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OPTICAL PROPERTIES OF
SOL-GEL DERIVED
Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (SBN) FOR
OPTOELECTRONIC
APPLICATION

HO MAN TAK MELANIE

MPHIL

THE HONG KONG POLYTECHNIC
UNIVERSITY

1999
ACKNOWLEDGEMENT

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ABSTRACT

$\text{Sr}_x \text{Ba}_{1-x} \text{Nb}_2\text{O}_6$ (SBN), one of the ferroelectric materials, is currently being investigated as the potential materials for the pyroelectric infrared detector, electro-optics, photorefractive and piezoelectrics devices. In our studies, both SBN powders and films have been successfully fabricated by sol-gel method. In the process of preparation of fine powders, there are several parameters, namely the annealing temperature and Sr/Ba ratio have been investigated in order to obtain the optimum conditions. Based on these results, the optimum processing parameters were identified so as to control the structural and optical properties of the SBN powders.

The structural behaviour was examined by X-ray diffraction and Raman spectroscopy, Scanning electron microscopy was employed to check the chemical composition of the samples. The dielectric properties were measured by an impedance gain analyzer. Finally, the nonlinear optical properties were examined by second harmonic generation. In conclusion, we have found out the relationship of the Sr:Ba ratio and the structural, electrical and optical properties of SBN powder.
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CHAPTER 1
INTRODUCTION

1.1 Background

Ferroelectric materials display a wide range of dielectric, ferroelectric, piezoelectric, electrostrictive and pyroelectric properties. They have been explored to manufacture various kinds of device such as piezoelectric or electro-acoustic transducers [1.1-1.2], high frequency surface-acoustic-wave (SAW) devices [1.3], pyroelectric infrared detectors [1.4], ferroelectric memory cells [1.5-1.6] and ferroelectric photoconductive displays [1.7-1.10]. The potential utilization of these properties in a new generation of devices has driven the intensive studies on the synthesis, characterisation, and determination of processing-property relationships of ferroelectric materials during the last ten years. Of various ferroelectric materials studied, strontium barium niobate (Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$, SBN) has received a great deal of attention owing to its large pyroelectric and electro-optic coefficients compared with other well-known ferroelectrics [1.11]. SBN is currently being investigated as potential materials for the pyroelectric infrared detector [1.12], electro-optics [1.13-1.14], photorefractive [1.15] and piezoelectrics [1.16].

SBN exhibits tetragonal tungsten bronze (TTB) type structure with its ferroelectric polar axis along the c-direction for $0.25 \leq x \leq 0.75$ [1.11]. On the contrary, SN and BN have different crystal structures with
type I and type II orthorhombic structure respectively [1.17]. Above its Curie temperature, the SBN crystal passes from the space group $P4\overline{bm}$ with the tetragonal structure into non-polar group $P \overline{4} b 2$ of monoclinic structure [1.11]. This Curie temperature, $T_c$, changes approximately linearly with $x$ ($T_c$ increases from $T_c \approx 57^\circ C$ at $x = 0.75$ to $T_c \approx 247^\circ C$ at $x = 0.25$). Beside the Curie temperature, many other physical properties of SBN also vary with its composition [1.11,1.18]. For example, single crystal SBN75 ($x = 0.75$) has high dielectric constant ($\varepsilon_3/\varepsilon_0 = 3400$) and pyroelectric coefficient ($31.0 \times 10^{-2} \, \mu C/cm^2K$) while single crystal SBN25 ($x = 0.25$) has low dielectric constant ($\varepsilon_3/\varepsilon_0 = 118$) and pyroelectric coefficient ($3.0 \times 10^{-2} \, \mu C/cm^2K$). Therefore, SBN with various composition are of important in different areas of application.

Several papers concerning the investigation of the properties (structural, dielectric, optical and ferroelectric) of SBN single crystal were published since the discovery of SBN solid solution [1.19-1.21]. Beside bulk SBN, thin films of SBN are of interest because of their potential applications in micro-electronic devices. Fabrication of SBN films has been reported by techniques such as sputtering [1.22], pulse-laser deposition [1.23], metal organic chemical vapour deposition [1.24] and sol-gel process [1.25-1.27].

Although SBN powder has advantages of easy fabrication and is ready to produce complex shape sample over the bulk and thin films, SBN powder has attracted much less attention compared with bulk and thin films. This may be due to the difficulties in preparation SBN powder.
using physical deposition techniques. Nevertheless, with sol-gel processing, preparing SBN powder is very easy as this has been demonstrated in other ferroelectric ceramic powder [1.28-1.29]. A literature survey has revealed that to completely form a single TTB phase SBN using mixed oxide route, the calcination temperature seems to be high and increases with an increasing mole ratio of strontium [1.30]. Thus, understanding the formation route of SBN powders through sol-gel method is extremely important to enable control of the composition and reduction of annealing temperature. In this thesis, we will fabricate SBN powders using sol-gel method. The optimal processing parameters will be identified. After fabricating the powders, the structural properties and the dielectric constant of these powders will be studied. In addition, the nonlinear optical properties of SBN films as a function of annealing temperature will be investigated.
1.2 Outlines of the thesis

This thesis is divided into eight chapters. Firstly, a brief review on previous work on this field is presented. Some physical and the structural properties of SBN are given in chapter 2. Since sample preparation plays an important role in materials research, the details of sample preparation using sol-gel method will be reviewed in chapter 3. The structural qualities of the samples were examined and investigated by X-ray diffractometry (XRD) and Raman spectroscopy (RS). The basic theories and experimental procedures of these two methods, as well as the results and discussions will be presented in chapter 4 and 5 respectively. After that, the experimental procedure, results and discussions of dielectric properties of our SBN samples will be reported in chapter 6. Then, the results and discussions of the nonlinear optical properties of SBN will be presented in chapter 7. It is followed by the conclusion of this thesis. Some suggestions for further study are also recommended.
CHAPTER 2

CHARACTERISTIC OF STRONTIUM BARIUM NIOBATE

Strontium barium niobate (SBN) is one of the well-known ferroelectrics with large electro-optic and pyroelectric coefficients. In this chapter, we will begin with the definition of ferroelectricity. After that, we will discuss the structure of SBN in section 2. Finally, the characteristics of SBN will be followed in section 3.

2.1 FERROELECTRICITY

2.1.1 Introduction

Ferroelectricity was discovered as early as 1921 by Valasek in Rochelle salt. Ferroelectrics are classes of materials that polarised permanently and spontaneously. They usually possess one or more ferroelectric phases that are particular states exhibiting spontaneous polarisation. This spontaneous polarisation can be reoriented by an external field, i.e. its direction of polarisation can be changed under external electric field. Since it performs similar behaviours under electric field like ferromagnetic materials under magnetic field, that is why they were named.
2.1.2 Polarisation and pyroelectric effect

Spontaneous polarisation is defined by the value of the dipole moment per unit volume, or by the value of the charge per unit area on the surface perpendicular to the axis of spontaneous polarisation. Since electrical properties are strongly correlated with the crystal structure [2.1], the axis of spontaneous polarisation is usually called crystal axis.

Although a crystal with polar axis exhibits piezoelectric effect, it does not necessarily have a spontaneous polarisation vector, because the net result of electric moments along all polar axis may be equal to zero. Therefore, only a crystal with a sole polar axis exhibits a spontaneous polarisation vector $P_s$ along this axis. In general, this spontaneous polarisation cannot directly be measured from the charges on the surfaces of the crystal, because these charges are compensated by external and/or internal carriers carrying on electric current, or by charges on the boundaries of twins. The value of the spontaneous polarisation $P_s$ depends on temperature. Figure 2.1 show the temperature dependence of spontaneous polarisation in two typical ferroelectric crystals, BaTiO$_3$ [2.2] and TGS (triglycine sulfate) [2.3]. As temperature changes, a variation of the charge density can be observed on those surfaces of the sample which are perpendicular to the unique polar axis in a crystal without twins, or in a poled polycrystal (ceramic) with oriented grains. This is the pyroelectricity in crystals exhibiting spontaneous polarisation.
Usually, a spontaneous polarisation can be written in the form

\[ P_s = \iiint_{V} \mu dV \text{ volume} \]  \hspace{1cm} (2-1)

where \( \mu \) is the dipole moment per unit volume. This formula implies that a polycrystalline material (ceramic or a composite) may have a remanent polarisation.

The pyroelectric effect is described in terms of a coefficient. If the change in temperature \( \Delta \Theta \) in a crystal is gradual and small in magnitude, the change in the spontaneous polarisation vector is

\[ \Delta P_s = \rho \Delta \Theta \]  \hspace{1cm} (2-2)

where \( \rho \) is the pyroelectric coefficient vector with three components:

\[ P_n = \frac{\partial P_{sn}}{\partial \Theta}, \text{ (m = 1, 2, 3)} \]  \hspace{1cm} (2-3)

The unit of the pyroelectric coefficient is \( \text{C m}^{-2} \text{ K}^{-1} \) (or \( \mu \text{C cm}^{-2} \text{ K}^{-1} \)).
According to the piezoelectric equations [2.1], the electric displacement vector \( D \) in a crystal is expressed as

\[
D = P_s + \varepsilon E + dT
\]  

(2-4)

where \( E \), \( \varepsilon \), \( d \), and \( T \) denote the electric field, the dielectric permittivity, the piezoelectric coefficient, and the stress respectively. When temperature changes, while \( E \) and \( T \) remain constant, eq.(2-4) can be rewritten in the form

\[
\Delta D = p \Delta \Theta, \quad p = (\partial D / \partial \Theta)_{E,T}
\]  

(2-5)

In general, the sign of the pyroelectric coefficient depends on the orientation of the piezoelectric axis (unique direction axis) in a crystal. According to the recommendation of *IRE Standards on Piezoelectric Crystals* [2.4], the positive end of the axis is that where positive charges are generated if a tensile stress is applied along this axis. When a crystal is heated and positive charges are generated at the positive end of the piezoelectric axis, the pyroelectric coefficient is defined to be positive. For most crystals, their pyroelectric coefficients are negative because spontaneous polarisation decreases as temperature increases.

### 2.1.3 Ferroelectric domains and hysteresis loop

Most pyroelectric crystals exhibit a spontaneous polarisation \( P_s \) in a certain temperature range and the direction of \( P_s \) can be reversed by an external electric field. In general, uniform alignment of electric dipoles only occurs in certain regions of a crystal, while in other regions of the crystal spontaneous polarisation are called the domain wall. The
ferroelectric domains were first demonstrated in a study of spontaneous birefringence [2.5,2.6].

It has not been understood clearly what the origin of the ferroelectric is. From a phenomenological viewpoint, a possible explanation is that the system with polydomain is in a state of minimum free energy. From a microscopic viewpoint, two possible explanations have been proposed. One of the explanations is that the domains are caused by a change in the electrostatic forces acting on the crystal's faces owing to the spontaneous polarisation that occurs as the crystal transforms from the paraelectric state to the ferroelectric state. Another explanation is that the domain structure is caused by defects and internal stresses in a crystal exhibiting piezoelectricity in the paraelectric state.

Anisotropy in a ferroelectric crystal is obviously large, and the orientation of dipoles usually coincides with the direction of spontaneous polarisation. It is hard to envisage that the dipole orientation changes gradually at a domain wall has the normal tendency to decrease its width in order to reduce the elastic energy generated by the strain near the wall. Therefore, a ferroelectric domain wall is very thin, and its thickness is about the scale of a few lattice cells.

The structure of a ferroelectric domain depends on the structure of the ferroelectric crystal. Some structural factors cause lattice distortion (including spontaneous deformation) at the wall to be as small as possible (in other words, to make two surfaces cut along the wall to be
Chapter 2 Characteristics of strontium Barium Niobate

identical) and the polarisation component along the direction normal to the wall to be continuous. Therefore, no electric charges accumulate on the wall and the electrostatic energy is a minimum. In a ferroelectric crystal, the variety of domain patterns and the number of types of domain walls depend on the number of all conceivable orientations of the dipole moment when the spontaneous polarisation occurs from the prototype phase (i.e., the phase with the highest symmetry below the melting point of the crystal).

Ferroelectric domain structure can be observed by various methods:

a) birefringence induced by a mechanical stress or an electric field, which is then observed by a polarising microscope [2.7, 2.8];

b) chemically etched samples observed by scanning electron microscopes [2.9, 2.10];

c) powder pattern method (such as sulphur powder carrying negative charges, lead oxide red powder carrying positive charges, and carbon powder carrying positive charges)[2.11, 2.12];

d) X-rays[2.13], and

e) liquid crystal display [2.14, 2.15]

A ferroelectric crystal always has a polydomain structure when it has just been grown. However, a crystal with a single domain can be obtained when an appropriate external electric field of high strength acts on it. A strong field may reverse the spontaneous polarisation.
2.2 STRONTIUM BARIUM NIOBATE

SBN belongs to the class of tetragonal tungsten-bronze-type ferroelectric oxides which is the second largest class of ferroelectrics following perovskite type ferroelectric. Similar with the perovskite structure, TTB type structure contains oxygen octahedra and maintains a crystallographic structure based on that of the TTB type K$_x$WO$_3$ and Na$_x$WO$_3$ (x < 1)[2.16]. In each TTB unit cell, there are four types of sites, namely, six A sites (with two $A_1$ sites and four $A_2$ sites), four C sites, ten B sites (with two $B_1$ sites and eight $B_2$ sites) and thirty oxygen ions (at the corners of the octahedra). The site occupancy formula may thus be written as $(A_1)_2 (A_2)_4 (C)_4 (B_1)_2 (B_2)_8 O_{30}$. The sites $A_1$, $A_2$, $C$, $B_1$ and $B_2$ can be either partially or fully occupied by different cations. In the case of niobates, the $B_1$ and $B_2$ sites are occupied by Nb$^{5+}$, while either alkaline earth ions or alkali ions, or both occupy the $A_1$, $A_2$ and $C$ sites. The number of occupied sites depends on the valence and number of these cations in accordance with the requirements of electroneutrality, and on their size in accordance with crystallographic constraints. For example, in Sr$_{3x}$Ba$_{5.5x}$Nb$_{10}$O$_{30}$ with $5x = 3.62$, the site occupancy of $A_1$, $A_2$, $C$, $B_1$ and $B_2$ are 3.62 Sr, 1.38 Ba, 0, 2Nb and 8Nb respectively. Since the six A sites are occupied by only five cations, therefore it belongs to the type of incompletely filled TTB-type structure. The condition is just like that of PbNb$_2$O$_6$ which has six A sites with only five Pb$^{2+}$ ions arbitrarily occupied. A schematic diagram showing a projection of the TTB structure on the (001) plane is shown in Figure 2.2.
Figure 2-2  Schematic diagram showing a projection of the tungsten-bronze-type structure on the (001) plane. The orthorhombic cell and the tetragonal cell are shown by solid lines and dotted lines, respectively [2.16].

2.2.1 The origin of ferroelectricity

Ferroelectric properties and some other properties of TTB type niobate crystal like SBN are strongly influenced by the composition and cation distribution. Generally, the origin of ferroelectricity lies in the displacement of the cations at A and B sites from the centrosymmetric oxygen planes in the paraelectric phase (as shown in Fig. 2.2) with decrease in temperature below Tc. At this regime, spontaneous polarisation occurs in the direction of the c-axis. SBN60 undergoes a structural phase transition between 60 and 80 K. During this phase transition, the crystal symmetry changes from point group 4mm to point
group \( m \) and the direction of the ferroelectric polar axis tilts away from the \( c \)-axis in the tetragonal lattice cell towards the \( \alpha \)-axis in the monoclinic lattice cell as the temperature decreases. The difference between the high-frequency dielectric constants and the low-frequency dielectric constants indicates that the phase transition is of a diffuse nature. The experimental data on specific heat suggest that this phase transition is not a first-order transition[2.16].

2.3 CHARACTERISTICS OF SBN

The \( \text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 \) solid-solution series (for \( 0.2 < x < 0.8 \)) has the TTB-type structure and belongs to the point group \( 4mm \) symmetry at room temperature. This crystal possesses excellent pyroelectric and linear electro-optic properties with low half-wave voltages[2.16]. Owing to its good mechanical and undeliquescent properties, SBN is an ideal pyroelectric and linear electro-optic material. In addition, SBN and doped SBN crystals can be used in holographic memory and other nonlinear optical devices. This is primarily because of the photorefractive effect (optically induced change of refractive index), in which only \( 5/6 \) of the \( A \) sites in the SBN lattice are filled and the vacancies at the other \( 1/6 \) \( A \) sites act as carrier trapping centres.

The ratio of Sr ions to Ba ions in SBN solid-solution crystals can be continuously varied in a wide range, as can be seen in the phase diagram for the pseudo-binary system \( \text{SrNb}_2\text{O}_6 - \text{BaNb}_2\text{O}_6 \) determined by
Carruthers and Grasso [2.17]. In view of the BaO—SrO—Nb$_2$O$_5$ ternary system, the compositional range of solid solubility varies from an additional 4 mol % (Ba + Sr) to an additional 1 mol% (Nb$_2$O$_5$). For different applications, SBN crystals with different physical properties can be grown by changing the composition of the melt. For example, crystalline Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ has a melting point of about 1500 ºC. From a melt of this composition, either colourless or transparent yellow crystals can be grown, which have a density of 5.4 g/cm$^3$ and a Moh's hardness of 5.5. By changing the Sr/Ba ratio, the Curie temperature $T_c$ of SBN can be made to vary in the range from 60 ºC to 250 ºC. The TTB type ferroelectric SBN crystals possess a spontaneous polarisation of 32 µC/cm$^2$ (Sr/Ba = 75/25) at room temperature and a polar axis along the $c$-axis of the tetragonal lattice[2.18, 2.19].

Polycrystalline ferroelectric thin films of SBN (grain size approximately 2-3 µm) having approximately the same nonlinear properties as SBN single crystals have been reported [2.20]. For a light beam traversing along a direction perpendicular to the $c$-axis under a driving electric voltage of 30 V, this modulator was found to operate effectively at several hundred kHz. The photocurrent effect in SBN has also been investigated [2.21]. This effect is due to excitation of the photocarriers generated during illumination, such that the electrical conductivity and the permittivity of the crystal are changed.
SBN shows also strong pyroelectric effects. The temperature dependence of polarisation and the pyroelectric current of a SBN crystal is shown in Fig. 2-3.

Figure 2-3 Temperature dependence of the polarisation change (a) and of the pyroelectric current; (b) in SBN crystals [2.18].
SBN crystal has a relatively large pyroelectric coefficient at room temperature. In order to be considered for use as infrared pyroelectric detectors, a large pyroelectric coefficient, a small specific heat and a fairly low relative permittivity are required. The characteristics of these detectors (at room temperature) can be improved by changing the ratio of Sr/Ba. These detectors have a high stability in air without a protective window, which is necessary in the case of TGS. A thin plate of SBN has a high absorption capacity in the infrared region above 10 μm without blackening. There is no apparent piezoelectric response in this plate below a frequency of 50 MHz. This material is therefore widely used for fast detectors. Zook and Liu [2.22] have reviewed the pyroelectric effect in thin SBN film. The main shortcoming of SBN is that its dielectric constant is not low enough for application at high frequencies. Thus, SBN thin film detectors are mainly used for small area, low-frequency application.

The birefringence of a SBN plate can be changed when a d.c. field is applied. The optical response shows two effects: the linear electro-optic effect and the electro-optic memory effect. With an increase of the applied field, the birefringence first increases along AB in Fig. 2-4 and reaches a linear region BC, which corresponds to the linear electro-optic effect. In the region of high electric field, the crystal is poled completely. The part AB corresponds to the change of birefringence due to the inversion of polarisation. A remanent birefringence (AD), which can be switched by a pulsed voltage, occurs with the remanent polarisation. Making use of the
memory effect of remanent birefringence, a light valve device with a longitudinal mode was fabricated [2.23, 2.24]. By controlling the amplitude of the voltage, partial inversion of the remanent polarisation can be achieved. These SBN devices can be used in ferroelectric displays or holographic storage more efficiently than the PLZT devices, because they possess lower light loss and are able to work without transverse field or bias strain.

Figure 2-4 Dependence of the birefringence of an SBN crystal on the applied d.c. field [2.23].
CHAPTER 3
SAMPLE PREPARATION

3.1 THE FORMS OF SAMPLE

Ferroelectric materials have been fabricated into different forms, namely, single crystal, powder, and film. Different forms have different properties and hence have different area of applications. Generally speaking, single crystal has the best electrical, structural and magnetic properties because crystal usually has smallest degree of deflection. However, there are some restrictions in application of single crystal because of their size, mechanical strength and cost.

As the idea of miniature comes to the world, it is necessary to reduce the size of the samples. Films seem to be one of the solutions. Films are basically divided into thick films and thin films. Both of them play their own role in electronic devices. Thin films are good for low voltage devices. However, due to their small thickness, some properties will be very weak. In this case, thick films are needed to enhance desirable properties. Thick films are generally applied in comparatively higher voltage devices.

On the other hand, powders have the advantages of ease of fabrication and low cost. They can also be pressed into bulk form with large size, complex shape and good stress resistance. In addition, powders perform some special effects. As the particle size of powders decreases to nano-meter, some of the properties will be enhanced due to
quantum effect. Nano-size semiconductor quantum dots with enhanced nonlinear properties are successful fabricated [3.1].

3.2 CERAMIC FABRICATION PROCESS

There are quite a number of methods for the preparation of ceramics. They can be grouped into three categories:

a) gas-phase reactions including chemical vapour deposition (CVD), metallorganic chemical vapour deposition (MOCVD), directed metal oxidation and reaction bonding.

b) liquid precursor methods involving liquid state reactions like sol-gel processing and polymer pyrolysis.

c) Fabrication from powders, for example, melt casting and firing of compacted powders (mixed oxide route).

Table 3.1 summarises the three different methods. The products of these methods are usually films or monoliths.

Table 3-1 Common ceramic fabrication methods [3.2].

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Methods</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases</td>
<td>Chemical vapour deposition</td>
<td>Films, monoliths</td>
</tr>
<tr>
<td>Gas-liquid</td>
<td>Directed metal oxidation</td>
<td>Monoliths</td>
</tr>
<tr>
<td>Gas-solid</td>
<td>Reaction bonding</td>
<td>Monoliths</td>
</tr>
<tr>
<td>Liquids</td>
<td>Sol-gel process</td>
<td>Films, fibres.</td>
</tr>
<tr>
<td></td>
<td>Polymerisation</td>
<td>film, fibres</td>
</tr>
<tr>
<td>Solids (powders)</td>
<td>Melt casting</td>
<td>Monoliths</td>
</tr>
<tr>
<td></td>
<td>Sintering of powders</td>
<td>Films, monoliths</td>
</tr>
</tbody>
</table>
For powder preparations, two groups of methods are commonly used. These two methods are mechanical methods and chemical methods. Tables 3.2 and 3.3 summarise the advantages and disadvantages of these two methods. In general, mechanical methods are used to prepare common and traditional ceramics, while chemical methods are used to prepare advanced ceramics [3.2].

One of the most convenient methods for fabricating ceramic powder is the mix-oxide route. However, in this method, the calcination temperature is usually very high which make this method not cost and energy effective. Recently, sol-gel process shows attractive advantages over the others. Advantages of sol-gel process include excellent homogeneity, ease of chemical composition control, high purity, low processing temperature and inexpensive equipment required.

Table 3-2 Common mechanical preparation methods for ceramics

<table>
<thead>
<tr>
<th>Mechanical Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commination</td>
<td>Inexpensive wide applicability</td>
<td>Limited purity, limited homogeneity, large particles size</td>
</tr>
<tr>
<td>Mechanochemical syntheiss</td>
<td>Fine particle size, good for nonoxides, low processing temperature</td>
<td>Limited purity, limited homogeneity</td>
</tr>
<tr>
<td>Chemical Methods</td>
<td>Example</td>
<td>Advantages</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>--------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td><strong>Solid-state reactions</strong></td>
<td>Mixed Oxide Route</td>
<td>Simple apparatus,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>inexpensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Liquid solution:</strong></td>
<td>spray drying,</td>
<td>High purity, small</td>
</tr>
<tr>
<td></td>
<td>spray pyrolysis,</td>
<td>particles, composition</td>
</tr>
<tr>
<td></td>
<td>freeze drying, sol-gel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>processing</td>
<td>control, chemical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>homogeneity</td>
</tr>
<tr>
<td></td>
<td>Nonaqueous liquid reaction</td>
<td>High purity, small</td>
</tr>
<tr>
<td></td>
<td></td>
<td>particles</td>
</tr>
<tr>
<td><strong>Vapour-phase reaction</strong></td>
<td>Gas-solid reaction</td>
<td>Inexpensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas-liquid reactions; reaction between gases</td>
<td>High purity, small particles</td>
</tr>
</tbody>
</table>

Table 3-3 Common chemical preparation methods for ceramics
3.3 SOL-GEL METHOD

3.3.1 Terminology

Sol-gel method is a wet chemical process that contains two important stages: sol and gel. A sol, by definition, is a colloidal suspension of solid particles in a liquid. The term colloid is defined as a suspension in which the dispersed phase is so small (~1-100 nm) that gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charge. Because of the small inertia of the dispersed phase, it exhibits Brownian motion. After some chemical reactions taken place, a sol will transform into a gel that is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. In sol-gel process, the precursors are the starting compounds used for preparation of a colloid which consists of a metal or metalloid element surrounded by various ligands (appendages not including another metal or metalloid atom). In our experiment, the precursors are metal alkoxides. These metal alkoxides are members of the family of metalorganic compound which has an organic ligand attached to a metal or metalloid atom.

3.3.2 The types of system

Sol-gel method is an excellent method for the preparation of ceramic materials. There are two types of system in sol-gel method, namely, the non-silicate and the silicate system. For non-silicate system,
it is further divided into transition metal, aluminate and borate system. In our case, SBN belongs to the transition metal non-silicate system.

3.3.3 Characteristics of metal alkoxides

Generally, metal alkoxides are very reactive due to the high electronegative -OR group [3.3,3.4]. These metal alkoxides are different from the most commonly used precursors like silicon alkoxides (Si(OR)\(_4\)) in several ways [3.3]:

1. The transition metals are less electronegative than that of the alkaline earth metal, therefore, they are less stable toward hydrolysis, condensation, and other nucleophilic reactions;

2. Transition metals can have several stable co-ordinations. When the co-ordinations are unsaturated, they are able to expand their co-ordinations via olation, oxolation, alkoxy bridging, or other nucleophilic association mechanisms;

3. Due to the high reactivity of transition metals, therefore, the presence of unwanted moisture and the condition of hydrolysis should be in strict control;

4. The rate of nucleophilic reactions is increased due to its high reactivity.

3.3.4 The mechanism of hydrolysis and condensation

In the absence of catalyst, hydrolysis and condensation both occur by nucleophilic substitution (S\(_N\)) mechanisms involving nucleophilic
addition ($A_N$). Afterwards, proton will be transferred from the attacking molecule to an alkoxide or hydroxo-ligand within the transition state and the protonated species as either alcohol (alcoxolation) or water (oxolation) will be removed [3.5, 3.6]. The thermodynamics of hydrolysis, alcoxolation, and oxolation (defined in Figure 3-1) are governed by (1) the strength of the entering nucleophile; (2) the electrophilicity of the metal; (3) the partial charge, and (4) stability of the leaving group.

Since the transition state involves an associative mechanism accompanied by a proton transfer, kinetics are governed by the extent of unsaturated co-ordinations of the metal, $N-z$, and the transfer ability of the proton. Larger values of ($N-z$) and greater acidities of the protons reduce the associated activation barriers and enhance the kinetics. The thermodynamic of olation depends on the strength of the entering nucleophile and the electrophilicity of the metal. The kinetics of olation are systematically fast because ($N-z$) > 0 such that no proton transfer occurs in the transition state.

Another factor that influences reaction kinetics is the extent of oligomerization ($molecular$ $complexity$) of the metal alkoxides. The molecular complexity depends on the nature of the metal atom. Within a particular group, it increases with the atomic size of the metal, thus explaining the tendency of divalent transition metal alkoxides to polymerise rendering them insoluble [3.7].
Chapter 3

Sample Preparation

\[
\begin{align*}
\text{H-O + M-OR} & \rightarrow \text{O-} \rightarrow \text{M-OR} \rightarrow \text{HO-M} \leftarrow \text{O-} \\
\text{H} \quad (a) & \quad \text{H} \quad (b) & \quad \text{H} \quad (c) & \quad \text{H} \\
\quad \rightarrow \text{M-OH} + \text{ROH} & \quad \text{hydrolysis} & \\
\quad \text{M-O + M-OR} & \rightarrow \text{M-O} \leftarrow \text{M-OR} \rightarrow \text{M-O-M} \leftarrow \text{O-} \\
\text{H} \quad (a) & \quad \text{H} \quad (b) & \quad \text{H} \quad (c) & \quad \\
\quad \rightarrow \text{M-O-M} + \text{ROH} & \quad \text{alcoxolation} & \\
\end{align*}
\]

\[
\begin{align*}
\text{M-O + M-OH} & \rightarrow \text{M-O} \leftarrow \text{M-OH} \rightarrow \text{M-O-M} \leftarrow \text{O-} \\
\text{H} \quad (a) & \quad \text{H} \quad (b) & \quad \text{H} \quad (c) & \\
\quad \rightarrow \text{M-O-M} + \text{H}_2\text{O.} & \quad \text{Oxolation} & \\
\quad \text{When } N-z > 0, \text{ condensation can occur by oxolation:} & \\
\left\{ \begin{array}{l}
\text{M-OH + M} \leftarrow \text{O-} \rightarrow \text{M-O-M} + \text{ROH} \\
\text{M-OH + M} \leftarrow \text{O-} \rightarrow \text{M-O-M} + \text{H}_2\text{O.}
\end{array} \right.
\end{align*}
\]

Figure 3-1 Definition of hydrolysis, alcoxolation, oxolation and oxolation.
It is observed that alkoxy bridges are more stable toward hydrolysis than associated solvent molecules and in some cases terminal OR ligands. Therefore, starting from a particular alkoxide, the kinetics and resulting structure can be controlled by appropriate choice of solvent [3.3].

The size and electron-providing or -withdrawing characteristics of the organic ligand also affect the hydrolysis and condensation kinetics. As observed in inorganic systems, the initial condensation products are oligomeric species that subsequently aggregate to form gels or precipitates. The oligomer size depends on $R$: the larger the size $R$, the smaller the oligomer. The $R$ group also exerts an influence on the morphology (particle size and surface area) and crystallisation behaviour of the resulting gel [3.8,3.9], perhaps by altering the size and structure of the primary oligomeric building blocks.

3.3.5 The structure of products after condensation

The structure of products after condensation depends on the rate of four reactions: hydrolysis, oxolation, alcoxolation, and olation. All the four reactions depend on the nature of the metal atom and alkyl groups and the molecular complexity as well as external parameters such as $r$, the choice of catalyst, concentration, solvent and temperature. However, it is very difficult to find out the progress of structural change because of its rapid reaction rates of transition metal oxide systems [3.10].
3.3.6 Chemical modification

Chemical modification of transition metal alkoxides with alcohol is commonly employed to retard the hydrolysis and condensation reaction rates in order to control the condensation pathway of the evolving polymer. In most cases, the modification occurs by an $S_N$ reaction between a nucleophilic reagent (XOH) and the metal alkoxide to produce an new molecular precursor [3.6]:

$$\text{XOH} + \text{M(OR)}_z \rightarrow \text{M(OR)}_{z-x}(\text{OX})_x + \text{ROH}$$

or when M is co-ordinatively unsaturated ($N-z > 1$) by nucleophilic addition (A$_N$):

$$\text{XOH} + \text{M(OR)}_z \rightarrow \text{M(OR)}_{z}(\text{XOH})_{N-z}$$

The hydrolysis and condensation behaviour of the modified precursor depends, of course, on the stability of the modifying ligands, which is not always possible to predict on the basis of the stability of the parent compound, M(OX)$_z$. Alcohol exchange reactions occur readily with metal alkoxide precursors:

$$\text{M(OR)}_x + x \text{R'OH} \rightarrow \text{M(OR)}_{x-x}(\text{OR'})_x + x \text{ROH}$$

Hydrolysis rates decrease with steric bulk of the alkoxy ligands, while chemical modification of transition metal precursors normally involves exchange of a bulky ligand for a less bulky one [3.11].
3.4 EXPERIMENTAL PROCEDURE

3.4.1 Preparation of SBN sol

It is well known that transition metal oxide gels are the basis of ferroelectric materials such as BaTiO$_3$ and Pb(Zr$_{x}$Ti$_{1-x}$)O$_3$. SBN, which composed of both alkaline earth and transition metals, belongs to this type. Naturally, the first step is to prepare the metal alkoxides. Strontium and barium metal were dissolved in 2-methoxyethanol to form strontium alkoxide and barium alkoxide respectively. The 2-methoxyethanol acted as both the solvent and stabilizer. Niobium(V) chloride (NbCl$_5$) was used to prepare niobium alkoxide by also adding potassium hydroxide into 2-methoxyethanol. The use of KOH was to get rid of the chloride ion. The KCl was precipitated out and could be easily separated from the solution by filtration. The three metal alkoxides were mixed in desire stoichiometric ratio according to the composition formula Sr$_x$ Ba$_{1-x}$ Nb$_2$ O$_6$. In our experiments, x = 0, 0.3, 0.5, 0.6, 0.75, 0.78, 0.8, and 1 were prepared.

3.4.2 Preparation of SBN powder from sol

In order to obtain powders, small amount of water was added to the sol for hydrolysis. The solution was allowed to stand overnight for complete reaction. After hydrolysis, the unwanted species like water and alcohol were removed by drying the gel in oven at 100 °C for 72 hours. Pieces of yellowish brown loosely packed solid were acquired. The solid was ground manually using mortal and pestle. The yellowish brown
powder was then put into a high temperature furnace for annealing at different temperatures ranging from 600 °C to 1400 °C. Finally, fine SBN powder was obtained. The procedure of the sol-gel processing of SBN powders is shown schematically in Fig. 3-2.

![Diagram](image)

**Figure 3-2** The flow chart of preparation route of SBN sol.
3.4.3 Preparation of SBN thin films

In general, sol-gel derived SBN films can be fabricated by dip coating or spin coating method. For dip coating, the substrate is lowered into the SBN sol and withdrawn at a constant speed. In spin coating, the SBN sol is dropped on to the substrate which is spinning at a high speed. Dip coating is currently the more widely used. One requirement is that the contact angle between the sol and the surface of the object should be low so that the solution wets and spreads over the surface. Usually water is present in the sol but moisture from the atmosphere is sufficient to cause hydrolysis and condensation reactions. The final film is obtained after annealing at high temperature. For thicker films, repeated dipping is necessary.

There are various advantages and disadvantages in each of the coating techniques. To decide which is the most suitable one, the size and properties of the future samples have to be considered carefully. For example, spin coating is not suitable for large-area samples. Comparison between these methods is tabulated in the following table[3.12]:

**Table 3-4 Comparison between dip coating and spin coating.**

<table>
<thead>
<tr>
<th></th>
<th>Dip coating</th>
<th>Spin Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of sample</td>
<td>Not limited</td>
<td>Limited by the size of spin coater</td>
</tr>
<tr>
<td>Special Equipment</td>
<td>Not necessary</td>
<td>A spin coater is needed</td>
</tr>
<tr>
<td>No. of surface coated in each run</td>
<td>Two</td>
<td>One only</td>
</tr>
<tr>
<td>Homogeneity thickness</td>
<td>Not even</td>
<td>Even</td>
</tr>
<tr>
<td>Edge effects</td>
<td>may occur for samples which are not axissymmetric</td>
<td>No such problem</td>
</tr>
</tbody>
</table>

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Ho Man Tak Melanie
For dip coating, the thickness of the film is related with the viscosity of the sol. Landau and Levich [3.13] reported that the theory is found to be a good match with the experimental data. For low capillary numbers defined by

\[ N_{ca} = \frac{\eta U}{\gamma_{lo}} \]  

(3-1)

where \( U \) is the withdrawal speed, \( \eta \) is the dynamic viscosity, and \( \gamma_{lo} \) is the surface tension of the solution, the thickness of the liquid film can be expressed in the form [3.13]:

\[ t = 0.944 N_{ca}^{1/6} \left( \frac{\eta U}{\rho g} \right)^{1/2} \]  

(3-2)

where \( \rho \) is the density of the solution and \( g \) is the acceleration due to gravity. From equation (3-1) and (3-2), the thickness of the film is predicted to vary as \( (U\eta)^{2/3} \). If the final solid film is densified to full density, \( \rho_f \), the thickness of the final film is

\[ t_f = 0.944 \frac{\rho - \rho_a}{\rho_f - \rho_a} N_{ca}^{1/6} \left( \frac{\eta U}{\rho_f} \right)^{1/2} \]  

(3-3)

However, the above equation is not suitable for spin coating. Since the physics behind is different. It is found that the thickness of film prepared by spin coating varies inversely as \( \omega^{2/3} \), where \( \omega \) is the angular velocity of the spin coater, and as \( \eta^{1/3} \) [3.14-3.17].
The first step is to prepare SBN solution as described in previous sections. In our studies, spin-coating method was used for better homogeneity. The coating process was done in a glove box to prevent hydrolysis of SBN sol because of air moisture. The duration of spinning was 10 s at speed of 3000 rpm. Another 20 s was needed for drying and gelation in between successive coatings in order to obtain multi-coating. Totally, 20 layers of coating were made for each of the samples. The samples were then annealed at different temperatures with range between 500 °C to 800 °C. The thickness of these samples was ~ 1.3 μm.
CHAPTER 4

X-RAYS DIFFRACTOMETRY

4.1 BACKGROUND

X-ray is a kind of electromagnetic wave and behaves like other electromagnetic waves, such as gamma rays from radioactive atoms, ultra-violet, visible light, infra-red, microwaves, and radio wave. Generally, x-ray is produced when electrons from a heated filament are accelerated by a potential difference and strike a metal target. The wavelengths are of the order of 0.1 nm (or 1 Å).

4.1.1 The history of X-ray

In 1895 Wilhelm Conrad Röntgen found that some photographic plates, which were kept carefully in his laboratory, became fogged. In order to find out the cause of the fogging, he traced the photographic plates to a high voltage gas-discharge tube. This tube seemed to emit a radiation that could penetrate paper, wood, glass, rubber, and even thick aluminium. However, Röntgen could not find out whether the radiation was a stream of particles or a train of waves, hence, he decided to call it X-rays [4.1.4.2].

It waited until 1912, Max von Laue proposed that a crystalline solid, which consisted a regular array of atoms, might form a natural three-dimensional 'diffraction grating' for X-rays. If a collimated beam of
continuous distributed X-rays was allowed to fall on a crystal, the atoms in the crystal became diffraction centres and constructive interference in certain direction would be resulted. If these diffracted beams fell on a photographic film, they formed an assembly of spots called 'Laue spots'. The atomic arrangements in the crystal could be deduced from a careful study of the positions and intensities of these Laue spots, just like the way what we had done for the deduction of structure of an optical grating. The detailed profile of the slits can be deduced by studying the positions and intensities of the lines in the interference pattern.

4.1.2 Bragg law

The study of the atomic structure of crystals by X-ray analysis was started in 1914 by Sir William Bragg and his son Sir Lawrence Bragg. They found that a monochromatic beam of X-rays was reflected from a plane in the crystal rich in atoms, so-called atomic plane, which acted like a mirror. X-rays have high energies and short wavelengths (on the order of the atomic spacing in solids), therefore, when a beam of X-rays impinged on a solid material, a portion of this beam would be scattered in all directions by the electrons, and strong enough for us to detect.
In Fig. 4-1, A-A' and B-B' are the two parallel planes of atoms which have the same \( h, k, \) and \( l \) values (Miller indices). The distance between them, that is the interplanar spacing, is \( d_{hkl} \). If a parallel, monochromatic, and coherent beam of X-rays with wavelength \( \lambda \) is incident on these two planes at an angle \( \theta \), then two rays (labelled 1 and 2) are scattered by atoms \( P \) and \( Q \). If the path length difference between 1-P-1' and 2-Q-2' (i.e. \( \overline{SQ} + \overline{QT} \)) is equal to a whole number, \( n \), of wavelengths, constructive interference of the scattered rays 1' and 2' occurs at an angle \( \theta \) to the planes. The condition for diffraction is

\[
n\lambda = \overline{SQ} + \overline{QT}
\]

or

\[
n\lambda = d_{hkl} \sin \theta + d_{hkl} \sin \theta = 2d_{hkl} \sin \theta
\]
Equation (4-2) is known as Bragg's law. Here \( n \) is the order of reflection, which can be any integer \((1, 2, 3, \ldots)\) and \( \sin \theta \) does not exceed unity \((\sin \theta \leq 1)\). This equation gives us a simple relation between X-ray wavelength, interatomic spacing, and angle of the diffracted beam. Non-constructive interference will give a very low-intensity diffracted beam, so Bragg's law only applied to constructive interference only.

The magnitude of the distance between two adjacent and parallel atomic planes (i.e., the interplanar spacing \( d_{hkl} \)) is a function of the Miller indices \((h, k, l)\) as well as the lattice parameters. Consider the case of a crystal with cubic structure,

\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{4-3}
\]

in which \( a \) is the lattice parameter (unit cell edge length). There are six more crystal lattice cells that are similar, but much complex than that in equation (4-3). They are listed in Table 4-1.

Because of the simple nature of Bragg's law, it provide just one of the essential conditions for diffraction by real crystals. It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners. However, atoms situated at other sites (e.g., face and interior unit cell postions as with face centre cubic and body centre cubic) act as extra scattering centers. They can produce out-of-phase scattering at certain Bragg angles. The net result is the absence of some diffracted beams which, according to Equation (4-2), should be present. For example, for the body centre cubic crystal structure, \( h + k + l \) must be
even if diffraction is to occur, whereas for face centre cubic crystal, \( h, k, \)
and \( l \) must all be either odd or even [4.3].

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Axial Relationships</th>
<th>Interaxial Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>( a = b = c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>( a = b \neq c )</td>
<td>( \alpha = \beta = 90^\circ, \gamma = 120^\circ )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( a = b \neq c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>( a = b = c )</td>
<td>( \alpha = \beta = \gamma \neq 90^\circ )</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha = \gamma = 90^\circ \neq \beta )</td>
</tr>
<tr>
<td>Triclinic</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha \neq \beta \neq \gamma \neq 90^\circ )</td>
</tr>
</tbody>
</table>

4.1.3 Diffraction techniques

For powder or polycrystalline specimen consisting of many fine and randomly oriented particles, the most common diffraction technique employed is to expose the samples to monochromatic X-rays. Each powder particle is a crystal by itself. The sample, which has a large number of these single crystal with random orientations, will ensure that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

A diffractometer is an apparatus used to determine the angles at which diffraction occurs for powders; its features are represented.
schematically in Figure 4-2. A specimen, in the form of a flat plate, is supported so that it can rotate about the axis which is perpendicular to the plane of the page. The monochromatic X-ray beam is generated, and the intensities of diffracted beams are detected with a counter. It should be noted that the specimen, X-rays source, and counter are all coplanar.

The counter is mounted on a movable carriage which may also be rotated about the axis; its angular position in terms of $2\theta$ is marked on a graduated scale. Carriage and specimen are mechanically coupled such that rotation of the specimen through $\theta$ is accompanied by a $2\theta$ rotation of the counter; this assures that the incident and reflection angles are maintained equal to one another (Figure 4-2). Collimators are incorporated within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam. As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of the diffraction angle, $2\theta$, which is measured experimentally.

Other powder techniques have been devised wherein diffracted beam intensity and position are recorded on a photographic film instead of being measured by a counter.
Figure 4-2 Schematic diagram of x-ray diffractometer [4.3].
4.1.4 Application of X-ray diffractometry

X-ray is a common experimental technique used in various types of material investigations. For example, crystallographic orientations of single crystals are measured by x-ray diffraction (or Laue) photographs [4.2]. Other uses of X-rays include qualitative and quantitative chemical identifications (the composition of a material) [4.4], and the determination of residual stresses and crystal size [4.5].

Determination of crystal structure

One of the primary use of X-ray diffractometry is the determination of crystal structure. The unit cell size and geometry can be resolved from the angular positions of the diffraction peaks, whereas arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

Determination of crystal size

As the principle of X-ray diffraction depends on the path difference between two adjacent atomic planes, therefore, a strong signal can only obtained at Bragg's angle. With other incident angles, other plane of the crystallites were involved. The reflective beam of X-rays of these planes cancel each other. However, as the particle size decreases, the number of atomic plane decreases, then, not all the reflected rays are cancelled. These weak reflective rays contribute to the strong one. Therefore, peak
broadening occurs. This is called the particle size effect of peak broadening.

The crystallite size broadening ($\beta$) of a peak can be written in terms of the mean crystallite dimension ($\tau$) using the Scherrer equation[4.5]:

$$\tau = \frac{K\lambda}{\beta, \cos \theta}$$ (4-4)

where $\beta$, is the line broadening due to the effect of small crystallites. $\beta$, is given by ($B-b$), where $B$ is the breadth of the observed diffraction line at full width half maximum (FWHM), and $b$ the instrumental broadening or breadth of a peak from a specimen that exhibits no broadening beyond inherent instrumental peak width. Note that $\beta$, must be given in radians; $K$ is the shape factor, which usually takes a value of about 0.9.

Then equation (4-4) becomes:

$$\tau = \frac{0.9\lambda}{(B-b)\cos \theta}$$ (4-5)

If the equipment setting is suitable, crystallite sizes as small as 10 Å can be measured.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 The apparatus

All experimental data were obtained from X-ray diffractometer (Philip Model PW3710) with copper as the tube anode. The emitted wavelengths are 1.54060 Å and 1.54439 Å, with the intensity ratio of 0.5.
The divergence and receiving slit size are 0.25° and 0.1 mm respectively. All unwanted signal which would cause peak broadening was filtered by a monochromator. Concerning the scanning mode, continuous scanning from \( \theta = 20^\circ \) to \( 60^\circ \) with step size equal to 0.02° was used throughout the experiments.

### 4.2.2 The sample holder

A home-made sample holder was used for powder measurements. It composed of several pieces of slide glass assembled as shown in Figure 4-3. The powders were placed in the well flatly. This ensured that the interaction volumes of each sample were constant.

**Figure 4-3 Top view and cross section of sample holder for powder.**
4.2.3 Procedure

Different composition of SBN powders with \( x \) varied from 0 to 1 were annealed in various temperatures, ranging from 600 °C to 1400 °C. Equal amount of each sample was put in the sample holder for X-ray measurement. In these measurements, the scan step and integral time were fixed at 0.02° and 1 s respectively. The raw data were recorded by a personal computer for data analysis.

4.3 RESULT AND DISCUSSION

4.3.1 Composition effect

The structural changes in \( \text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 \) were studied as a function of \( x \). All the powders, with \( x = 0, 0.3, 0.5, 0.6, 0.75, 0.8, \) and 1, were annealed at 1200 °C. Figure 4-4 shows the XRD patterns of these SBN powders. Using Scherrer's relation that assumes the small crystallite size causing line broadening, we obtained an average crystallite size of \( \sim 27 \) nm for all of our samples. Table 4-1 summarises the \( x \) dependence of the average crystallite size for different Sr/Ba ratio.

<table>
<thead>
<tr>
<th>( x )</th>
<th>Sample</th>
<th>Approximate crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>BN</td>
<td>18</td>
</tr>
<tr>
<td>0.3</td>
<td>SBN30</td>
<td>29</td>
</tr>
<tr>
<td>0.5</td>
<td>SBN50</td>
<td>26</td>
</tr>
<tr>
<td>0.6</td>
<td>SBN60</td>
<td>25</td>
</tr>
<tr>
<td>0.75</td>
<td>SBN75</td>
<td>28</td>
</tr>
<tr>
<td>0.8</td>
<td>SBN80</td>
<td>28</td>
</tr>
<tr>
<td>1</td>
<td>SN</td>
<td>36</td>
</tr>
</tbody>
</table>
Figure 4-4 XRD spectra of (a) BN, (b) SBN30, (c) SBN50, (d) SBN60, (e) SBN75, (f) SBN80 and (g) SN.
In Figure 4-4, SN (Fig. 4-4g) shows a strong peak at \( \theta = 29.1^\circ \) while BN (Fig. 4-4a) exhibits two characteristic peaks at \( \theta = 28.4^\circ \) and \( 29.8^\circ \). For \( x = 0.5 \) (Fig. 4-4c), a XRD pattern of single TTB phase SBN is obtained. This XRD pattern is consistent with the reported by VanDamme et. al [4.6]. As \( 0.8 > x > 0.5 \) (Fig. 4-4d, Fig.4-4e and Fig. 4-4f), the spectra contain SBN-like XRD patterns with the additional feature at \( \theta = 29.1^\circ \). This extra feature becomes stronger as \( x \) increases. The origin of this feature appears to arise from the SN phase. This result indicates that at \( x > 0.5 \), a mixture of TTB phase SBN and SN are present. The intensity ratios of SN/SBN increased with increasing mole ratio of strontium. On the other hand, for \( x = 0.3 \) (Fig. 4-4b), the X-ray spectrum suggests the presence of a mixture of TTB phases SBN and BN.

4.3.2 Temperature effect

In order to understand the formation route of sol-gel derived SBN powders, we studied the evolution of structural properties of SBN30, SBN50, SBN60, SBN75 and SBN80 powders as a function of annealing temperature ranging from 600 °C to 1400 °C. Figure 4-5a to Fig. 4-5e shows the XRD spectra of these SBN powders annealed at different temperatures respectively. For SBN50, the TTB structure can be observed with the annealing temperature as low as 1000 °C. The structure completely developed at 1200 °C. At higher temperature like 1400 °C, it is found that there is no change in the structure of SBN50. Therefore, it seems that SBN50 can be formed at lower annealing
temperature. Consider SBN60 (Fig. 4-5c), at annealing temperature below 1000 °C, the XRD spectrum is SN-like. As the annealing temperature is increased, the characteristic SBN peaks are observed while the SN peak at 2θ = 29.1° gets weaker. At 1400 °C, the spectrum is essentially the same as the TTB phase SBN60 single crystal. Similar features are also observed in SBN75 (Fig. 4-5d) and SBN80 (Fig. 4-5e). However, in the spectrum of SBN80 at 1400 °C, the observation of SN peak at 2θ = 29.1° indicating that the SN phase still exists in the powders.

On the other hand, Figure 4-5a shows the XRD spectra for SBN30 annealed in different temperatures. At annealing temperature 600 °C, weaker peaks corresponding to the BN phase are observed. As the temperature increases to 1000 °C, these peaks are enhanced. As the annealing temperature increased to 1200 °C, the intensity of these characteristic peaks of BN (2θ = 28.4° and 29.8°) diminishes with the enhancement of the SBN characteristic peaks. When the annealing temperature is increased to 1400 °C, the spectrum becomes SBN liked, with no BN phase is observed.

In summary, for SBN50, the annealing temperature for a complete TTB phase SBN structure is 1200 °C. While for SBN60, SBN75 and SBN30, this temperature increases to about 1400 °C. However, for SBN80, even at 1400 °C annealing temperature, mixed phases of orthorhombic SN and TTB phase SBN are obtained. We believe that the formation of SBN consists of two parallel reaction processes of BN and
SN at low temperatures, and thereafter these two phases form a solid solution of SBN at a much higher temperature. From Fig. 4-4 and 4-5, the ratios of intensity of SN/SBN are observed to increase with increasing mole ratio of strontium. This result indicates that the temperature for a complete formation of the TTB phase SBN is higher with larger $x$. This evidence is consistent with the results in SBN powders prepared by the mixed-oxide route [4.7].
Figure 4-5(a) XRD spectra of SBN30 with different annealing temperatures.
Figure 4-5(b) XRD spectra of SBN50 with different annealing temperatures.
Figure 4-5(c) XRD spectra of SBN60 with different annealing temperatures.
Figure 4-5(d) XRD spectra of SBN75 with different annealing temperatures.
Figure 4-5(e) XRD spectra of SBN80 with different annealing temperatures.
CHAPTER 5
RAMAN SPECTROSCOPY

5.1 INTRODUCTION
The subject of inelastic light scattering was first investigated theoretically by Brillouin[5-1], who published a study of light scattering by density waves in liquids in 1922. A year later Smekal extended this fundamental work to two level atoms [5-2]. As a result of Smekal's prediction elementary excitations would produce shifts in the frequency of the scattered photon. Inelastic light scattering was first observed experimentally by Raman [5-3] in 1928. This phenomenon is often called the Smekal-Raman effect, but is now more commonly known as Raman scattering. This method is an excellent non-destructive probe of elementary excitations in a crystal. The basic idea of Raman scattering is that an incident photon of energy $\hbar \omega_L/2\pi$ interacts with elementary excitations within the system and raises the energy of the system to an intermediate state of different energy. The system then relaxes to a lower stationary state with the emission of a photon. The energy of the final state, $\hbar \omega_S/2\pi$, may be less or greater than the energy of the initial state, and is called Stokes or anti-Stokes scattering respectively. The frequency shift, $\mid \omega_L - \omega_S \mid$, also called the Raman shift, is the characteristic of the excitations that occur in the sample. In general, Stokes and anti-Stokes scattering yield equivalent information, and since
Stokes scattering intensities are normally stronger, Stokes spectra are often sufficient and preferred.

5.2 RAMAN SCATTERING THEORY

5.2.1 Quantum theory of Raman scattering

The Hamiltonian describing the interaction of an electromagnetic field with a solid can be written as [5.4 - 5.6],

\[ H = H_e + H_i + H_{ei} + H_p + H_{er} + H_{ir} + H_{ep} \]  \hspace{1cm} (5-1)

where \( H_e \), \( H_i \) and \( H_p \) are the Hamiltonians of the electrons, the ions and photons respectively. \( H_{ei} \), \( H_{er} \) and \( H_{ir} \) represents the electron-ion, electron-radiation and ion-radiation interaction respectively. The last term \( H_{ep} \) is the electron-phonon interaction. Under the adiabatic approximation, \( H_e + H_i + H_{ei} \) can be solved and the electron and phonon ground eigenstates and eigenvectors can be determined.

In order to simultaneously describe spontaneous and stimulated light scattering, a second-quantization notation will be used. By using photon creation and annihilation operators \( \hat{a}_k^\dagger \) and \( \hat{a}_k \) respectively, the Hamiltonian \( H_p \) can be rewritten as:

\[ H_p = \sum_k \frac{1}{2\omega(\mathbf{k})} (\hat{a}_k^\dagger \hat{a}_k^\dagger + \hat{a}_k \hat{a}_k) \]  \hspace{1cm} (5-2)

The thermodynamic expectation value is given by

\[ \langle H_p \rangle_k = \omega(\mathbf{k})(n_k + \frac{1}{2}) = V\omega_c <E^2>_k = \frac{V\omega^2}{c^2 <A^2>_k} \]  \hspace{1cm} (5-3)
where \( n_k \) is the thermal equilibrium statistical factor and \( V \) the volume under consideration. \( \mathbf{E}(r) \), the electric field operator, and \( \mathbf{A}(r) \), the corresponding vector potential operator, can be obtained from Maxwell's equations [5-7,5-8]:

\[
\mathbf{A}(r) = \sum_k \left( \frac{1}{2\varepsilon_0 V \omega(k)} \right)^{\frac{1}{2}} (a_k e^{ikr} + a_k^* e^{ikr}) \mathbf{e}_k \tag{5-4}
\]

\[
\mathbf{E}(r) = \sum_k \left( \frac{\omega(k)}{2\varepsilon_0 V \omega(k)} \right)^{\frac{1}{2}} (a_k e^{ikr} + a_k^* e^{ikr}) \mathbf{e}_k \tag{5-5}
\]

where \( \mathbf{e}_k \) represents the polarization vectors of the electric fields and the equations apply to photons propagating in free space. Consider the kinetic energy of the electron:

\[
\frac{1}{2} \sum_j \left[ (p_j + \mathbf{A}(r_j))^2 \right] = \frac{1}{2} \sum_j (p_j)^2 + \frac{1}{2} \sum_j [\mathbf{A}(r_j)]^2 + \frac{1}{2} \sum_j [p_j \cdot \mathbf{A}(r_j) + \mathbf{A}(r_j) \cdot p_j] \tag{5-6}
\]

\[
= \frac{1}{2} \sum_j (p_j)^2 + H_\sigma + H_\sigma^* \tag{5-7}
\]

where \( j \) runs over all electrons. The electron-photon Hamiltonian \( H_{\sigma r} \) has two terms: \( H_\sigma^* \), linear in the electromagnetic field, and a quadratic term \( H_\sigma \). The expression for \( H_{\sigma r} \) in terms of \( a_k \) and \( a_k^* \) are easily obtained from equation (5-4) and (5-6):

\[
H_{\sigma r} = \sum_j \frac{1}{2} \left( \frac{\omega}{2\varepsilon_0 V} \right)^{\frac{1}{2}} a_{kL} e^{ikLr} e_L \cdot (p_j + \frac{1}{2} k_L) + \omega \frac{1}{2} a_k^* e^{ikr} e_L (p_j - \frac{1}{2} k_j) \tag{5-7}
\]
\[ H_{\epsilon} = \sum_j \frac{1}{2V\varepsilon_0 \omega_j^2 \omega_L^2} (\mathbf{e}_s \cdot \mathbf{e}_L) e^{i(\mathbf{k}_j \cdot \mathbf{r})} \] 

To obtain the first order Raman cross section, we consider a photon bringing the system from the ground state to an excited state. By using the adiabatic approximation, we can write the state function as the product of two terms, namely, the electronic part and the vibrational part. Considering the scattering process involves only the phonon from the initial vibrational state \( n_0 \) to the final vibrational state \( n_f \) while the electronic wave functions \( \psi_0 \) the initial and final state are the same, we notice that the Hamiltonian \( H_{\epsilon} \) does not contribute to the scattering. Hence, the sole contribution to the phonon scattering arises from \( H_{\epsilon} \). Using second-order perturbation theory, the stokes cross section becomes [5-6]:

\[
\frac{\partial^2 \sigma}{\partial \omega \partial \Omega} = \frac{\omega^2}{\omega_L^2} \left[ \sum_{i,n_i} <0,n_i|e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_s \cdot (\mathbf{p} - \frac{1}{2} \mathbf{k}_L)|i,n_i> \times 
<0,n_0|e^{i\mathbf{k}_L \cdot \mathbf{r}} \mathbf{e}_L \cdot (\mathbf{p} + \frac{1}{2} \mathbf{k}_L)|0,n_0> \frac{1}{\omega_{i,n_i} - \omega_{0,n_0} - \omega_L} + \text{NRT}\right] \delta(\omega_{0,n_0} - \omega_{0,n_0} - \omega_L)
\]

(5-9)

where the angular brackets represent the thermodynamic average over \( n_0 \) and \( n_f \). In equation (5-9) we have only written the resonant terms explicitly which exhibits resonance for \( \omega_{i,n_i} - \omega_{0,n_0} \approx \omega_L \). The nonresonant terms (NRT) are obtained from the resonant terms by permuting \( \mathbf{e}_L, \mathbf{k}_L \).
with \( e_s, k_s \) and changing \(-\omega_L \) into \( +\omega_s \). Similar to the classical case [5-4], by defining the transition susceptibility of the solid as:

\[
\chi_s = \frac{4\pi V^{-1}}{\omega_s \omega_L} < \sum_{i, n_i} < \omega, n_o + |p|, n_i > \times < i, n_i | p | 0, n_o > \times \frac{1}{\omega_{i, n_i} - \omega_{s, n_o} - \omega_L} + NRT >
\]

(5-10)

we get the first order Stokes cross section as

\[
\frac{\partial^2 \sigma_s}{\partial \omega_k \partial \Omega} = \frac{\omega_s^4 V}{(4\pi)^2 c^2} |e_s \chi_s e_L|^2
\]

(5-11)

On comparison to the classical scattering theory [5.8], we find the relation

\[
\chi_s = \frac{\partial \chi}{\partial \xi} < \xi^{+} >^2
\]

(5-12)

where the susceptibility \( \chi_s \) is defined as the dipole moment per unit volume induced by a unit field.

Since our interest is not the absolute cross section, the most important part is the factor \( |e_s \chi_s e_L|^2 \) which allows us to derive the selection rules. The above discussion is suitable for most nonresonant \((\omega_L \neq (\omega_o + \omega_t)\) in equation 5-9) Raman processes in solids. For the near-resonant situation the cross section will be strongly modified from the nonresonance case.
5.2.2 Resonant light scattering

To obtain the phonon Raman scattering cross section under resonant situation, we can apply the Born-Oppenheimer wavefunction approximation to the eigenstates in order to evaluate the transition susceptibility $\chi_s$ in equation (5.10). First, we define a normal coordinate dependent electronic polarizability $P_\omega(\xi)$ which only depends on the initial and intermediate electronic states $|o>$ and $|i>$ respectively, and expand $P_\omega(\xi)$ in a power series of $\xi$:

$$P_\omega(\xi) = P_\omega(0) + \left( \frac{\partial P_\omega}{\partial \xi} \right)_o \xi + \ldots$$  \hspace{1cm} (5.13)

where $P_\omega(\xi) = <i | p | o>$. Substituting equation (5.13) into (5.10), we get [5-9, 5-10]

$$\chi_s = \sum_i \sum_{n_i} \chi_{i,n_i} = \sum_i \sum_{n_i} \frac{1}{\omega_{i,n_i} - \omega_{o,n_o} - \omega_L} + \sum_i \sum_{n_i} \frac{1}{\omega_{i,n_i} - \omega_{o,n_o} - \omega_L}$$

$$\neq \left( \frac{\partial P_\omega}{\partial \xi} \right)_o \xi + \ldots$$  \hspace{1cm} (5.14)

The first term on the right hand side of the expression is called the Frank-Condon polarizability and usually contributes to elastic scattering in solids. The second term is called the Herzberg-Teller term. We can evaluate this term by solving the first order electron-phonon interaction Hamiltonian $H_{ep}$ which arises from a mixture of intermediate state
i with other states \( j \) via the potential change induced by the phonon displacement. Applying the first-order theory, we get

\[
\left( \frac{\partial P_{i \rightarrow j}}{\partial \xi} \right)_0 = \sum_j P_{i \rightarrow j}(0) \frac{\langle i | H_{\text{ep}} | j \rangle}{\omega_i - \omega_j}
\]  \hspace{1cm} (5-15)

Including equation (5-15) into the Herzberg-Teller term, we notice that the matrix element \( \langle n_f | \xi | n_i \rangle = \delta_{n_f \rightarrow n_i} \) for one-phonon Stokes \( (n_f = n_i + 1) \) and anti-Stoke scattering \( (n_f = n_i - 1) \) respectively. With the static approximation [5-11], the Herzberg - Teller term simplifies as

\[
\sum_{i,j} \frac{\langle n_f | P_i(0) | n_i \rangle < i | H_{\text{ep}} | j > < n_j | P_j(0) | n_o \rangle}{(\omega_{j,n_o} - \omega_{n_o,n_i} - \omega_L)(\omega_{i,n_o} - \omega_{a,n_i} - \omega_L)}
\]  \hspace{1cm} (5-16)

When denominator of equation (5-16) becomes small, the Raman scattering cross section will be large. Experimentally, we achieve this condition by tuning the incident photon energy such that either \( \omega_L \) equals to \( \omega_i - \omega_o \) (incoming resonance: the incident radiation energy equal to an electronic transition) or \( \omega_s \) equal to \( \omega_i - \omega_o \) (outgoing resonance: the scattered radiation energy equal to an electronic transition).

### 5.2.3 Conservation laws and selection rules

The kinematics of Raman scattering processes are governed by conservation law of energy and momentum:

\[
\omega_i = \omega_L \pm \omega_R \hspace{1cm} ; \hspace{1cm} \mathbf{k}_i = \mathbf{k}_L \pm \mathbf{k}_R
\]  \hspace{1cm} (5-17)

Momentum conservation for phonons can be re-expressed as
\[ q_R \approx 0 \]  \hspace{1cm} (5-18)

which is reasonable for typical values of photon and crystal wavevectors. The range of wavevectors, from forward to back scattering is

\[ 0 < q < 2.6 \times 10^7 \text{ m}^{-1} \]  \hspace{1cm} (5-19)

and is thus two or three orders of magnitudes smaller than the typical Brillouin zone edge \((-\pi/d, d \text{ being a lattice constant})\). Raman scattering is thus often described as a probe of zone centre \( q = 0 \) phonons.

The dependence of the Raman scattering cross section on a tensor in equation (5-11) has led to the definition of a “Raman tensor” \( R \) as

\[ \frac{d\sigma}{d\omega} \sim |e_s \cdot R \cdot e_L|^2 \]  \hspace{1cm} (5-20)

The spatial properties of the scatterer can be described by the irreducible representations of its symmetry group. Let \( \Gamma_R \) be the irreducible representation appropriate to the excitation, while \( \Gamma_{VS} \) and \( \Gamma_{VL} \) be the irreducible representations for the polar vectors \( e_s \) and \( e_L \) in the point group of the crystal. For the scattering cross section equation (5-20) to be invariant, \( \Gamma_R \) must contain components that vary like the irreducible representations

\[ \Gamma_R = \Gamma_{VS}^* \times \Gamma_{VL} = \Gamma_{R1} + \Gamma_{R2} + \ldots \]  \hspace{1cm} (5-21)

Poulet and Matthew [5.12] give a full account of the calculation of selection rules and symmetry properties of the Raman tensor. These are tabulated in a variety of references [5.12, 5.13].
5.3 EXPERIMENTAL PROCEDURE

Figure 5-1 is a schematic representation of the set-up for our Raman measurements. Raman spectra for the powders were excited by 488 nm laser light from a CW argon gas laser (Coherent Innova 70). The output power was kept at 50 mW to avoid laser annealing of the samples. All measurements were performed at room temperature. An interference filter (Oriel Model no. 52640) with a bandwidth of 3 nm was employed to filter the unwanted laser lines (plasma emission). A camera lens (Canon FD 85mm 1:1.8) was used for collecting the scattered light which was analysed and detected using a double grating monochromator (Spex 1403) equipped with a cooled photomultiplier tube (Hamamatsu R928). All spectra were recorded in the small-angle scattering geometry. The resolution here obtained could be as good as 0.1 cm\(^{-1}\). A nonlinear least-square fitting routine was used to fit the spectra with the Lorentzian type bands plus a linear background. From each fitting three parameters (position, intensity and full width at half maximum) for each peak were obtained. The errors in determining the parameters of the spectral lines were equal to ±1 cm\(^{-1}\) for the positions and ±2 cm\(^{-1}\) for the widths.
5.4 RESULT AND DISCUSSION

5.4.1 Composition effect

Figure 5-2a shows the unpolarized Raman spectrum in the vicinity of the optical phonon frequencies for single crystal Sr_{0.6}Ba_{0.4}Nb_{2}O_{6} (SBN60). In general, two groups of lines corresponding to the fundamental vibrations can be separated in the vibrational spectrum of SBN: (1) peaks in the region below 150 cm\(^{-1}\) are assigned to the relative movement of the metal cations with respect to the octahedra framework. They are usually called external vibrations; and (2) peaks in the region between 200-800 cm\(^{-1}\) belong to deformation vibration of the oxygen framework. They are called internal vibrations to distinguish them from the external vibrations. Similar to the spectrum given by Amzallag et. al [5.14], two broad and strong A_{1}(TO) phonons at 260 cm\(^{-1}\) and 635 cm\(^{-1}\), one weak B_{1}(TO) phonon at 155 cm\(^{-1}\), and one weak B_{2} phonon at 420 cm\(^{-1}\) are observed. Since there are 132 optical phonon modes in the unit
cell, it is possible that several nearly degenerate modes may occur and appear as one band. This degeneracy would contribute to the broadening of the band and asymmetric line-shape.

Figure 5-2b and 5-2h shows the spectra of BN and SN respectively. The spectra of SN and BN, which carry far more features than the spectrum of single crystal SBN, are very similar to the spectra reported by Repelin [5.15]. All the peak frequencies and the assignments of SN, BN and single crystal SBN are given in Table 5-1.

Table 5-1 Symmetries, frequencies and assignment of several optical modes of SN powder, BN powder and single crystal SBN60 at room temperature.

<table>
<thead>
<tr>
<th>SrNb₂O₆</th>
<th>SBN60 Single Crystal</th>
<th>BaNb₂O₆</th>
<th>Symmetry</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>129(s)</td>
<td>116(s)</td>
<td>A₁</td>
<td></td>
<td>external bands movement of metal cation w.r.t. NbO₆</td>
</tr>
<tr>
<td>138</td>
<td>155</td>
<td>B₁</td>
<td></td>
<td>deformation O-Nb-O δ(O-Nb-O)</td>
</tr>
<tr>
<td>185</td>
<td>185</td>
<td>A₁</td>
<td></td>
<td>elongation Nb-O v(Nb-O) deformation O-Nb-O δ(O-Nb-O)</td>
</tr>
<tr>
<td>200</td>
<td>227</td>
<td>B₁</td>
<td></td>
<td>elongation O-Nb-O v(Nb-O) deformation O-Nb-O δ(O-Nb-O)</td>
</tr>
<tr>
<td>227</td>
<td>227</td>
<td>B₁</td>
<td></td>
<td>deformation O-Nb-O</td>
</tr>
<tr>
<td>269</td>
<td>260</td>
<td>A₁ B₁</td>
<td></td>
<td>deformation O-Nb-O δ(O-Nb-O) elongation Nb-O v(Nb-O)</td>
</tr>
<tr>
<td>290</td>
<td>304</td>
<td>A₁ B₁</td>
<td></td>
<td>deformation O-Nb-O δ(O-Nb-O) deformation Nb-O-Nb δ(Nb-O-Nb) elongation Nb-O v(Nb-O)</td>
</tr>
<tr>
<td>325</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>354</td>
<td>366</td>
<td>B₂</td>
<td></td>
<td>deformation O-Nb-O δ(O-Nb-O) torsion</td>
</tr>
<tr>
<td>388</td>
<td>379</td>
<td>A₁</td>
<td></td>
<td>elongation Nb-O v(Nb-O)</td>
</tr>
<tr>
<td>429</td>
<td>420</td>
<td>B₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>475</td>
<td>492</td>
<td>B₁</td>
<td></td>
<td>elongation Nb-O v(Nb-O)</td>
</tr>
<tr>
<td>581(s)</td>
<td>550</td>
<td>A₁</td>
<td></td>
<td>elongation Nb-O v(Nb-O)</td>
</tr>
<tr>
<td>629</td>
<td>635</td>
<td>A₁ B₁</td>
<td></td>
<td>elongation Nb-O v(Nb-O)</td>
</tr>
<tr>
<td>688(s)</td>
<td>713</td>
<td>B₁</td>
<td></td>
<td>elongation Nb-O v(Nb-O)</td>
</tr>
</tbody>
</table>
Figure 5-2 Raman spectra of (a) SBN60 single crystal, (b) BN, (c) SBN30, (d) SBN50, (e) SBN60, (f) SBN75, (g) SBN80 and (h) SN are annealed at 1200°C.
The observed external A
mode in BN is smaller than that in SN because of the heavier mass of the metal cations in BN. As x = 0.8 (Fig. 5-2g), the SBN spectrum is identical to that of SN except that the peaks become broader with the evolution of two broad underneath features around 250 cm
and 650 cm
. These broad features become more prominent while the SN peaks get weaker as x decreased to 0.6 (Fig. 5-2e). As x = 0.5 (Fig. 5-2d), the spectrum is akin to the TTB phase SBN single crystal except that the phonon peaks are broader. As x is further reduced to 0.3 (Fig. 5-2c), the two broad features with individual phonon peaks, which resemble phonons in BN, are observed. Similar to XRD results, these findings indicate that for x < 0.5, the powders consist of a mixture of TTB phase SBN and BN powders, and as x > 0.5, the powders are composed of mixed TTB phase SBN and SN powders. However, for x = 0.5, the powders are mainly single TTB phase SBN powders.

5.4.2 Temperature Effect

In order to understand the formation route of sol-gel derived SBN powders, we studied the evolution of structural properties of SBN30, SBN50, SBN60, SBN75 and SBN80 powders as a function of annealing temperature. Figures 5-3a, 5-3b, 5-3c 5-3d and 5-3e show the Raman spectra of these SBN powders respectively. As mentioned in Chapter 4, SBN50 (Fig5-3b) started to give TTB structure when the annealing temperature is at 1000 °C. The structure completed when the annealing temperature is equal to 1200 °C. For SBN60 (Fig5-3c), at low annealing
temperature, the Raman spectrum is SN-like. As the annealing temperature is increased, the phonon peaks become broader with the evolution of two broad underneath features around 250 and 650 cm\(^{-1}\). These broad features become more noticeable while the SN peaks get weaker at higher annealing temperature. At 1400 °C, the spectrum is essentially the same as the TTB phase SBN60 single crystal (Fig. 5-2a). This indicates that TTB phase SBN peaks are enhanced while the orthorhombic SN phase are suppressed as the annealing temperature is increased. Similar effects are also observed for SBN75 and SBN80. Compare Figures 5.3c and 5.3d carefully, at 1200 °C, the SBN75 spectrum contains a very smooth SBN profile with only a weak characteristic SN peak at 688 cm\(^{-1}\). On the other hand, for SBN80, the spectrum is more SN like with several noticeable SN peaks observed at 227, 269, 290, 320 and 581 cm\(^{-1}\). As the annealing temperature further increased to 1400 °C, the SBN75 spectrum is very similar to that of single crystal with no SN peak is observed. This implies that the powders contain mainly TTB type SBN structure. However, for SBN80, there are still few characteristic SN peaks remaining in the spectrum indicating that SBN80 powders contain both orthorhombic SN and TTB phase SBN powders. These results consist with the results observed in our XRD measurements.

Figure 5-3a shows the Raman spectra of SBN30 with various annealing temperatures ranging from 600 °C to 1400 °C. At 600 °C, it is obvious that crystalline BN phase is occurred. As the temperature
further increases ($< 1200 \, ^\circ\text{C}$), the peak intensities of these BN peaks increase. At 1200 $^\circ\text{C}$, two broad peaks at 250 cm$^{-1}$ and 650 cm$^{-1}$ start to develop with the BN peaks get weaker. At 1400 $^\circ\text{C}$, the spectrum becomes very similar to that of SBN60 single crystal.

Based on these findings, it seems that the formation of SBN arises from two parallel routes: BN and SN are formed at lower annealing temperature, then the two phases combine and form SBN. For $x = 0.5$, that is SBN50, the complete formation temperature for TTB phase SBN is around 1200 $^\circ\text{C}$. However, for $x < 0.5$ and $x > 0.5$, a higher annealing temperature is need. This temperature depends on the Sr/Ba ratio. The temperature will increase with the deviation of this Sr/Ba ratio from 0.5. Therefore, we proposed that annealing temperatures play an important role in the formation of SBN. Higher annealing temperature is needed for $x \neq 0.5$. Based on these results of the Raman spectra and XRD patterns at various temperatures, the following formation mechanism is proposed:

$$
\begin{align*}
x \text{Sr(OR)$_2$} + (1-x) \text{Ba(OR)$_2$} + 2 \text{Nb(OR)$_2$} & \xrightarrow{\text{reflux}} x \text{SrNb}_2(\text{OR})_2 + (1-x) \text{BaNb}_2(\text{OR})_2 \\
& \xrightarrow{\text{hydrolysis}} x \text{SrNb}_2\text{O}_6 + (1-x) \text{BaNb}_2\text{O}_6 \\
\text{amorphous powder} & \xrightarrow{600^\circ\text{C} - 900^\circ\text{C}} x \text{SrNb}_2\text{O}_6 + (1-x) \text{BaNb}_2\text{O}_6 \\
\text{crystalline powder} & \xrightarrow{1000^\circ\text{C} - 1400^\circ\text{C}} \text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 \text{ Powders}
\end{align*}
$$
Figure 5-3(a) The Raman spectra of SBN30 in different annealing temperatures.
Figure 5-3 (b) Raman Spectra of SBN50 in different annealing temperatures.
Figure 5-3 (c) Raman Spectra of SBN60 in different annealing temperatures.
Figure 5-3(d) Raman spectra of SBN75 in different annealing temperatures.
Figure 5-3(e) Raman spectra of SBN80 in different annealing temperatures.
CHAPTER 6

DIELECTRIC PROPERTIES

6.1 INTRODUCTION

For ferroelectric materials, dielectric properties are one of the most important properties because of their application in electrical and electronic devices. Ceramic materials that are good electrical insulators are regarded as dielectric materials. Although these materials do not conduct electric current when an electric field is applied, they are not inert to the electric field. The field causes a slight shift in the balance of charge within the material to form an electric dipole and this is where the term 'dielectric' originated from. Figure 6-1 shows the schematic diagram for the change of distribution of charges within the ferroelectric ceramics with an external applied field.

6.2 THEORY

6.2.1 Polarisation

The formation of an electrical dipole is called polarisation. There are several types of polarisation: (1) electronic polarisation; (2) orientation (dipolar) polarisation; (3) space charge polarisation, and (4) atomic or ionic polarisation.
Figure 6-1 The change of distribution of charges of a ceramic with two different polarization direction.

Electronic polarisation occurs in all dielectric materials. It results from a displacement of the centre of the negatively charged electron cloud relative to the positive nucleus of an atom by the electric field. Once the electric field is removed, they move back to their original positions, resulting in no polarisation. This effect, analogous to elastic stress and strain, is comparatively small to other mechanism because of the tiny displacement of electrons.
Orientation polarisation involves nonsymmetrical molecules that constrain permanent electric dipoles. One of the most common examples is water which has a chemical formula, H₂O, containing covalent bonds between the hydrogen and oxygen atoms. Because of the effect of lone pair electrons (not formed covalent bond with hydrogen electrons) the two hydrogen atoms are on one side of the oxygen atom. The hydrogen side of the molecule has a net positive charge and the oxygen side has a net negative charge. Under an electric field, the molecules will align with the positive side facing the negative electrode and the negative side facing the positive electrode. The effect of orientation polarisation is comparatively larger than electronic polarisation. This is because larger charge displacement is possible in the relatively large molecules compared to the spacing between the electron and nucleus in individual atoms.

The third source of polarisation is called space charge polarisation. Space charges are random charges caused by cosmic radiation, thermal deterioration, or are trapped in the material during the fabrication process.

The fourth type of polarisation is the atomic or ionic polarisation which occurs in ionic materials. It involves displacement of atoms or ions within a crystal structure when an electric field is applied. A wide range of polarisation effects is possible through this mechanism depending on the crystal structure, the presence of solid solution, and other factors. Examples include pyroelectricity, piezoelectricity, and ferroelectricity.
On the whole, the total polarisation $P$ of a substance is equal to the sum of the electronic, orientation, space charge and ionic polarisation. It is possible for one or more of these contributions to the total polarisation to be either absent or negligible in magnitude relative to the others. For example, ionic polarisation will not exist in covalent bonded materials in which no ions are present.

### 6.2.2 Dielectric constant

The degree of polarisability or charge storage capability of a material is identified by the term relative dielectric constant ($K'$). This is also referred to as relative permittivity. When an electric field is applied to two flat plates of a metal such that one plate becomes positive and the other negative, this applied electric field will cause polarisation in the material between the conductive plates. The relative dielectric constant compares the polarisability or charge storage capability of the material with that of a vacuum between the plates [6.1]:

$$K' = \frac{K_{\text{material}}}{K_{\text{vacuum}}} = \frac{\varepsilon^*}{\varepsilon_0} \quad (6.1)$$

Obviously, for vacuum, $K'$ equals to 1. For most of the materials, $K'$ will be larger than 1. For example, dry air at 0 °C and standard atmospheric pressure, $K'$ is 1.0006. Table 6-1 lists the relative dielectric constant for a variety of materials [6.1].

---

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### Table 6-1 Relative dielectric constant for different materials [6.1]

<table>
<thead>
<tr>
<th>Material</th>
<th>$K'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>5.9</td>
</tr>
<tr>
<td>LiF</td>
<td>9.0</td>
</tr>
<tr>
<td>KBr</td>
<td>4.9</td>
</tr>
<tr>
<td>MgO</td>
<td>2.5-7.3</td>
</tr>
<tr>
<td>BaO</td>
<td>6.6</td>
</tr>
<tr>
<td>BeO</td>
<td>34</td>
</tr>
<tr>
<td>Diamond</td>
<td>5.7</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>8.6-10.6</td>
</tr>
<tr>
<td>Mullite</td>
<td>6.6</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>15-170</td>
</tr>
<tr>
<td>Cordierite</td>
<td>4.5-5.4</td>
</tr>
<tr>
<td>Porcelain</td>
<td>6.0-8.0</td>
</tr>
<tr>
<td>Forsterite (Mg$_2$SiO$_4$)</td>
<td>6.2</td>
</tr>
<tr>
<td>Fused SiO$_2$</td>
<td>3.8</td>
</tr>
<tr>
<td>Steatite</td>
<td>5.3-7.5</td>
</tr>
<tr>
<td>High-lead glass</td>
<td>19.0</td>
</tr>
<tr>
<td>Soda-lime-silica glass</td>
<td>6.9</td>
</tr>
<tr>
<td>Zircon</td>
<td>8.8</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>1600</td>
</tr>
<tr>
<td>BaTiO$_3$ + 10% CaZrO$_3$ + 1% MgZrO$_3$</td>
<td>5000</td>
</tr>
<tr>
<td>BaTiO$_3$ + 10% CaZrO$_3$ + 10% MgZrO$_3$</td>
<td>9500</td>
</tr>
<tr>
<td>Paraffin</td>
<td>2.0-2.5</td>
</tr>
<tr>
<td>Beewax</td>
<td>2.07-3.0</td>
</tr>
<tr>
<td>Rubber, polystyrene, polycrylates</td>
<td>2.0-3.5</td>
</tr>
<tr>
<td>Phenolic</td>
<td>7.5</td>
</tr>
</tbody>
</table>
Note the wide range in values of dielectric constant for different materials. Materials with low dielectric constant are used for electrical insulator applications. For example, Al$_2$O$_3$, BeO, AlN, and some polymers are used for insulation in integrated circuits (substrates and packages). Rubber and other flexible polymers are used for insulation on electrical wire. Electrical porcelain, forsterite, and steatite are used as electrical insulators. Materials with high dielectric constant are used in capacitors for charge storage and other functions. Capacitors and their functions will be discussed later in this chapter.

The dielectric constant is affected by temperature. The nature of the effect depends on the source of polarisation. Electronic polarisation is relatively insensitive to temperature, so temperature has little effect on the dielectric constant. Molecular orientation polarisation is opposed by thermal agitation, so the dielectric constant goes down as the temperature increases. Atomic/ionic polarisation tends to increase with temperature due to an increase in charge carriers and ion mobility. The dielectric constants of BeO and some Al$_2$O$_3$-based compositions are shown as a function of temperature in Figure 6-2 [6.1]. The fact that the dielectric constant increased with temperature suggests that atomic/ionic polarisation is the dominant mechanism.
The frequency of the applied electric field or the frequency of other electromagnetic fields impinging on the material also affects the dielectric constant. The polarisation requires time to respond to an applied field. Electronic polarisation occurs very rapidly and is present even at high frequencies. For example, visible light is of relatively high
frequency (10\textsuperscript{15} cycles per second) and has an electric interaction with the electronic polarisation of a dielectric. This is discussed later in this chapter under optical properties. Molecular polarisation is only affected by low frequencies. In a high-frequency field, the molecules do not have time to realign with each cycle. Examples of the effect of frequency and the combined effects of frequency and temperature for several materials are illustrated in Figure 6.3 [6.1].

6.2.3. Dielectric Strength

Another important dielectric property is the dielectric strength which is the capability of the material to withstand an electric field without breaking down i.e. no electrical current can pass. It has unit of volts per unit thickness of the dielectric material. Volts per mil (10\textsuperscript{-3} inch) or volts per centimetre are often used.
Figure 6-3 Effect of frequency and temperature on the dielectric constant of (a) Al₂O₃ crystal (with the electric field aligned normal to the c axis) [6.3], (b) soda-lime-silica glass [6.4].
6.2.4. Dielectric loss

An ideal dielectric would permit no electric charge flow. Instead, only a displacement of charge via polarisation is allowed. If a thin plate of such an ideal material are placed between parallel plate electrodes to form a capacitor with an alternating (sine wave) applied electric field, the current will lead the voltage by a phase angle of $\pi/2$ or 90°. Under this circumstance, no power would be absorbed by the dielectric and the capacitor would have zero loss. However, real materials always have some loss. The phase angle between the current and voltage is not exactly 90°; the current lags slightly behind what it would be in an ideal dielectric. The angle of lag is defined as $\delta$ and the amount of lag becomes $\tan \delta$ which is referred to as the loss tangent and is equal to $K''/K'$. Here $K'$ is the relative dielectric constant and $K''$ is defined as the relative loss factor [6.1]. The dielectric loss and dielectric constant are usually larger in polycrystalline materials.

Dielectric loss results from two mechanisms: (1) ion migration; (2) ion vibration and deformation. The most important mechanism for ceramics is ion migration that is strongly affected by temperature and frequency. The losses due to ion migration increase at lower frequencies and higher temperature.
6.2.5. Capacitance

A dielectric material placed between two electrically conductive electrodes is called capacitor. When placed in an electric circuit, the capacitor is able to store electrical charge. The larger the degree of polarisability of the dielectric material, the higher the relative dielectric constant will be and the more charge that can be stored.

The amount of charge, \( Q \), that can be stored is equal to the applied voltage, \( V \), times the capacitance, \( C \):

\[
Q = CV
\]  \hspace{1cm} (6.2)

The unit of \( Q \) is the coulomb, which is an ampere-second. The unit of \( C \) is the farad. A capacitor has a capacitance of one farad when one coulomb charges it to an electric potential of one volt. One farad is a very large level of capacitance. Most capacitors have capacitance of a much lower level such as a microfarad \( (10^{-6} \text{ farad}) \), a nanofarad \( (10^{-9} \text{ farad}) \), or a picofarad \( (10^{-12} \text{ farad}) \).

The capacitance depends on the relative dielectric constant \( K' \) and the geometry of the capacitor. For a parallel-plate capacitor such as shown in figure 6.1, the capacitance is expressed as:

\[
C = \frac{E_0K'A}{t}
\]  \hspace{1cm} (6.3)

Where

\[ A = \text{total area of the electrodes} \]

\[ t = \text{thickness of the dielectric} \]

\[ E_0 = \text{permittivity of vacuum} \]
Thus the capacitance increases with the area and relative dielectric constant. However, it decreases when the thickness of the dielectric increases.

6.3 EXPERIMENTAL PROCEDURE

6.3.1 Sample treatment

Various compositions of SBN powders were fabricated as mentioned in chapter 3. The annealing temperature was kept at 1200 °C. Approximately same amount of powders were used to prepare all the pellets for dielectric measurements. The SBN powders were first mixed with ethanol which acted as both solvent and binder for disc forming. Then the mixture was put into a cylindrical mould and pressed into circular pellets with diameter of 6 mm and average thickness ~ 0.9 mm. The samples were then put into an oven at a temperature of 200 °C for 2 hour in order to remove all the ethanol inside the samples. After that, the samples were coated with silver paint on both sides. Two pieces of copper discs with diameter equals to 3 mm were used as electrodes. The samples discs were placed between the copper electrodes like sandwiches, and mounted on a sample holder (Figure 3-4). The sample holder was wired to the input terminal of the Helwett Packard 4194A impedance gain-phase analyser. The C_w/D mode was selected in the menu. Capacitance and dielectric loss at 1 kHz and 10 MHz were measured.
The thickness of each sample was measured accurately by a gauge in order to calculate the dielectric constants.

![Diagram of sample discs in sample holder]

**Figure 6-4** Sample discs in sample holder.
6.4 RESULTS & DISCUSSION

From equation 6-3, the relative dielectric constants $K'$ of each samples were calculated. These results were obtained by direction measurement of samples. It can be further transformed into $K_{\text{material}}$ by using equation 6-1. Figure 6-5 shows the dielectric constant and loss factor of SBN powders as a function of x. It is seen that the dielectric constant of our SBN powders has a maximum at $x = 0.5$. These results contradict those reported for single crystal SBN [6.2] in which, the dielectric constant increases as x is increased from 0.25 to 0.75.

In order to elucidate these discrepancies, we consider the structure characteristics of SBN powders as discussed in chapter 4 and 5. We believe that the reduction in dielectric constant at $x > 0.5$ is due to the presence of unwanted SN phase in addition to the TTB phase SBN. It is this unwanted SN phase, which has a much lower dielectric constant, deteriorates the dielectric properties of our SBN powders. In order to verify this, we measured the temperature dependence of the dielectric constant of SBN60 powder. Figure 6-7 shows the dielectric constant of SBN60 powders as a function of annealing temperature. At 1200 °C, the dielectric constants measured at 1 kHz and 10 MHz are 55 and 48 respectively. These values are smaller than that of SBN50 powders (Fig.6.5). As we increased the annealing temperature to 1400 °C, the dielectric constant of SBN60 powder measured at 1 kHz and 10 MHz increased to 86 and 70 respectively. On the other hand, as we increased the annealing temperature to 1400 °C, the dielectric constant of SBN50
remains the same as that of SBN50 annealed at 1200 °C. This means that at annealing temperature of 1400 °C, the dielectric constant of SBN60 is larger than that of SBN50. Therefore, we believe that the enhancement of the dielectric constant for SBN60 between 1200 °C and 1400 °C is due to complete conversion of SBN powders into TTB phase SBN60.
Figure 6-5 The graphs of dielectric constant and loss tangent at
(a) 1 KHz and (b) 10 MHz against strontium content(x).
Figure 6-6 Relationship between dielectric constant and annealing temperature of SBN60 powder.
CHAPTER 7

NONLINEAR OPTICAL PROPERTIES

7.1 INTRODUCTION

Some anisotropic dielectric crystals exhibit a nonlinear polarisation effect. SBN, being in 4mm point group, is one of those materials. In the past, nonlinear effect in conventional materials is so small that it cannot be detected experimentally. However, the availability of lasers has made it possible to study optical nonlinearities in a wide variety of materials. Nonlinear techniques and materials have enormous potential for applications in dynamic holography, wavefront reversal, optical computer and communication. Therefore it is of great interest for us to study the nonlinear optical properties of SBN.

7.1.1 Theoretical background

Based on the Maxwell equations in electromagnetic theory of light, the dielectric and magnetic susceptibility were independent of the strengths of the applied fields.

\[
P = \varepsilon \cdot E; \quad M = (\varepsilon - 1) \cdot H
\]

Equation (7-1) is what we get from classical models. Later, people modified this equation with quantum theories. After several transformations the phenomena observed in the steady state can be
described by a dielectric polarisation density expanded as a power series in the electric field [7.1]:

\[ P_a = X_{a\beta} E_\beta + X^{(2)}_{a\beta\gamma} E_\beta E_\gamma + X_{a\beta\gamma\delta} E_\beta E_\gamma E_\delta + \ldots \] (7-2)

where the subscripts denote Cartesian co-ordinates. The complex tensor coefficients of the higher-order terms are called nonlinear susceptibilities. The first term is responsible for the linear effect. The second term is accountable as the second-harmonic generation (frequency doubling), it governs phenomena like sum and difference-frequency generation, and for parametric amplification and oscillation. The third one is responsible for the third-harmonic generation, stimulated Raman scattering, Brillouin scattering, self-focusing and optical phase conjugation. The unit of the coefficients are in m/V. The nonlinear optical effects are useful in spectroscopy, saturated absorption, stimulated Raman gain, four-wave mixing, multi-quantum absorption sum frequency generation, etc.

### 7.1.2 Second harmonic generation

Second harmonic generation (SHG) is governed by the second term in eq (7.2). It is due to the lacking of centre-of-inversion symmetry in the samples. The driving polarisation is,

\[ P_a^{(2)}(\omega_3) = \chi^{(2)}_{a\beta\gamma}( -\omega_3, \omega_1, \omega_2 ) E_\beta(\omega_1) E_\gamma(\omega_2)e^{-i\omega_3 t} \] (7-3)

where \( \omega_3 = \omega_1 + \omega_2 \) in general. For SHG, \( \omega_1 = \omega_2 \) therefore SHG is also called frequency doubling and can be rewritten as:

---

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\[ P_j(2\omega) = \sum_{j,k} \varepsilon_{jk} d_{jk} E_j(\omega) E_k(\omega) \]  

(7-4)

where \( d_{ijk} \) is a tensor. For point group \( 4mm \) in which SBN belongs to, the \( d_{ijk} \) will be written [7.2]:

\[
\begin{pmatrix}
0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{24} & 0 & 0 \\
d_{31} & d_{31} & d_{33} & 0 & 0 & 0
\end{pmatrix}
\]  

(7-5)

Phase matching is an important requirement of SHG. If the condition is not matched, the doubled frequency could not be seen. Consider the momentum of a photon as \( k \), the following equations must be satisfied:

\[ 2k_1 = k_2 \quad \text{or} \quad 2k(\omega) = k(2\omega) \]  

(7-6)

where \( k = n\omega \kappa / c \), \( \kappa \) is a unit vector normal to the wavefront and \( c \) is the velocity of light. From eq. (7-6), the refractive indices can be written as:

\[ n(\omega) = n(2\omega) \]  

(7-7)

It means that the phase velocity of the fundamental-frequency radiation must be equal to the phase velocity of the SHG. Otherwise, the doubled frequency radiation will be cancelled out by interference within the crystal. The equation for phase matching is [7.1]:

\[ n_0^{2\omega} n_\tau^{2\omega} / [(n_\tau^{2\omega})^2 \sin^2 \theta_\perp + (n_\tau^{2\omega})^2 \cos^2 \theta_\perp]^{-1/2} = n_0^{\omega} \]  

(7-8)

and the solution is

\[ \sin^2 \theta = \frac{(n_\tau^{2\omega})^2 [(n_\tau^{2\omega})^2 - (n_\tau^{\omega})^2]}{(n_0^{\omega})^2 [(n_0^{2\omega})^2 - (n_\tau^{2\omega})^2]} \]  

(7-9)

where \( \theta_m \) is usually called the phase-matching angle, i.e., the angle at which the requirement of phase matching is satisfied.
7.2 EXPERIMENTAL PROCEDURES

7.2.1 The samples

Five samples were under investigation. They are SBN60 thin films coated on fused silica substrates. The thickness of the samples were ~ 1.3 μm. The samples were annealed in temperature range of 500 °C to 800 °C in order to study the dependence of SHG on the annealing temperature.

7.2.2 The setup

SHG properties were measured by a Q-switched Nd:YAG laser at a wavelength of 1.064 μm. The pulse width is 5 ns with a repetition rate of 10 Hz. Fig 7-1 shows the experimental setup for the SHG measurements. The laser beam was split so that the second-harmonic (SH) intensities from the sample (I_s) and from a Y-cut quartz reference (I_0) can be measured simultaneously. To eliminate the influence of the laser output fluctuations, the intensity ratio I_s/I_0 was measured. Both the incident fundamental and the transmitted SH light beams were polarised by using polarisers P_1 and P_2, respectively. Narrow-band filters and monochromators were placed before the detectors to ensure that only the SH intensities were measured.

For calibration, the SH intensity ratio I_Q/I_0 of a Y-cut quartz sample at the same position of the film was measured. Consequently, the second-order nonlinear optical susceptibility, d_{eff}, of the SBN film was determined by comparing the value of I_s/I_0 and I_Q/I_0.
7.3 RESULTS AND DISCUSSION

Figures 7-2a and 7-2b show the SHG intensity of SBN60 thin films annealed at 700 °C and 800 °C respectively in the P-P direction. Figure 7-3 shows the similar SH intensity characteristic graphs in the P-S direction. The P direction is defined as parallel to the plane of incidence; and the S direction is perpendicular to the plane of incidence. The plane of incident is referred to the laser beam. For thin film sample with a thickness much less than the coherence length, the SH intensity generated by a fundamental light with intensity $I(\omega)$ is given by:

$$I_{(2\omega)} \propto [ l_s^2 I^2(\omega) d_{eff}^2 / n^2(\omega) n(2\omega)]$$

(7-10)

where $l_s$ is the film thickness, $d_{eff}$ is the measured effective second-order nonlinear optical susceptibility, $n(\omega)$ and $n(2\omega)$ are the indices of
refraction at frequencies $\omega$ and $2\omega$, respectively, and $l_c$ is the coherence length of the film. For the SH intensity ratio of the SBN film to quartz, $I_s/I_Q$, the factor $n^2(2\omega)n(\omega)/n^2Q(2\omega)nQ(\omega) \sim 3.6$. Taking into account the transmission of the film and substrate $T$ to the SH, eq (7-10) becomes

$$ I_s/I_Q \sim (l_s/l_c)^2 Td_{11}^2/(3.6 \ d_{11,Q}^2) $$ (7-11)

where $l_s,Q \sim 20 \mu m$ is the coherence length of the quartz and $d_{11,Q} = 0.34 \ pm/N$ is the $d_{11}$ of the quartz. This yields,

$$ d_{\text{eff}} \sim (I_c/Q)(l_s/T)(I_s/I_Q) (I_Q/I_0)^{1/2} d_{11,Q} $$ (7-12)

Therefore, by the above equation (7-12) the values of $d_{15}$, $d_{31}$, $d_{33}$ of SBN60 annealed in 700 °C, 800 °C can be calculated. The $d_{33}$, $d_{15}$ and $d_{13}$ of the single crystal and the measured values of our SBN60 films are listed in table 7-1:

| Table 7-1 List of nonlinear optical susceptibility of SBN60 thin films and single crystal. |
|---------------------------------|-----------------|-----------------|-----------------|
| SBN60 Single crystal           | SBN60 thin film annealed in 700 °C | SBN60 thin film annealed in 800 °C |
| $d_{15}$                       | 5.98            | 0.068           | 0.208           |
| $d_{31}$                       | 4.31            | 0.220           | 0.466           |
| $d_{33}$                       | 11.3            | 1.093           | 2.177           |
Figure 7-2 The SH intensity of SBN60 thin film on fused silica substrate annealed in (a) 700 °C and (b) 800 °C in P-p direction.
Figure 7-3 The SH intensity of SBN60 thin film on fused silica substrate annealed in (a) 700 °C and (b) 800 °C in P-S direction.
In order to observe the effect of annealing temperature on the SHG, Figure 7-4 shows the measured $d_{33}$ as a function of the annealing temperature.

![Figure 7-4 The values of $d_{33}$ of SBN60 thin films with different annealing temperature.](image)

It is seen that the annealing temperature has a strong effect on the nonlinear optical properties of the SBN films. From the X-ray data on the sol-gel derived SBN films [7.5], films annealed above 700 °C are in TTB phase SBN. This consists with our observation in Figure 7-4 in which the $d_{33}$ increase by an order of magnitude. However, with annealing temperature increased to 800 °C, the $d_{33}$ is further increased by two folds. This increment at 800 °C indicates that beside the
percentage of the TTB phase in the films will affect the SHG signal, other structure properties of the films may be also important. For example, the packing density of the films, the geometry of the domain walls and the grain size of the films will also have a strong influence on the SHG signal. Generally speaking, inhomogeneities within the bulk of the films typically produce small but distribution variations of refractive index that will induce scattering in the waveguide. We believe that at higher annealing temperature, the porosity of the films was improved so that the measured SHG signal was enhanced. From table 7-1, we also notice that the measured d values are much smaller than those of the single crystal. This may be due to the scattering of laser beam by the back layer of the samples and/or no highly preferred orientation of film growth.

In summary, we have measured the nonlinear optical properties of our sol-gel derived SBN60 films. The measured values are about 1 order of magnitude less than those measured in single crystal. Further improvement of the films qualities will be needed in order to increase the nonlinear optical properties of our films.
CHAPTER 8
CONCLUSION

In our study, strontium barium niobate (Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$) powders were successfully fabricated by sol-gel method. Various values of $x$ from 0 to 1 namely BN, SBN30, SBN50, SBN60, SBN75, SBN78, SBN80, SN were fabricated. Their structural properties and dielectric properties have been measured. In addition to powders, SBN films were also successfully produced. Their nonlinear optical properties were studied by second harmonic generation experiments.

By analysing the Raman and X-ray spectra, we suggest that at annealing temperature = 1200 °C, the SBN powders were a mixture of BN and TTB phase SBN for $x < 0.5$, and SN and TTB phase SBN for $x > 0.5$. This indicates that pure TTB phase SBN powders with $x = 0.5$ could only be obtained at higher annealing temperatures. The formation of SBN seems to consist of two parallel reaction processes of BN and SN, and thereafter these two phases form a solid solution of SBN at a higher annealing temperature. Therefore, the dielectric constants were reduced for $x > 0.5$ because of the presence of the unwanted SN. Since SN has a low dielectric constant compare to SBN.

The nonlinear optical properties of sol-gel derived SBN films have been measured in our SBN thin films. It is found that the values of $d_{33}$, $d_{31}$ and $d_{13}$ are ~1 order of magnitude smaller than that of the SBN60.
single crystal. The reasons of such a phenomenon is probably due to the scattering of laser beam by the substrates and no preferred orientation of the thin films. All these factors made the thin film become not comparable with the bulk.

Future work

Firstly, SBN powders can be fabricated into 0.3 nano-composites which are one of the frontiers in material research. By embedding the SBN powders in optical transparent matrix, for example, sol-gel silica, the optical properties of the composite will be modified. Secondly, sol-gel derived SBN thick films can be fabricated. For opto-electronic devices, films of few microns thick will be needed. Furthermore, studies on improving the structural qualities of sol-gel derived films will also be interesting.
Chapter 1
REFERENCES


REFERENCES


Chapter 2


Chapter 3


**Chapter 4**


REFERENCES


Chapter 5


**Chapter 6**


**Chapter 7**


