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Department of Applied Physics

Preparation and Characterization of Sodium Potassium Niobate-based Electro-Optic Ceramics

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A thesis submitted in partial fulfillment of the requirements for

the degree of Master of Philosophy

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CERTIFICATE OF ORIGINALITY

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Abstract

The main objective of the present work is to develop new lead-free KNN-based electro-optic ceramics. The demand on the electro-optic (EO) materials increases with the rapid development of optic communication technology. The most widely used EO ceramics such as $(Pb_{1-x}La_x)(Zr_{1-y}Ti_y)_{1-x/4}O_3$ (PLZT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ -PbTiO₃ (PMN-PT) are contain a large amount (> 65%) of lead which is highly toxic. For environmental protection reasons, lead-free materials have been extensively studied in recent years as replacements for lead-containing materials. In this work, new lead-free, $(K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO_3 + x mol\% Bi_2O_3$ (abbreviated as KNN-La-xBi) electro-optic ceramics exhibiting good optical transparency and strong linear electro-optic responses have been successfully fabricated.

The two-step sintering technique has been used to fabricate the $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $(K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO_3$ (KNN-La) ceramics. The ceramics were first sintered at a higher temperature T_1 for a period t_1 . Then, the temperature was decreased rapidly to T_2 and held for t_2 . The effects of the sintering conditions on the the grain growth, dielectric, piezoelectric and optical properties of the ceramics have been studied.



Our results reveal that the technique is capable of suppressing the grain growth of the ceramics. The grain growth of the ceramics is mainly affected by the first-step sintering temperature T_1 and sintering time t_1 while the densification is controlled by the second-step sintering temperature T_2 and the dwelling time t_2 . The grain sizes of the KNN ceramics are reduced significantly from ~16 to ~3 µm after applying the two-step sintering technique. The grain sizes of the KNN-La ceramics are slightly reduced from 0.8 to 0.5 µm by the two-step sintering technique. Although the grain size of the KNN-La ceramics is reduced to ~ 0.5 µm, the ceramics only become translucent. Our results also show that the dielectric and piezoelectric properties of the ceramics are not deteriorated by the reduction of the grain size.

Excess Bi₂O₃ has been added as a sintering aid to lower the sintering temperature and suppress the grain growth of the KNN-La ceramics. Our results show that excess Bi₂O₃ is effective in promoting uniform densification as well as suppressing the grain growth of the ceramics. The KNN-La-xBi ceramics possess smaller and more uniform grains, and hence their optical properties are improved significantly. For the KNN-La-2Bi ceramic, the transmittance reaches a high value of 50% in the near-IR region. Our results also reveal that the ceramics possess a cubic-like crystal structure



and hence minimal optical anisotropy. The ceramics also exhibit a diffuse phase transition, suggesting that they have become more relaxor-like and contain more polar nano-regions. As a result, the optical properties of the ceramics are improved by the significant reduction of the light scattering at the grain boundaries as well as the domain walls. Although a relaxor-like behaviour is induced, the ceramics exhibit strong linear electro-optic response, giving a high effective linear EO coefficient of 120-145 pm/V.

Transparent KNN-La and KNN-La-xBi ceramics have also been successfully fabricated by hot-press sintering technique. The pressure applied during the hot-press sintering technique is effective in promoting uniform densification and hence reducing the pores in the ceramics. The light scattering by the pores is reduced, and thus resulting in the significant improvement of the optical properties of the ceramic. For the KNN-La-1Bi ceramic prepared by hot-press sintering technique, the observed transmittance is increased by more than 100%, reaching a high value of 55% in the near-IR region. However, probably due to the non-uniform shrinkage of the ceramics, the ceramics become easily broken during the sintering process.



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Chapter 1 Introduction

1.1 Motivation of Research

In recent years, the rapid development of optic communication technology gives rise to the increase in studies of electro-optic (EO) materials. Owing to the high EO effect, toughness, good transparency and low fabrication cost, EO ceramics such as (Pb_{1-x}La_x)(Zr_{1-y}Ti_y)_{1-x/4}O₃ (PLZT) and Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) have been widely applied in different optoelectronic devices such as optical filters, optical attenuators and switches [1-2]. However, the high percentage of lead used in the EO ceramics is harmful to the environment and human body. For environmental protection purposes, lead-free materials have been extensively studied in recent years as possible replacements for lead-based materials.

Potassium sodium niobate (KNN) is one of the good candidates for lead-free piezoelectric ceramics due to its high Curie temperature and good piezoelectric properties [3-4]. However, because of the low melting temperature and high volatility of alkali-elements, its sinterability is poor [5]. It is difficult to obtain dense and wellsintered KNN ceramics by conventional sintering. A number of studies have been



conducted to improve the sintering performance of KNN ceramics; these include the formation of new solid solutions with other ferroelectrics or non-ferroelectrics, e.g. KNN-SrTiO₃ [6] and KNN-LiSbO₃ [7], and the use of sintering aids, e.g. MnO_2 [8] and Bi_2O_3 [9].

Although KNN-based ceramics can be well-sintered to high densities by conventional sintering, they are opaque and hence there are few works reporting the optical properties. These should be due to the significant light scattering by their large grains and non-cubic crystal structure. It has been known that smooth surfaces, high densification, small grains and isotropic crystal structure are essential factors for ceramics exhibiting good optical properties. Obviously, an EO ceramics should exhibit a good optical transparency.

Recent studies have shown that the sinterability and piezoelectric properties of KNN ceramics can be improved by the doping of donor ions La³⁺ at the A-site [10]. The grain growth of the ceramic is inhibited and the grain size is reduced significantly. However, there is no study investigating the optical properties of La-doped KNN ceramics.

Chen and Wang have recently developed a new sintering technique, i.e., two-Chan Man Ting Page 2



step sintering technique, for obtaining fully dense nano-crystalline ceramics at low sintering temperatures [11]. The technique is promising and has been used to successfully fabricate dense KNN ceramics with enhanced piezoelectric properties [12]. However, there are no detailed investigations on the effects of the sintering conditions on the other physical as well as optical properties of the ceramics, in particular the grain size and transparency.

1.2 Objectives of Research

The main objective of this work is to develop new lead-free KNN-based electrooptic ceramics. La-doped KNN [$(K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO_3$] ceramics is chosen as the main composition for the study. The two-step sintering technique is used to fabricate the ceramics with the aim of suppressing their grain growth and then improving their optical transparency. Excess Bi₂O₃ is also used as a sintering aid to lower the sintering temperature and suppress the grain growth. The effects of the two-step sintering conditions on the dielectric, piezoelectric and optical properties of the ceramics are investigated. The linear electro-optic properties of the ceramics fabricated by the optimized condition are evaluated.



1.3 Scope and Outline of Thesis

The main objective of this work is to develop new lead-free KNN-based electrooptic (EO) ceramics by using the two-step sintering technique. The optical properties, microstructure, dielectric, ferroelectric and EO properties of the ceramics are studied. The hot-press sintering technique is also used to fabricate the ceramics for comparison purposes.

Chapter 1 (the current chapter) gives the brief introduction of the whole thesis. Motivation and objectives of research are described. The outline of the thesis which briefly describes the contents of each chapter is also given.

Chapter 2 gives the reviews of the literatures on the EO effect and EO ceramics, the factors affecting the optical properties of ceramics, KNN-based ceramics and the two-step sintering technique. The limitations and gaps in earlier research are also presented.

Chapter 3 describes the methodologies for fabrication and characterization of the ceramics. The experimental details for the fabrication of the ceramics by both the twostep sintering technique and the hot-press sintering technique are given in this chapter.



The methods for characterizing the optical properties, the microstructure, dielectric, ferroelectric and electro-optic properties of the ceramics are described.

Chapter 4 reports the results of the ceramics prepared by the two-step sintering technique. This chapter discusses the effects of the two-step sintering conditions on the properties of KNN and KNN-La ceramics. The properties of the KNN-La-xBi ceramics prepared by the optimized conditions are also characterized.

Chapter 5 reports the results of the ceramics prepared by the hot-press sintering technique. This chapter characterizes the properties of the KNN-La-xBi ceramics prepared by the optimized conditions.

Chapter 6 summarizes the major findings in the research.



Chapter 2 Literature Review

2.1 Introduction

In this chapter, background theory of electro-optic (EO) effect is introduced and a review of two most widely used electro-optic ceramics (Pb_{1-x}La_{0x})(Zr_{1-v}Ti_v)_{1-x/4}O₃ (PLZT) and Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) is given. In recent years, owing to environmental protection reasons, lead-free piezoelectric ceramics have been extensively studied for replacing the lead-based ceramics. Among varies lead-free ceramics, potassium sodium niobate (KNN) is considered to be a good candidate because of its good piezoelectric properties and high Curie temperature. Obviously, ceramics used as EO materials must have good optical properties. It is then important to understand the relationships between the structure and optical properties of ceramics in developing EO ceramics. Therefore, reviews of factors affecting the optical properties of ceramics and KNN-based ceramics are given. The two-step sintering technique has been shown to be effective in suppressing the grain growth which may be helping in improving the optical properties of ceramics. So a review of the technique is given.



2.2 Electro-optic effect in crystals

2.2.1 Refractive index

The refractive index of an isotropic material is defined as the ratio of the speed of electromagnetic wave in vacuum c to that in the material v as shown below:

$$n = \frac{c}{v} \tag{2.1}$$

According to the Maxwell's equations [13], the speed of electromagnetic wave in a material can be expressed as

$$v = \frac{1}{\sqrt{\epsilon_0 \epsilon_r \mu_0 \mu_r}} \tag{2.2}$$

where ε_0 and μ_0 are the permittivity and permeability of vacuum, respectively; ε_r and μ_r are the relative permittivity and relative permeability of the material, respectively. For non-magnetic materials, μ_r is approximately equal to 1. Therefore, the refractive index can be represented as [13]:

$$n = \sqrt{\varepsilon_r} \tag{2.3}$$



2.2.2 Index Ellipsoid (Optical indicatrix)

The induced polarization P depends linearly on the applied electric field E with the constant proportionality χ which is called susceptibility. For isotropic dielectrics, P and E are always in parallel and hence χ is scalar.

$$P = \varepsilon_0 \chi E \tag{2.4}$$

For anisotropic dielectrics, the polarization depends on both the direction and magnitude of the applied electric field and therefore the susceptibility is the second rank tensor [14].

$$\mathbf{P}_{i} = \varepsilon_{o} \chi_{ij} \mathbf{E}_{j} \tag{2.5}$$

The electric displacement field D (which corresponds to the stored electric charge per unit area) of anisotropic dielectrics is defined as [14]

$$D_i = \varepsilon_0 E_j + P_i \tag{2.6}$$

From Eqs.2.5 and 2.6,

$$D_{i} = \varepsilon_{o}E_{j} + \varepsilon_{o}\chi_{ij}E_{j} = \varepsilon_{o}(\delta_{ij} + \chi_{ij})E_{j}$$
(2.7)

Therefore,

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$$\mathbf{D}_{i} = \boldsymbol{\varepsilon}_{ij} \mathbf{E}_{j} \tag{2.8}$$

where $\varepsilon_{ij} [= \varepsilon_0 (\delta_{ij} + \chi_{ij})]$ is the permittivity of the dielectrics; and the relative permittivity $\varepsilon_{r,ij}$ hence equals to $\delta_{ij} + \chi_{ij}$.

The refractive index of anisotropic non-magnetic dielectrics is then given as follows:

$$n_{ij}^{2} = \varepsilon_{r,ij} \tag{2.9}$$

According to the above relation, the refractive index of anisotropic dielectrics depends on the orientations of dielectric. As a result, the phase velocity of electromagnetic wave propagating in anisotropic dielectrics depends on its propagating direction as well as its polarization [15].

It is customary to describe the optical theory of dielectrics in terms of the impermeability tensor B_{ij} as defined below [15]:

$$\mathbf{B}_{ij} = \left[\boldsymbol{\varepsilon}_{ij}\right]^{-1} \tag{2.10}$$

Hence,

$$\mathbf{E}_{i} = \mathbf{B}_{ij}\mathbf{D}_{j} \tag{2.11}$$

For anisotropic dielectrics, the energy density is given as [14]

$$\xi = \frac{1}{2}\vec{E} \cdot \vec{D} = \frac{1}{2}B_{ij}D_jD_i$$
(2.12)

or

$$2\xi = B_{11}D_1^2 + B_{22}D_2^2 + B_{33}D_3^2 + 2B_{12}D_1D_2 + 2B_{23}D_2D_3 + 2B_{31}D_3D_1$$
(2.13)

Eq.2.13 is an equation for an ellipsoid of constant energy density in the D space.

Defining $x_i = \frac{D_i}{\sqrt{2\xi\epsilon_o}}$, Eq.2.13 can be written as

$$\frac{x_1^2}{n_{11}^2} + \frac{x_2^2}{n_{22}^2} + \frac{x_3^2}{n_{33}^2} + 2\frac{x_1x_2}{n_{12}^2} + 2\frac{x_2x_3}{n_{23}^2} + 2\frac{x_3x_1}{n_{31}^2} = 1$$
(2.14)

The surface described by Eq.2.14 is called the optical indicatrix or index ellipsoid. By choosing a suitable coordinate system, e.g. x'_i , Eq.2.14 can be diagonalized to the form of:

$$\frac{{x_1'}^2}{{n_{11}'}^2} + \frac{{x_2'}^2}{{n_{22}'}^2} + \frac{{x_3'}^2}{{n_{33}'}^2} = 1$$
(2.15)

The ellipsoidal surface described by Eq.2.15 is shown in Figure 2.1 [15]. n'_{11} , n'_{22} and n'_{33} are equal to the semi-axes of the optical indicatrix, called the principal refractive indexes of the crystal. The x'_i coordinate system is called the principle-axis system.



Figure 2.1 The optical indicatrix [15]

The optical indicatrix defines the refractive indexes of electromagnetic waves that can propagate in the crystal. For a plane wave propagating along the OP direction in a crystal, the refractive index is given by the semi-axes of the central elliptical section (shaded region) of the indicatrix as shown in Figure 2.1 [15]. The refractive indexes are equal to OE and OR, respectively, for the waves with their polarization parallel to the major and minor axis.

For cubic crystals, $n'_{11} = n'_{22} = n'_{33}$, the indicatrix is a sphere and therefore they are isotropic [15]. The speed of wave is independent of its propagating direction as well as the orientation of its polarization. For uniaxial crystals (e.g. crystals with hexagonal,



tetragonal and trigonal symmetry crystal) with an optical axis parallel to the x'_3 -axis, $n'_{11} = n'_{22} \neq n'_{33}$. The indicatrix is symmetrical about the optical axis and the central section of the ellipsoid is a circle with a radius n'_{11} or n'_{22} [15]. The speed of wave propagated along the x'_3 -direction is not affected by its polarization orientation; i.e. there is no birefringence (defined as the difference in refractive indexes) for waves propagating along the optical axis. For biaxial crystals (e.g., crystals with orthorhombic, monoclinic and triclinic symmetry), the indicatrix is a triaxial ellipsoid with two circular inclined sections, of which the normal define the two optical axes.

2.2.3 Electro-optic effect and coefficients

Electro-optic effect is a change of optical properties in a materials resulting from the influence of an applied electric field. The optical and electro-optical properties of dielectrics are related to their refractive indexes which vary with the permittivity (Eq. 2.9). For anisotropic nonlinear dielectrics, the polarization P, permittivity ϵ and refractive index n are given as:

$$P_{i} = \varepsilon_{o}(\chi_{ij}^{(1)} + \chi_{ijk}^{(2)}E_{k} + \chi_{ijkl}^{(3)}E_{kl} + ...) E_{j}$$
(2.16)

$$\varepsilon_{ij}(E) = \varepsilon_0(\delta_{ij} + \chi_{ij}^{(1)} + \chi_{ijk}^{(2)}E_k + \chi_{ijkl}^{(3)}E_{kl} + ...)$$
(2.17)



$$n_{ij}^{2}(E) = n_{ij}^{2} + \chi_{ijk}^{(2)}E_{k} + \chi_{ijkl}^{(3)}E_{kl} + ..$$
(2.18)

where $\chi_{ij}^{(1)}$ is the linear susceptibility, $\chi_{ijk}^{(2)}$ and $\chi_{ijkl}^{(3)}$ are the second- and third-order susceptibilities, respectively. Practically, it is customary to express the change in refractive index in terms of the optical impermeability B as:

$$\Delta B_{ij} = \Delta \left(\frac{1}{n_{ij}^2}\right) = r_{ijk} E_k + R_{ijkl} E_k E_l$$
(2.19)

where r_{ijk} is the linear electro-optic coefficient and R_{ijkl} is the quadratic electro-optic coefficient. Accordingly, the first term of Eq.2.19 represents the linear electro-optic effect (Pockels effect) while the second term represents the quadratic electro-optic effect (Kerr effect) [15-18].

It has been shown that a reversal of electric field has no effects on the refractive index of a material with a centrosymmetric or random structure, such as glass and cubic crystals. Therefore, it has a zero linear electro-optic coefficient but non-zero quadratic electro-optic coefficient. In 1875, John Kerr performed experiments to study the effect of electric field on the optical properties of glass. Hence, the quadratic or non-linear electro-optic effect has been known as the Kerr effect. On the other hand, a reversal of electric field affects the refractive index of materials with non-centrosymmetric



structure such as uniaxial and biaxial crystals. In 1893, Pockels analyzed a linear electro-optic effect which was reported by both Wilhelm Röntgen and August Kundt separately in 1883. The linear electro-optic effect has then also called the Pockels effect. Non-centrosymmetric materials can also exhibit the Kerr effect [15].

2.3 Electro-optic ceramics

In recent years, the studies of electro-optic materials have increased along with the rapid development of optic communication technology. Organic, Polymeric and ferroelectric materials are three main categories of electro-optic materials. (Pb,La)(Zi,Ti)O₃ ferroelectric electro-optic ceramic is one of the most widely used electro-optic materials. It has been used to fabricate different types of electro-optic devices such as optical attenuator, modulator, electro-optic shutter and optical data recorder due to its good electro-optic effect, low optical loss, low fabrication cost and ceramic stiffness [19]. The electro-optic properties of two lead-based perovskite ferroelectric ceramics (Pb_{1-x}La_x)(Zr_{1-y}Ti_y)_{1-x/4}O₃ (PLZT) and Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) are described in the following sections and those of ferroelectric materials are listed in Table 2.1 for comparison.



2.3.1 (Pb_{1-x}La_x)(Zr_{1-y}Ti_y)_{1-x/4}O₃ (PLZT) ceramics

(Pb)(Zi, Ti)O₃ (PZT) is a well-known ferroelectric ceramics due to its promising ferroelectric and piezoelectric properties. PZT possesses a perovskite (ABO₃) structure as shown in Figure 2.2. The A site of the structure is occupied by Pb ions and B site is occupied by Zi and Ti ions. After doping of lanthanum ions into the A site, PZT ceramics become $(Pb_{1-x}La_x)(Zr_{1-y}Ti_y)_{1-x/4}O_3$ (abbreviated as PLZT 100x/1-100y/100y) electro-optic ceramics which have good transparency in a wide wavelength range. It has been shown that PLZT 10/65/35 ceramics possess pseudo-cubic perovskite structure [20]. This may be the reason for the good optical properties. Moreover, the PLZT 10/65/35 ceramics exhibit relaxor characteristics [20].



Figure 2.2 Perovskite structure



According the phase diagram shown in Figure 2.3, the electro-optic applications of PLZT ceramics can be divided into three categories: quadratic, linear and memory. Depending on the composition, both the Pockels and Kerr effects can be observed in the PLZT ceramics. The Pockels effect observed in PLZT ceramics is much stronger than that in lithium niobate (LiNbO₃) single crystal, which has been extensively used in telecommunication applications, e.g., optical modulator and electro-optic shutter. Therefore, PLZT ceramics have been considered as possible replacements for LiNbO₃. Because of the strong Kerr response, PLZT ceramics can also be used as light shutters and optical displays [2].



Figure 2.3 Phase diagram of PLZT showing relation between PLZT composition and structure for electro-optic applications [2]



2.3.2 Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) ceramics

Electro-optic ceramics with high stiffness and large electro-optic response have been longed for image display applications. PMN-PT ceramics are known to have superior electrostrictive properties and very good fracture stiffness [2]. Recently, PMN-PT ceramics with a high transmittance of about 70% at 633 nm as well as a high quadratic electro-optic coefficient of 28x10⁻¹⁶ m²/V⁻² have been developed and become promising candidates for electro-optic applications [19]. Similar to PLZT, the good optical properties of PMN-PT ceramics should be arisen from the pseudo-cubic structure while the strong Kerr response should be attributed to the relaxor characteristics.

Table 2.1 Electro-optic (EO) coefficients of ferroelectric materials: effective quadratic

	Composition	R _c	r _c
	La/Zr/Ti	$(x10^{-16} m^2/V^2)$	(pm/V)
PLZT	8.5/65/35	38.60	/
	9/65/35	3.80	/
	9.5/65/35	1.50	/
	10/65/35	0.80	/
	11/65/35	0.32	/
	12/65/35	0.16	/
	8/40/60	/	100
	12/40/60	/	120
PMN-PT	/	28	/
LiNbO ₃	/	/	17

(Kerr) EO coefficient R_c and effective linear (Pockel) EO coefficient r_c [1, 19, 21-22]

2.4 Factors affecting transparency of ceramics

In order to fabricate ceramics which can be used as EO materials, the ceramics should exhibit a good transparency. It is then important to familiarize with the factors affecting the optical properties of ceramics which are polycrystalline. The scattering of light at the sample surfaces, precipitate, pores, grains, and grain boundaries would reduce the forward transmission of light significantly as shown in Figure 2.4 [23-25].



Therefore, ceramics with smooth surfaces, higher densification, smaller grains and isotropic crystal structure are expected to exhibit good optical properties.



Figure 2.4 Light transmission mechanism in ceramics

Diffuse scattering of light at rough surfaces prohibits the light to get into ceramics and therefore reduce the transparency of ceramics significantly. The optical properties of ceramics can be improved by proper polishing of the rough surfaces because the diffuse scattering of light at smooth surfaces can be neglected [25]. Moreover, the difference between the refractive indexes of air and ceramics causes a reflection loss at the air-ceramic interfaces [25]. The reflection loss at the air-ceramic interfaces [25]. The reflection loss at the air-ceramic interface [25]. The reflection loss at the air-ceramic interface [25]. The reflection loss at the air-ceramic interface can be calculated by $R = (n-1)^2/(n+1)^2$ where R is the reflectance and n is the refractive index of ceramic. The reflection loss can be eliminated by proper



antireflection coating at the ceramic surfaces.

According to Mie scattering theory, the incident light will be scattered significantly by a sphere if the wavelength of the light is close to the size of sphere. Therefore, transparent ceramics should not contain spherical objects of sizes as large as the wavelength of visible light (400 - 700 nm). Pores and precipitates should be eliminated to improve the transparency of ceramics. Recent studies of transparent Nddoped YAG ceramics show that the impact on the light scattering by pores is reduced significantly when the porosity is lower than 0.01% [26]. Enhancing densification to eliminate pores in ceramics is important for promoting the optical properties of ceramics. Ceramics with fine grains are expected to have smaller pore size and therefore can minimize the light scattering effect. A study on nanometer polycrystalline MgAl₂O₄ shows that the transmittance of ceramics at 633nm is higher than 50% even the porosity is more than 1% [27]. This may be because the pore size is much smaller than the visible light wavelength. Dense ceramics with fine grains which are much smaller than the visible light wavelength are normally transparent to visible light.

Except for cubic crystals, the optical properties of crystals along different crystalline axes are not the same [28]. The different atomic distance in all directions for


crystals without cubic symmetry results in different vibrational frequencies and hence different refractive indexes [28]. This optical anisotropy can be found in crystals with tetragonal, rhombohedral and orthorhombic symmetry leading to the phenomenon of birefringence [28]. For polycrystalline ceramics, the grains are randomly oriented. At the grain boundaries, the birefringence will lead to a discontinuity of refractive index due to the difference in crystallographic directions between the neighboring grains [25]. Grain boundary reflection, grain boundary refraction and grain boundary scattering which deteriorate the transparency of ceramics may occur at grain boundary [25]. However, recent study has shown that the influences of birefringence in the tetragonal ZrO_2 ceramics become less important when the grains are smaller than 20 nm [29]. This may be because the scattering of light by grains can be neglected when the grain size is much smaller than the wavelength of incident light. For the birefringent ceramics, grain size may be critical for the optical properties of ceramics.

2.5 Sodium Potassium Niobate-based Ceramics

The lead oxide powder used in the preparation of lead-based materials is notorious for its toxicity. For environmental protection purposes, lead-free materials have been widely studied in recent years as possible replacements for lead-based



materials. Potassium sodium niobate is considered to be a good candidate for lead-free piezoelectric ceramics because of its high Curie temperature and good piezoelectric responses [3-4]. The compositions which are close to the polymorphic phase boundary at 52.5% Na have the highest electromechanical coupling coefficients and the best piezoelectric properties because of the coexistence of the tetragonal and orthorhombic phases [5, 30-33]. K_{0.5}Na_{0.5}NbO₃ (abbreviated as KNN) is thus the most studied composition among the whole compositional range. According to the binary phase diagram KNbO₃-NaNbO₃ as shown in Figure 2.5, the Curie temperature of KNN is at about 420°C, and the tetragonal phase transforms to the orthorhombic phase at about 200°C upon cooling. The KNN exhibits orthorhombic perovskite structure (where the A site is occupied by K⁺ and Na⁺ while B site is occupied by Nb⁵⁺) at room temperature [31, 33-35].



Figure 2.5 Binary phase diagram KNbO₃-NaNbO₃ [33, 35]

As also shown in Figure 2.5, the solidus and liquidus lines for KNN are at 1140°C and 1280°C respectively. The phase stability for KNN is thus limited to 1140°C. The low eutectic temperature (1140°C) and the high volatility of the alkali-elements (K and Na) in KNN will cause evaporation of the alkali-elements at high sintering temperatures and hence non-stoichiometry [5]. Therefore, KNN has a poor sinterability and it is difficult to obtain dense and well-sintered KNN ceramics by using conventional sintering.

A number of studies have been carried out to improve the sintering performance of KNN ceramics; these include the formation of new solid solutions with other



ferroelectrics or non-ferroelectrics, e.g. KNN-SrTiO₃ [6] and KNN-LiSbO₃ [7], and the use of sintering aids, e.g. MnO₂ [8] and Bi₂O₃ [9]. In general, the density of pure KNN ceramics prepared by conventional sintering is about 90-95% of the theoretical density (4.51 g/cm³). It has been shown that the density of KNN-SrTiO₃ ceramic prepared by conventional sintering can reach 4.52 g/cm³ [6]. On the other hand, by using 1 mol% Bi₂O₃, the density of KNN-based ceramics prepared by conventional sintering can increase from 4.21 to 4.47 g/cm³ [9]

Recent studies have also showed that the sinterability and piezoelectric properties of KNN ceramics can be improved by the doping of donor ions La^{3+} at the A-site [10]. It has been found that the piezoelectric coefficient d_{33} increases significantly from 95 to 135 pC/N after the doping 1.25 mol% of La^{3+} [10]. The density of the ceramic also increases to about 4.4 g/cm³ [10]. More importantly, the grain growth of the ceramic is inhibited and the grain size is reduced significantly as shown in Figure 2.6 [10]. The La-doped KNN ceramics also exhibit relaxor-like characteristics. These suggest that the scattering of light can be reduced in these ceramics. This is similar to the case of PZT ceramics which become transparent and exhibit strong electro-optical responses after the doping with La^{3+} [20]. Nevertheless, there is little work reporting the



optical and electro-optic properties of La-doped KNN ceramics.



Figure 2.6 Microstructure of (a) pure KNN and (b) KNN doped with 1.25mol% La [10]

2.6 Two-step Sintering technique

There are few works reporting their optical properties of KNN-based ceramics even though they can be well-sintered to high densities by conventional sintering. This may be because they are opaque due to the optical anisotropy of the crystal structure and the significant light scattering by the large grains. In conventional sintering, the sample is heated at a high temperature for a certain time. Both grain-boundary migration (which leads to the grain growth) and grain-boundary diffusion (which leads to the densification by eliminating inter-particle pores) are activated [11]. As their driving forces, both proportional to the reciprocal of the grain size, are comparable in magnitude, a coarse-grain ceramic is usually produced [11]. In order to produce dense



and fine-grained ceramics, researchers have proposed various sintering techniques such as microwave-sintering technique [36], atmosphere sintering technique [37], sparkplasma-sintering technique [38] and hot-press sintering technique [32]. Most of the techniques require special equipment and complicated procedures which increase the cost of the fabrication.

It has been shown that the grain growth of a ceramic can be effectively suppressed by a new sintering technique, i.e., two-step sintering technique [11]. It does not require any special equipment and therefore it is easy to be implemented. In 2000, Chen and Wang developed the two-step sintering technique which is a promising approach to obtain fully dense nano-crystalline ceramics at low sintering temperatures [11]. They have suggested that the activation energy of grain-boundary migration is larger that of grain-boundary diffusion. Grain-boundary migration can facilitate the grain growth while grain-boundary diffusion leads to densification by eliminating interparticle pores [11]. According to the sintering technique, the sample is first heated to a high temperature and then cooled down rapidly and held at a low temperature for suppressing the grain growth in the final stage of the sintering process. Both processes are activated at higher temperature, while only the grain-boundary diffusion is activated



at lower temperature. The technique has been demonstrated for Yttria Y_2O_3 ceramics [11]. The grain growth of the ceramics can be effectively suppressed as shown in Figure 2.7(a) [11]. After the doping with 1% Mg, the grain size of the ceramics is reduced to about 60 nm as shown in Figure 2.7(b) [11]. The technique has also been successfully used to fine-grained perovskite BaTiO₃ [39-41] and BiScO₃-PbTiO₃ [42]ceramics. As shown in Figure 2.8, the grain sizes of the ceramics are about 70 and 200nm, respectively [39, 42].



Figure 2.7 (a) Grain size of Y_2O_3 in two-step sinternig (b) Microstructure of fully dense

Y₂O₃ doped with 1% Mg [11]



Figure 2.8 Microstructure of (a) BaTiO₃ and (b) BiScO₃-PbTiO₃ ceramics [39, 42]

A recent study has shown that dense KNN ceramics (with a high relative density of 95%) can be obtained at a low sintering temperature of 980°C by the two-step sintering technique [12]. Probably due to the reduction in volatilization loss of alkali elements, the ceramics exhibit better piezoelectric properties ($d_{33} = 121$ pC/N, which is about 50% high than that of a ceramic prepared by the normal sintering process). However, there are no detailed investigations on the effects of the sintering conditions on the other physical and optical properties of the ceramics, in particular the grain size and transparency.



Chapter 3 Fabrication and Characterization of KNNbased ceramics

3.1 Introduction

In the previous chapter, reviews of KNN and KNN-based ceramics are given. As mentioned before, there are few works reporting the optical properties of KNN ceramics. The opacity of KNN ceramics may be due to the light scattering by large grains and pores. Literature has indicated that the two-step sintering technique is effective in producing dense KNN ceramics with better piezoelectric properties. The two-step sintering technique may be able to improve the optical properties of KNN ceramics. Moreover, although KNN-La ceramics and PLZT ceramics have several similar properties, there are few reviews showing the optical and electro-optic properties of KNN-La ceramics. In this work, the two-step sintering technique has been adopted to fabricate K_{0.5}Na_{0.5}NbO₃ (KNN) ceramics (K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO₃ (KNN-La) ceramics. Excess Bi₂O₃ was added so as to improve the optical properties of the KNN-La ceramic. For comparison purpose, the hot-press sintering technique has also been used to fabricate the KNN-La ceramics. Fabrication of ceramics were generally divided into three steps including powders preparation, compaction and sintering. In this chapter,



the procedures for powders preparation and compaction are described. The experiment details for the two-step sintering technique and the hot-press sintering technique are introduced. The characterizing methods of ceramics are also described.

3.2 Preparation of ceramic powders

The KNN and KNN-La powders were prepared by mixed-oxide method using analytical-grade metal oxides and carbonate powders: $K_2C_2O_4$ (99.5%), $Na_2C_2O_4$ (99%), Nb₂O₅ (99.99%), La₂O₃ (99.99%) and Bi₂O₃ (99.99%). The powders were weighted according to the chemical formulas: (a) $K_{0.5}Na_{0.5}NbO_3$ (KNN), (b) $(K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO_3 \ (KNN-La) \ and \ (c) \ (K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO_3 \ + \ x \ mol\%$ Bi₂O₃ (abbreviated as KNN-La-xBi) with x equal to 0.5, 1 and 2. Bi₂O₃ was added as a sintering aid to lower the sintering temperature and inhibit the grain growth [43-44]. In order to avoid any contaminations affecting the properties of samples, all apparatuses used were cleaned by deionized water. $K_2C_2O_4$ and $Na_2C_2O_4$ were first dissolved in deionized water. Nb₂O₅ and Bi₂O₃ were then added and mixed thoroughly. The mixture was then dried and calcined at 850°C for 5 h to decompose the carbonates and form the perovskite structure. After the calcination, the mixture was ball milled in ethanol using zirconia balls for 24 h to refine the powders particle size and improve the homogeneity



[45].

3.3 Compaction

After ball milling, the powders were dried and then mixed thoroughly with a polyvinyl alcohol (PVA) binder solution. The concentration of the PVA binder solution is 5 wt% in water and the ratio of powders to PVA binder solution is 1 : 0.3. A uniaxial pressure of ~43 MPa was applied to compact 0.7 g of powders into the desired shape and size at room temperature. The excess air between powders in the die was driven out and compacted green disk samples were obtained. The diameter of the disk samples was 15.2 mm and the thickness as about 1.2 mm.

3.4 Sintering technique for synthesis of KNN-based ceramics

3.4.1Two-step sintering technique

In two-step sintering technique, the disk samples were heated in a high temperature furnace (Carbolite RHF1600). They were first heated to an intermediate temperature T_1 (1100-1200°C) with a heating rate of 3°C/min and held for t_1 (10-20 min). Then, the temperature was decreased rapidly to T_2 (1000-1100°C) with a cooling rate of 20°C/min and held for t_2 (600-960 min). After that, they were cooled down to



room temperature with a cooling rate of 9°C/min. The temperature and time profile for the two-step sintering technique is shown in Figure 3.1. KNN and KNN-La ceramics were used to investigate the effect of sintering time and temperature on the grains size of ceramics. The sintering conditions for KNN and KNN-La ceramics are shown in Table 3.1 and 3.2, respectively. A KNN-La ceramic was prepared by the conventional sintering technique for comparison purpose. The optimized conditions for preparing KNN, KNN-La and KNN-La-xBi ceramics by two-step sintering are summarized in Table 3.3.





Table 3.1 Sintering conditions for KNN ceramics:

Sample	$T_1(^{\circ}C)$	t_1 (min)	$T_2(^{\circ}C)$	t_2 (min)
KNN 1100/10/1000/600	1100	10	1000	600
KNN 1120/10/1000/600	1120	10	1000	600
KNN 1150/10/1000/600	1150	10	1000	600
KNN 1120/10/1000/900	1120	10	1000	900

Table 3.2 Sintering conditions for KNN-La ceramics:

Sample	$T_1(^{\circ}C)$	t ₁ (min)	T_2 (°C)	t ₂ (min)
KNN-La 1170/960/0/0	1170	960	/	/
KNN-La 1180/10/1100/960	1180	10	1100	960
KNN-La 1180/20/1100/960	1180	20	1100	960
KNN-La 1180/10/1080/960	1180	10	1080	960

Table 3.3 Optimized sintering conditions for KNN, KNN-La and KNN-La-xBi ceramics:

Sample	$T_1(^{\circ}C)$	\mathbf{t}_1 (min)	T_2 (°C)	t ₂ (min)
KNN	1120	10	1000	600
KNN-La	1180	20	1100	960
KNN-La-0.5Bi	1200	10	1100	960
KNN-La-1Bi	1190	10	1100	960
KNN-La-2Bi	1180	20	1090	960



3.4.2 Hot-press sintering technique

Hot-press sintering technique is a process that produces dense ceramics through the applications of heat and pressure simultaneously [46]. A disk sample was fed into a die and was pressed to a pressure at a high temperature for a certain period to facilitate densification. Ceramics were provided with the major part of the driving force for elimination of porosity by the pressure between a punch and a holder. Dense ceramics were thus produced by hot-press sintering technique. The most widely used electrooptic ceramics such as PLZT and PMN-PT can be produced by hot-press sintering technique [19-20].

For comparison, KNN-La and KNN-La-xBi ceramics were also prepared by the hot-press sintering technique. In the experiment, the sample surrounded by ZrO_2 powders was placed into a SiO₂ mold as shown in Figure 3.2. A Al₂O₃ punch of diameter 50.5 mm was put onto the ZrO₂ powders to ensure that the pressure acting on the sample was uniformly distributed. ZrO₂, SiO₂ and Al₂O₃ are the materials which do not react with the ceramic materials under high temperature and pressure. A uniaxial pressure ~3 MPa was applied on the sample when the sintering temperature reached 900°C. The pressure was then increased to ~6.5 MPa at 1000°C. Finally, it was



increased to ~16 MPa at the sintering temperature T listed in Table 3.4. The uniaxial pressure was removed upon cooling to 900 °C. The temperature and pressure profile for the hot-press sintering technique is shown in Figure 3.3.

Table 3.4 Optimized sintering temperature T for KNN-La and KNN-La-xBi ceramic

Sample	T (°C)
KNN-La	1180
KNN-La-0.5Bi	1180
KNN-La-1Bi	1170
KNN-La-2Bi	1160



Figure 3.2 Set-up for the hot-press sintering technique



Figure 3.3 Temperature and pressure profile for the hot-press sintering technique



3.5 Characterization of KNN-based ceramics

3.5.1 Optical properties and optical band gap energy

For measuring the optical properties, the sintered ceramics of diameter 13 mm were finally polished to a thickness of 0.5 mm using 1- μ m diamond paste. The refractive index n of the (un-poled) ceramics was measured at 633 nm using a prism coupler (Metricon Model 2010). The optical transmittance T of ceramics was measured in the range of 300-900 nm using a UV-VIS spectrophotometer (Shimadzu UV-2550). The absorption coefficient α was then calculated using [47]:

$$\alpha = \frac{1}{t} \ln(\frac{1}{T}) \tag{3.1}$$

where t was the thickness of sample. From the calculated absorption spectrum, the optical band gap energy E_g of ceramics was determined. According to the Tau equation [48], the relationship between E_g and α for direct transition was given as:

$$(\alpha hv)^2 = A(hv - E_g)$$
(3.2)

where v was the photon frequency, A was a constant and h was Planck's constant. E_g was then obtained by plotting $(\alpha hv)^2$ versus hv and extrapolating the linear portion of the curve to zero.



3.5.2 Microstructure and Crystalline structure

The microstructure of ceramics was observed using a scanning electron microscopy (SEM) (JEOL, JSM-6490). Both the fracture and top surfaces of the ceramics were observed. To reveal the microstructure, the polished surface of the ceramics was first thermally etched at a high temperature about 150°C below the sintering temperature for 30 min.

X-ray Diffraction (XRD) can be used to characterize the crystal structure of crystalline materials. Each material possesses its own crystalline atomic structure. When an X-rays beam bombards crystal atoms, waves with the same frequency are re-radiated as shown in Figure 3.4. The re-emitted X-rays interfere with each other either constructively or destructively. In order to produce the diffraction pattern, the Bragg's Law shown below must be satisfied

$$n\lambda = 2d_{hkl}\sin\theta \qquad (3.3)$$

where n is the order of the intensity maximum, λ is the X-ray wavelength, d_{hkl} is the inter-planar spacing of a set of lattice planes with Miller indices h, k, l and θ is the incident angle of X-ray beam. A unique X-ray diffraction can be produced from



particular crystalline materials and therefore X-ray diffraction can be used to analyze the crystal structure of ceramics. The lattice constants of crystals can also be estimated from the XRD pattern. In this work, the crystalline structure of the ceramics was examined using a Rigaku SmartLab X-ray diffractometer equipped with CuK_{α} radiation ($\lambda = 1.54$ Å).



Figure 3.4 Bragg diffraction of X-rays from crystal planes

3.5.3 Ferroelectric Hysteresis loop and piezoelectric properties measurement

The characteristics of ferroelectrics can be indicated by the ferroelectric hysteresis loop which shows the relation between the net macroscopic polarization of a ferroelectric material and the applied electric field. In this study, the hysteresis loops of ceramics were measured using a modified Sawyer-Tower circuit at 200 Hz [49]. Two



capacitors: the ferroelectric capacitor (sample) C_F and a reference capacitor C_R were included in the Sawyer-Tower circuit. In order to obtain the resultant hysteresis loop, the value of C_R used in the measurement should be much larger (about 1000 times) than that of C_F. The voltage drop at C_R can be neglected and hence $C_FV_i \approx C_RV_{o}$. The experimental setup of the hysteresis loop measurement is shown in Figure 3.5. Copper electrodes were first deposited on the surfaces of the samples by sputtering. The sample was then immersed into a silicone oil bath in order to prevent electrical breakdown in air. An a.c. signal generated by a function generator (HP 8116A) was amplified by a high voltage amplifier (Trek 609D-6) and then applied to the sample. A digital oscilloscope (HP54645A) was used to measure the input voltage V_i applied to the sample and the output voltage V_{o} across C_{R} . The data were finally recorded by the computer for further analysis. The polarization P of the sample was calculated as:

$$P = \frac{C_R V_o}{A}$$
(3.4)

where A is the area of the sample.



Figure 3.5 Experimental Set-up of the Hysteresis loop measurement

The piezoelectric properties of the ceramics were measured after poling. In the poling process, dipoles which random oriented in an as-prepared polycrystalline were reoriented in a particular direction by a high d.c. field. The poling field for the KNN and KNN-La ceramics were 3 kV/mm and 5 kV/mm, respectively. The ceramics were poled at 180°C for 30 min and the electric field was removed upon cooling at 60°C. The piezoelectric coefficient d_{33} was measured using a piezo- d_{33} meter (ZJ-3A, China).

3.5.4 Dielectric properties measurement

The capacitance C and the dielectric loss tand of ceramics were measured using an impedance analyzer (HP4194A). The relative permittivity ϵ_r was then be calculated

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by:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$
(3.5)

where A is the area of the sample, d is the thickness, ε_0 is the permittivity of vacuum. The relative permittivity was also measured a function of temperature for studying the phase transition of the ceramics. The experimental set-up for the measurement is shown in Figure 3.6. A ceramic connected to the impedance analyzer was put into a Carbolite furnace in which the temperature was increased from 25 to 480 °C. The temperature dependence of C of the sample was measured and thus the temperature dependence of ε_r was calculated. The temperature in the furnace was measured using a thermocouple which was connected to a Keithley multimeter. The data measured by the impedance analyzer and the multimeter were recorded and processed by a computer.



Figure 3.6 Experimental set-up of dielectric properties measurement

3.5.5 Electro-optic properties measurement

Electro-optic properties of the ceramics were measured with a transverse geometry using a modified Sénarmont system as shown in Fig 3.7 [50]. Coplanar Au/Cr electrodes, with a parallel spacing of 1 mm, were adopted for the poling and measurement. To improve the uniformity of the electric fields, the coplanar electrodes were deposited on both the top and bottom surfaces of the sample. In the measurement, the sample is inserted in the light path with its polarization (i.e., the poling direction) oriented along the z-axis. A small ac field (E_0) with a frequency (f) of 1 kHz is applied along the z-axis. The polarizer and the quarter-wave ($\lambda/4$) plate are positioned so that their optical axes (P and Q) make an angle of α and β , respectively, with the z-axis. An



ESP 3000 motion controller is used to rotate the analyzer during the measurement. The angle between the optical axis of the analyzer (A) and z-axis is indexed as γ . A laser beam at 633 nm propagates along the y-axis and is incident normally on the polarizer, sample, $\lambda/4$ plate, analyzer as well as the photo-detector.

If the polarization amplitude of the incident light beam is denoted as E_{in} , then the two polarization components of the light beam incident on the sample are given as:

$$E_{x} = E_{in} \sin \alpha e^{i(ky - \omega t)}$$
(3.6)

$$E_z = E_{in} \cos \alpha \, e^{i(ky - \omega t)} \tag{3.7}$$

where ω is the angular frequency of the light beam and t is time. After passing through the sample, the components become:

$$E_{x} = E_{in} \sin \alpha e^{ikn_{1}(E)L} e^{i(ky-\omega t)}$$
(3.8)

$$E_{z} = E_{in} \cos \alpha e^{ikn_{3}(E)L} e^{i(ky-\omega t)}$$
(3.9)

where L is the thickness of the sample (along the y-direction). If Γ is defined as the phase retardation:

$$\Gamma = k[n_3(E) - n_1(E)]L$$
(3.10)

Eq. 3.9 becomes

$$E_{z} = E_{in} \cos(\alpha) e^{ikn_{1}(E)L} e^{i\Gamma} e^{i(ky-\omega t)}$$
(3.11)

After passing through the $\lambda/4$ plate, the components of the light beam are given, with the reference to the Q-Q' system, as:

$$E_{0} = E_{in}[\sin\alpha\sin\beta + \cos\alpha\cos\beta \cdot e^{i\Gamma}]e^{i(ky-\omega t) + kn_{1}(E)L}$$
(3.12)

$$E_{Q'} = E_{in} [\sin \alpha \cos \beta - \cos \alpha \sin \beta \cdot e^{i\Gamma}] e^{i\pi/2} \cdot e^{i(ky - \omega t) + kn_1(E)L}$$
(3.13)

In practice, $\alpha = \beta = 45^{\circ}$. Moreover, only the beam with its polarization parallel to the optical axis of the analyzer can pass through the analyzer. Accordingly, the polarization component and then the intensity of the beam received by the photo-detector are given as:

$$E_{A} = \frac{E_{in}}{2} \{ [\cos \gamma + \cos(\Gamma - \gamma)] + i \cdot [\sin \gamma + \sin(\Gamma - \gamma)] \} \cdot e^{i(ky - \omega t) + kn_{1}(E)L} \quad (3.14)$$

and

$$I_{A} = \frac{I_{in}}{4} \{ 2[1 + \cos\gamma\cos(\Gamma - \gamma)] + \sin\gamma + \sin(\Gamma - \gamma) \} = \frac{I_{in}}{2} [1 + \cos(\Gamma - 2\gamma)] \quad (3.15)$$

Euler's formula has been used in deriving Eq. 3.14. Depending on the properties of the photo-detector (as characterized as G), a signal with a voltage of V_s is generated:

$$V_{s} = \frac{GI_{in}}{2} [1 + \cos(\Gamma - 2\gamma)]$$
(3.16)

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As the fully poled KNN-based ceramics possess uniaxial symmetry, having the optical axis aligned along the poling field direction (i.e., the z-axis), the equation of the optical indicatrix is given as:

$$\frac{{x'_1}^2}{{n'_0}^2} + \frac{{x'_2}^2}{{n'_0}^2} + \frac{{x'_3}^2}{{n'_e}^2} = 1$$
(3.17)

where n_o and n_e are the ordinary and extraordinary refractive index, which equals to the semi-minor and semi-major axis of the indicatrix, respectively, i.e., referring to Figure 2.1, $n_o = n_{11}$ ' and $ne = n_{33}$ '. Under an electric field, the optical indicatrix will be modified. As mentioned in Chapter 2, the change in the refractive indexes for the Pockels effect is given as (Eq. 2.19) :

$$\Delta\left(\frac{1}{n_{ij}^{2}}\right) = r_{ijk}E_{k} \tag{3.18}$$

For simplicity, Eq. 3.18 is normally re-written in matrix notation as:

$$\Delta\left(\frac{1}{n_p^2}\right) = r_{pk} E_k \tag{3.19}$$

where p = 1, 2, 3, ... 6. In rewriting the equation, the scheme: $11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3$, 23 or $32 \rightarrow 4, 13$ or $31 \rightarrow 5$ and 12 or $21 \rightarrow 6$ is adopted. For materials with uniaxial symmetry, the first-order EO matrix, i.e., r_{pk} , is given as:

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$$\begin{bmatrix} 0 & 0 & r_{13} \\ 0 & 0 & r_{13} \\ 0 & 0 & r_{33} \\ 0 & r_{51} & 0 \\ r_{51} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(3.20)

Therefore, the equation of the optical indicatrix for the KNN-based ceramics under an electric field E_0 along the z-axis (Figure 3.7) becomes:

$$\left(\frac{1}{n_0^2} + r_{13}E_0\right)x_1'^2 + \left(\frac{1}{n_0^2} + r_{13}E_0\right)x_2'^2 + \left(\frac{1}{n_e^2} + r_{33}E_0\right)x_3'^2 = 1$$
(3.21)

For a light beam propagating along the y-axis, the refractive indexes are given as (Figure 2.1):

$$\frac{1}{n_1^2(E)} = \frac{1}{n_0^2} + r_{13}E_0$$
(3.22)

and

$$\frac{1}{n_3{}^2(E)} = \frac{1}{n_e{}^2} + r_{33}E_0 \tag{3.23}$$

In general, $r_{13}E_o \ll 1/{n_o}^2$ and $r_{33}E_o \ll 1/{n_e}^2.$ Eqs. 3.22 and 3.23 hence become

$$n_1(E) = \frac{n_0}{(1+n_0^2 r_{13} E_0)^{1/2}} = n_0 - \frac{1}{2} n_0^3 r_{13} E_0$$
(3.24)

and

$$n_{3}(E) = \frac{n_{e}}{(1+n_{e}^{2}r_{33}E_{o})^{1/2}} = n_{e} - \frac{1}{2}n_{e}^{3}r_{33}E_{o}$$
(3.25)

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The phase retardation Γ now becomes:

$$\Gamma = \frac{2\pi L}{\lambda} [n_3(E) - n_1(E)] = \frac{2\pi L}{\lambda} [(n_e - n_o) - \frac{1}{2} (n_e^3 r_{33} - n_o^3 r_{13}) E_o]$$
(3.26)

If define an effective EO coefficient $r_{\rm c}$ as

$$r_{c} = r_{33} - r_{13} \frac{n_{o}}{n_{e}}$$
(3.27)

Eq. 3.26 becomes:

$$\Gamma = \frac{2\pi L}{\lambda} [(n_e - n_o) - \frac{1}{2} r_c n_e^{3} E_o]$$
(3.28)

As

$$E_{o} = \frac{V_{o}}{d} \sin\omega t \tag{3.29}$$

where V_o is the amplitude of the applied a.c. voltage, $\omega = 2\pi f$ (where f = 1 kHz) and d is the spacing between the coplanar electrodes, Γ can be simplified as:

$$\Gamma = \Gamma_{\rm o} - \Gamma_{\rm m} \sin \omega t \tag{3.30}$$

where

$$\Gamma_{\rm o} = \frac{2\pi L}{\lambda} \left(n_{\rm e} - n_{\rm o} \right) \tag{3.31}$$

$$\Gamma_{\rm m} = \frac{\pi L}{\lambda} \frac{r_{\rm c} n_{\rm e}^{3} V_{\rm o}}{d}$$
(3.32)

The detected voltage V_s (Eq. 3.16) now becomes:

$$V_{s} = \frac{GI_{in}}{2} [1 + \cos(2\gamma - \Gamma_{o} + \Gamma_{m}\sin\omega t)]$$
$$= \frac{GI_{in}}{2} [1 + \cos(2\gamma' + \Gamma_{m}\sin\omega t)]$$
(3.33)

where $2\gamma' = 2\gamma - \Gamma_0$. Using the Jabobi-Anger expansion and Bessel functions, Eq. 3.33 can be approximated as:

$$V_{\rm s} = \frac{GI_{\rm in}}{2} (1 + \cos 2\gamma' - \Gamma_{\rm m} \sin 2\gamma' \sin \omega t)$$
(3.34)

The d.c. component $V_{s,dc}$ and a.c. component $V_{s,ac}$ of the detected signal are:

$$V_{s,dc} = \frac{GI_{in}}{2} (1 + \cos 2\gamma') = GI_{in} \cos^2 \gamma'$$
(3.35)

$$V_{s,ac} = -\frac{GI_{in}}{2}\Gamma_{m}\sin 2\gamma'\sin\omega t = V_{s,ac,o}\sin\omega t$$
(3.36)

In the measurement, γ and then γ' will vary from 0 to 360°, by rotating the analyzer in a step of 2°. In this work, the difference between the maximum and minimum values of V_{s,dc} is measured using a HP 54645A digital oscilloscope as:

$$V_{s,dc,p-p} = V_{s,dc,max} - V_{s,dc,min} = GI_{in}$$
(3.37)

The different between the maximum and minimum amplitude of $V_{s,ac}$ is measured using

a Stanford SR830 lock-in amplifier as:

$$V_{s,ac,p-p} = V_{s,ac,o,max} - V_{s,ac,o,min} = GI_{in}\Gamma_m$$
(3.38)

From Eqs. 3.37 and 3.38, Γ_m is obtained and the effective EO coefficient r_c can be calculated as:

 $r_{c} = \frac{\lambda d}{\pi L n_{e}^{3} V_{o}} \frac{V_{s,ac,p-p}}{V_{s,dc,p-p}}$ (3.39)



Figure 3.7 Schematic diagram for the setup of a modified Sénarmont system



Chapter 4 Characterization of KNN-based ceramics prepared by Two-step sintering technique

4.1 Introduction

In the previous chapter, the processes for fabricating KNN-based ceramics including powders preparation, compaction and sintering were described. The methods for evaluating the optical, microstructural, ferroelectric, piezoelectric, dielectric and electro-optic properties of the ceramics were elaborated. In this chapter, the KNN-based ceramics prepared by the two-step sintering technique will be characterized. The effects of the sintering conditions, including T_1 (first-step sintering temperature), t_1 (sintering time), T_2 (second-step sintering temperature) and t_2 (dwelling time) (Figure 3.1), on the properties of the KNN and KNN-La ceramics are firstly discussed. The properties of the KNN-La-xBi ceramics prepared by the optimized sintering conditions are then discussed. The samples are abbreviated, for example, as KNN T1/t1/T2/t2, where T_1 and T_2 are in °C and t_1 and t_2 are in min.

4.2 Effect of sintering conditions

In this section, the effects of the sintering conditions on the properties of the



KNN and KNN-La ceramics are discussed. It has been known that the sintering conditions for KNN-based ceramics by conventional sintering are very stringent. It is hence not surprised that the sintering temperature and time ranges for fabricating the KNN and KNN-La ceramics with a dense structure by the two-step sintering technique are also very narrow.

The SEM micrographs of the fracture surfaces of KNN ceramics sintered at different T_1 and t_2 are shown in Figure 4.1. The grain size, relative permittivity ε_r , dielectric loss tan δ and piezoelectric properties d₃₃ of the ceramics are summarized in Table 4.1. The grain size is estimated by averaging the size of those grains shown in the micrographs. The literature values for a KNN ceramic prepared by conventional sintering at 1100°C for 4 h (abbreviated as KNN 1100/240/0/0) are also listed in Table 4.1 for comparison [10]. In general, the grain size of the ceramics, except KNN 1150/10/1000/600, prepared by the two-step sintering technique is much smaller than that prepared by the conventional sintering technique. This should be attributed to the suppression of the grain-boundary migration by the low second-step sintering temperature T₂ (1000°C, Table 3.1). The observed ε_r and d₃₃ of the KNN ceramics prepared by the two-step sintering technique are higher than that prepared by the



conventional sintering technique. This may be partly attributed to the reduced volatilization loss of alkali elements. Nevertheless, the results clearly show that the twostep sintering process is effective in inhibiting the grain growth of KNN ceramics without deteriorating the dielectric and piezoelectric properties.

The grain growth is facilitated by the grain-boundary migration process which occurs only at T_1 , but not at T_2 . Therefore, it is obvious that an increase in T_1 will lead to an increase in the grain size as shown in Table 4.1 and Figures 4.1(a) - (c). The results also suggest that T_1 is a major parameter affecting the grain growth of the ceramics and hence should be controlled for producing ceramics with small grains and good electrical properties.

As shown in Figures 4.1 (b) and (d), there is no significant difference in the grain size and densification between the KNN 1120/10/1000/600 and KNN 1120/10/1000/900 ceramics. This suggests that a dwelling time t₂ of 600 min (or 10 h) is long enough for facilitating the densification of KNN ceramics.



Sample	tanð	٤r	d ₃₃	Grain Size
	(%)	@1kHz	(pC/N)	(μ m)
KNN 1100/240/0/0	5	200	95	16
KNN 1100/10/1000/600	2	250	120	2.7
KNN 1120/10/1000/600	4	400	100	3.5
KNN 1150/10/1000/600	6	300	90	6.3
KNN 1120/10/1000/900	4	350	110	3.5

Table 4.1 Grain size, dielectric and piezoelectric properties of KNN ceramics







Figure 4.1 SEM micrographs of the fracture surfaces of ceramics: (a) KNN



1100/10/1000/600 (b) KNN 1120/10/1000/600 (c) KNN 1150/10/1000/600 and (d) KNN 1120/10/1000/900

Although the two-step sintering technique is capable of inhibiting the grain growth of the KNN ceramics, they remain opaque. This should be due to the large grain size of the ceramics. It has been shown that grains size of KNN ceramics can be reduced by the doping with donor ions La³⁺ at the A-site. Therefore, the KNN-La ceramics were fabricated, by both the two-step sintering technique and conventional technique (for comparison). The observed grain size, ε_r , tan δ and d_{33} of the ceramics are summarized in Table 4.2, while the SEM micrographs of their fracture and thermally etched surfaces are shown in Figures 4.2 and 4.3, respectively. It should be noted that the sintering conditions for preparing KNN-La ceramics are different from those for KNN ceramics. For example, the sintering temperatures T_1 and T_2 have to be increased to 1180 and 1100°C, respectively, for achieving good densification. Although a dwelling time of 600 min (or 10 h) is long enough for densifying the ceramics, a longer t_2 (960 min or 16 h) has been used for sintering the KNN-La ceramics with the intention of improving their optical properties.

In general, the two-step sintering technique is able to inhibit the grain growth of


the KNN-La ceramics (Table 4.2). However, the reduction in the grain size is much smaller than that for the KNN ceramics (Table 4.1). This may suggest that there exists a limit of grain size for ceramics fabricated by the mixed-oxide method. As also shown in Figures 4.2 and 4.3, the ceramics prepared by the two-step sintering technique contain more small grains (~0.5 μ m). However, pores are observed in the ceramics (Fig. 4.2), which may be part of the causes for the poor optical properties of the ceramics (discussed in the following section). Similarly, probably due to the reduced volatilization loss of alkali elements resulting from the lower sintering temperature (T₂), the observed d₃₃ of the ceramics prepared by the two-step sintering is larger while tan δ is smaller.

Sample	tanð	ε _r	d ₃₃	Grain Size
	(%)	@1kHz	(pC/N)	(µm)
KNN-La 1170/960/0/0	6	1000	80	0.80
KNN-La 1180/10/1100/960	3	1000	95	0.45
KNN-La 1180/20/1100/960	3.5	1100	80	0.58
KNN-La 1180/10/1080/960	3	1000	85	0.53

Table 4.2 Grain size, dielectric and piezoelectric properties of La-doped KNN ceramics









Figure 4.2 SEM micrographs of the fracture surfaces of ceramics: (a) KNN-La 1170/960/0/0 (b) KNN-La 1180/10/100/960 (c) KNN-La 1180/20/1100/960 (d) KNN-La 1180/10/1080/960











1170/960/0/0 (b) KNN-La 1180/10/1100/960 (c) KNN-La 1180/20/1100/960 (d) KNN-La 1180/10/1080/960

The grains of the KNN-La 1180/20/1100/960 ceramic are larger than those of the KNN-La 1180/10/1100/960 ceramic. This may be due to the longer sintering time t_1 at T_1 . As discussed before for the KNN ceramics, T_1 should be the major parameter affecting the grain size. Therefore, sintering the sample at T_1 for longer time should increase the grain size. On the other hand, the grain size is not affected significantly by the second-step sintering temperature T_2 as shown in Table 4.2 and Figures 4.3 (c) - (d). According to Chen and Wang [11], only the grain-boundary diffusion process which leads to the densification by eliminating inter-particle pores is supposed to be activated at T_2 . The grain-boundary migration process which facilitates the grain growth is suppressed at T_2 . So it is apparent that the grain size does not depend significantly on T_2 .

In summary, the two-step sintering technique is capable of suppressing the grain growth of the KNN and KNN-La ceramics without deteriorating their dielectric and piezoelectric properties. The grain growth of the ceramics is mainly affected by the first-step sintering temperature T_1 and sintering time t_1 while the densification is controlled by the second-step sintering temperature T_2 and the dwelling time t_2 . Although the grain size of the ceramics is greatly reduced to about 0.5 µm after the



doping of La^{3+} and the application of the two-step sintering technique, the ceramics only become translucent (Figure 4.4b). This may be due to the non-uniform grain sizes as well as non-uniform densification.

4.3 Properties of the ceramics prepared

4.3.1Optical properties and optical band gap energy

Figure 4.4 shows the photographs of the KNN, KNN-La and KNN-La-xBi ceramics. The optimized sintering conditions for the KNN, KNN-La and KNN-La-xBi ceramics are listed in Table 3.3. As mentioned in the previous section, even after applying the two-step sintering technique to suppress the grain growth, the KNN ceramics remain opaque (Figure 4.4a) while the KNN-La ceramics only become translucent (Figure 4.4b). However, as shown in Figures 4.4 (c)-(e), the optical transparency of the ceramics has been improved significantly after the addition of Bi₂O₃. The optical transmittance spectra of the KNN-La and the KNN-La-xBi ceramics measured in the range of 300-900 nm are shown in Figure 4.5. It can be seen that the transmittance T of the KNN-La ceramic is almost zero in the whole range of the measurement, while the observed T for the KNN-La-xBi ceramics starts to increase from about 400 nm and reaches a high value (25-50%) at 900 nm. As shown in Figure



4.5, the observed T for the KNN-La-2Bi ceramic is about 100% larger than that of the KNN-La-0.5Bi and the KNN-La-1Bi ceramics.

As also demonstrated in Figure 4.4, the improvement in the optical transparency of the KNN-La-xBi ceramics should be partly due to the reduction of the white spots which are formed as a result of the light scattering at pores within the ceramics (Fig. 4.2). This should be attributed to the more uniform densification resulting from the addition of excess Bi₂O₃. It has been shown that excess Bi₂O₃ is effective in promoting liquid phase sintering and then densification [44]. In fact, white spots embedding in a transparent background have been observed for all the KNN-La-xBi ceramics as well as the KNN-La under an optical microscope. As a transparent background has been observed, it is suggested that the low transmittance of the ceramics, especially for the KNN-La-0.5Bi and the KNN-La-1Bi ceramics, should be partly resulted from the "unoptimized" fabrication processing.

It should be noted that reflection loss arising from the difference in refractive indexes occurs at the air-ceramic interfaces. This suggests that the optical transparency of the ceramics can be further improved by the deposition of proper anti-reflection coating on both surfaces of the ceramics. The reflection loss at the air-ceramic interface



can be calculated by $R = (n-1)^2/(n+1)^2$ where R is the reflectance and n is the refractive index of ceramic. The refractive index of the KNN-La-xBi ceramics has been measured

to be 2.257, so the estimated reflection loss is about 30%.

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Figure 4.4 Photographs of (a) KNN and (b) KNN-La (c) KNN-La-0.5Bi (d) KNN-La-1Bi and (e) KNN-La-2Bi ceramics





Figure 4.5 Optical transmittance spectra for the KNN-La and KNN-La-xBi ceramics

The zero transmittance at wavelengths shorter than 400 nm should be arisen from the interband transitions, suggesting that the optical band grap energy E_g of the ceramics can be obtained from those measurements. The plots of $(\alpha hv)^2$ versus hv for the KNN-La-xBi ceramics are shown in Figure 4.6. As mentioned in Section 3.5.1, E_g can be determined by extrapolating the linear portion of the curve to zero. The calculated E_g for the KNN-La-0.5Bi, KNN-La-1Bi and KNN-La-2Bi ceramics are 3.04, 3.04 and 3.12 eV, respectively. This suggests that the doping of La³⁺ and the addition of Bi₂O₃ only have a minor effect on the band gap of the ceramics. As shown in Figures 4.6 (a) - (b), the linear portion of the curves for the KNN-La-0.5Bi and the KNN-La-1Bi



ceramics is short, so the extrapolated E_g value may have a larger experimental error. It has been shown that the optical band gap energy of KNN nanorods is 3.09 eV which is only about 1% lower than the observed value for the KNN-La-2Bi ceramic [51]. For KNN, the optical band gap enegy is the minimum energy required for the transition of an electron from the top of the valence bands occupied by O_{2p} electron state to the bottom of the conduction bands dominated by the empty Nb_{4d} elecron states.





Figure 4.6 Plots of $(\alpha h\nu)^2$ versus hv for the KNN-La-xBi ceramics. The optical band gap energy E_g is obtained by extrapolating the linear portion of the curve to zero.

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4.3.2 Microstructure and Crystalline structure

The SEM micrographs of the fracture and thermally etched surfaces of the KNN-La-xBi ceramics are shown in Figures 4.7 and 4.8, respectively. It can be seen that the grains of the KNN-La-xBi ceramics are generally smaller than those of the KNN-La ceramics (Figure 4.3). This should be attributed to the addition of excess Bi₂O₃. It has been shown that Bi₂O₃ is effective in suppressing the grain growth of perovskite ceramics [43-44]. Bi₂O₃ may settle at the grain boundaries and reduce their mobility during the densification. As a result, the mass transportation becomes weakened and the grain growth is suppressed. The improvements in the optical transparency of the KNN-La-xBi ceramics should then be partly attributed to the reduced scattering of visible and IR lights by the smaller grains. Although the grains of the KNN-La-2Bi ceramic are larger than those of the KNN-La-0.5Bi and KNN-La-1Bi ceramics, they are still smaller than 1 μ m and around 0.5 μ m, so the resulting scattering should not be significant. It has also been observed that the number of pores observed in the KNN-La-2Bi ceramic is lesser than those in the KNN-La-0.5Bi and KNN-La-1Bi ceramics (Fig. 4.7). These should hence lead to the higher observed T for the ceramic (Fig. 4.5). On the other hand, the number of pores observed in the KNN-La-xBi ceramics is generally lesser



than those observed in the KNN-La ceramic (Figure 4.2 c). This may be part of the causes for the improvements in the optical properties for the KNN-La-xBi ceramics.







Figure 4.7 SEM micrographs of the fracture surfaces of ceramics: (a) KNN-La-0.5Bi (b)

KNN-La-1Bi (c) KNN-La-2Bi







Figure 4.8 SEM micrographs of the thermally etched surfaces of ceramics: (a) KNN-La-0.5Bi (b) KNN-La-1Bi (c) KNN-La-2Bi

The X-ray diffraction patterns of the KNN, KNN-La and KNN-La-xBi ceramics are shown in Figure 4.9. All the ceramics possess a single-phase perovskite structure and no secondary phase is observed (Figure 4.9a). Because of the similar ionic radii, La^{3+} (1.06 Å) enters the A-sites of the lattices for replacing Na⁺ and K⁺ (1.02 and 1.38 Å)



as following the designated formulae. As discussed above, the excess Bi_2O_3 may settle at the grain boundaries for suppressing the grain growth. Probably due to the small amount, they cannot be observed in the XRD patterns. Indeed, some of them may evaporate or diffuse, in the form of Bi^{3+} (0.96 Å), into the A-sites to compensate the loss of the alkaline elements Na⁺ and K⁺ (1.02 and 1.38 Å). This may be evidenced by the slightly change of the diffraction peaks as shown in Figure 4.9(b).

As shown in Figure 4.9(b), two diffraction peaks (202) and (020) in the KNN ceramic become a single peak in the KNN-La ceramic as well as the KNN-La-xBi ceramics. It seems that the ceramics have a tendency to transform into another phase, e.g., pseudocubic. However, in consideration of the results on phase transition given below, it is suggested that the crystal structure of the KNN-La and KNN-La-xBi ceramics should remain orthorhombic, probably with very similar lattice constant a, b and c. Similar results have also been observed for other KNN-based ceramics, e.g., Ta-modified KNN [52], KNN-BaTiO₃ [53] and KNN-AgSbO₃ [54] ceramics.

The lattice constants of the ceramics were refined using all the diffraction peaks shown in Figure 4.9 by the Rietveld method. An orthorhombic Amm2 model was used in the refinement for the ceramics. As shown in Table 4.3, the lattice constant a



decreases while b increases after the doping of La^{3+} . It can also be seen that the lattice constants of the KNN-La ceramic become very close to each other, differing only by a very small amount (~0.03 Å or < 1%), suggesting that the ceramic possesses a cubiclike crystal structure with minimal optical anisotropy. The undesirable optical properties of the KNN-La ceramic should be arisen from the pores formed in the ceramics. After the addition of excess Bi₂O₃ the lattice constants of the ceramics become closer to each other, differing only ~0.025 Å. Owing to the similar lattice constants, the optical anisotropy of the ceramics is reduced. The birefringence at the grain boundaries is then minimized and the optical properties of the ceramics are improved (Figure 4.4 c-e). It has been known that the cubic-like structure of the electro-optically useful PLZT, with c being typically about 1% larger than a, is one of the major causes for their high transparency [15].





Figure 4.9 X-ray diffraction patterns of the KNN, KNN-La and KNN-La-xBi ceramics (a) 20-70°C (b) 44-47°C

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Sample	a (Å)	b (Å)	c (Å)	Difference (Å)
KNN	4.007	3.945	4.007	0.062
KNN-La	3.996	3.965	3.996	0.031
KNN-La-0.5Bi	3.992	3.968	3.992	0.024
KNN-La-1Bi	3.990	3.965	3.990	0.025
KNN-La-2Bi	3.990	3.965	3.990	0.025

Table 4.3 Lattice constants a, b and c and their differences for the ceramics prepared by optimized conditions

4.3.3 Dielectric and Ferroelectric properties

The temperature dependences of the relative permittivity ε_r (measured at 100 kHz) for the KNN, KNN-La and KNN-La-xBi ceramics are shown in Figure 4.10. The KNN ceramic exhibits two transition peaks: one is associated with the paraelectric cubic-ferroelectric tetragonal phase transition at 424 °C (T_C) and the other is the ferroelectric tetragonal-ferroelectric orthorhombic phase transition at 225 °C (T_{O-T}). After the doping of La³⁺, both the cubic-tetragonal and tetragonal-orthorhombic phase transition peaks are broadened and the observed T_C and T_{O-T} decrease slightly to 395 °C and 210 °C, respectively. It has been reported that the KNN-La ceramic is a relaxor-like ferroelectric and exhibits a diffuse phase transition. After the addition of excess Bi₂O₃,



the cubic-tetragonal phase transition peak becomes further broadened and shifts significantly to lower temperatures (310-340°C). On the other hand, there is no significant change for the tetragonal-orthorhombic phase transition peak; the observed T_{O-T} remains at a high temperature of around 210°C. This provides additional evidence for the suggestion that the crystal structure of the ceramics should remain orthorhombic even though their diffraction peaks (202) and (020) merge into one.

On the other hand, the change of the cubic-tetragonal phase transition suggests that some of the excess Bi^{3+} may enter the KNN lattices, causing the crystal structure to become more cubic (Figure 4.9b). Nevertheless, the results suggest that a diffuse phase transition is induced in the KNN-La as well as the KNN-La-xBi ceramics. A diffuse phase transition has been observed in a number of ABO₃-type perovskites [52-57]. In those compounds, either the A-sites or the B-sites are occupied by two or more cations. It is known that a large difference in ionic radii of the A-site cations or B-site cations is favorable for the formation of ordered structures [55]. As La^{3+} (1.06 Å) has a similar size of Na⁺ and K⁺ (1.02 and 1.38 Å), the substitution of La^{3+} in the KNN lattices should increase the A-site disordered degree and hence the local compositional fluctuation. As a result, the ceramics become more relaxor-like and exhibit a diffuse phase transition.



Accordingly, the KNN-La and KNN-La-xBi ceramics should contain considerable amount of polar nano-regions, and hence the light scattering (arisen at the domain walls) is greatly reduced and the optical transparency is improved (Figures 4.4-4.5).

The relative permittivity ε_r and dielectric loss tanð measured at 100 kHz and room temperature for the ceramics are summarized in Table 4.4. The observed ε_r increases significantly from 430 to 1020 while tanð decreases from 7.1% to 4.3% after the doping of La³⁺. The doping of La³⁺ may improve the sinterability and hence the densification of the ceramics, resulting in an improvement of the dielectric properties. The observed ε_r retains at a high value (>1100) for the KNN-La-0.5Bi and KNN-La-1Bi ceramics. However, it decreases significantly to 780 for the KNN-La-2Bi ceramic. This may be attributed to the excess Bi₂O₃ accumulated at the grain boundaries. The observed tanð for the KNN-La-xBi ceramics remains almost unchanged, having a value smaller than 4%. This suggests that they can readily be used in practical applications.





Figure 4.10 Temperature dependence of relative permittivity (measured at 100kHz) of the KNN, KNN-La and KNN-La-xBi ceramics

The P-E hysteresis loops for the KNN, KNN-La and KNN-La-xBi ceramics are shown in Figure 4.11. Probably due to the relaxor-like characteristics, the KNN-La and KNN-La-xBi ceramics exhibit a slanted P-E hysteresis loop. Moreover, the observed remanent polarization P_r decreases sharply from 13.5 to 10.6 μ C/cm² after the doping of La³⁺. This should be because the ceramics become more relaxor-like. The observed remanent polarization P_r decreases from 10.6 to 6.5 μ C/cm² with increasing the amount of Bi₂O₃.







Figure 4.11 P-E hysteresis loops of the cermaics: (a) KNN (b) KNN-La (c) KNN-La-0.5Bi (d) KNN-La-1Bi and (e) KNN-La-2Bi

4.3.4 Electro-optic properties

The d.c. component $V_{s,dc}$ and a.c. component $V_{s,ac}$ measured from the photodetector with the rotating angle γ of the analyzer varying from 0 to 360° are shown in Figure 4.12. The observed $V_{s,dc}$ and $V_{s,ac}$ change sinusoidally with γ . According to Eqs. 3.37 and 3.38, the phase retardation Γ_m can be obtained from the ration of $V_{s,ac,p-p}$ to $V_{s,dc,p-p}$. The field induced phase retardation Γ_m of the KNN-La-xBi ceramics were measured as a function of an a.c. field E at room temperature. As shown in Figure 4.13,



good linear relationships between Γ_m and E are obtained for the KNN-La-xBi ceramics, suggesting that they are linear EO material. According to Eq. 3.39, the effective EO coefficient r_c for the ceramics has been calculated from the slope of the plots.



Figure 4.12 Voltage signals $V_{s,dc}$ and $V_{s,ac}$ measured from the photo-detector with γ varying from 0 to 360°





30

Electric field (V/mm)

40

50

60

70

. 20

10

0.00

0



Figure 4.13 The plots of the field induced phase retardation Γ_m as a function of an a.c. applied field for the ceramics: (a) KNN-La-0.5Bi (b) KNN-La-1Bi (c) KNN-La-2Bi

The effective linear (Pockel) EO coefficient r_c of the KNN-La-xBi ceramics have been measured and the results are listed in Table 4.4. The measurements were carried out one day after the poling. In general, the observed r_c decreases with increasing the amount of Bi₂O₃. For the KNN-La-1Bi ceramic which has high transmittance of 30% in the near-IR region, the observed r_c reaches a high value of 120 pm/V, which is about 7 times larger than that of LiNbO₃ (17 pm/V) single crystal and as good as the PLZT 12/40/60 (120 pm/V) ceramics.



Table 4.4 Relative permittivity ε_r , dielectric loss tand, remanent polarization P_r , piezoelectric coefficient d_{33} and effective linear (Pockel) EO coefficient r_c for the ceramics prepared by optimized conditions

Sample	tanð	ε _r	Pr	d ₃₃	r _c
	(%)	@100kHz	$(\mu C/cm^2)$	(pC/N)	(pm/V)
KNN	7.3	430	13.5	100	/
KNN-La	4.3	1020	10.6	80	/
KNN-La-0.5Bi	4.0	1230	8.6	62	145
KNN-La-1Bi	3.9	1130	6.9	38	119
KNN-La-2Bi	3.3	780	6.5	/	0.7

4.4 Conclusions

In this chapter, the effect of the two-step sintering conditions on the properties of the KNN and KNN-La ceramics has been investigated. The grain growth of the ceramics is mainly affected by the first-step sintering temperature T_1 and sintering time t_1 while the densification of the ceramics is controlled by the second-step sintering temperature T_2 and dwelling time t_2 . It has been shown that the two-step sintering technique is capable of suppressing the grain growth of the KNN and KNN-La ceramics without deteriorating their dielectric and piezoelectric properties. However, the optical properties of the KNN and KNN-La ceramics prepared by the two-step sintering



technique have not been improved by a lot. Therefore, the KNN-La-xBi ceramics have been prepared by the two-step sintering technique. Our results show that the optical properties of the ceramics have been improved significantly. Besides the optical properties, the microstructure, dielectric, ferroelectric and electro-optic properties of the KNN-La-xBi ceramics have been investigated. Although a relaxor-like behaviour is induced, the ceramics exhibit strong linear electro-optic response. For the KNN-La-1Bi ceramic, it exhibits a reasonably high transmittance of 30% in the near-IR region as well as a high effective linear electro-optic coefficient of 120 pm/V.



Chapter 5 Characterization of KNN-based ceramics prepared by Hot-press sintering technique

5.1 Introduction

In the previous chapter, the KNN-La-xBi ceramics with good optical and electro-optic properties have been fabricated by the two-step sintering technique. Their properties have been investigated. The good optical properties are probably due to the small grains and isotropic crystal structure. The light scattering produced by the pores might not be completely minimized. In this chapter, KNN-La-xBi ceramics were prepared by the hot-press sintering technique in order to improve the densification and reduce the pores in the ceramics. The hot-press sintering technique is a promising method for fabrication of electro-optic ceramics such as PLZT. However, only one ceramic can be prepared by the technique every time while five or more ceramics can be prepared by the two-step sintering technique. The constraint of quantity of ceramic and the special equipment required in the hot-press sintering technique would increase the cost of fabrication. The optical and electro-optic properties of the KNN-La and KNN-La-xBi ceramics prepared by hot-press sintering under the optimized sintering conditions are discussed. The optimized sintering temperatures for the ceramics are



listed in Table 3.4.

5.2 Properties of the ceramics prepared

Photographs of the KNN-La and KNN-La-xBi ceramics are shown in Figure 5.1. It can be seen that the optical transparency of the KNN-La-xBi ceramics has been improved significantly. There are only few white spots observed in the KNN-La-1Bi ceramics. This may be the reason for the significant improvement in the optical properties. However, the ceramics prepared by the hot-press sintering technique become very brittle. Even after sintering the samples under different conditions, including the temperatures at which the pressure is increased and decreased, and the rate of increasing and decreasing the pressures, they are broken. The breakage may occur during the sintering or the removal of the samples from the embedded ZrO₂ powders which have become stuck together after the high-temperature sintering. The breakage may be caused by the non-uniform shrinkage of the ceramics under the simultaneously applied heat and pressure.



Figure 5.1 Photographs of (a) KNN-La (b) KNN-La-0.5Bi (c) KNN-La-1Bi and (d) KNN-La-2Bi ceramics.

The optical transmittance spectra of the KNN-La and the KNN-La-xBi ceramics measured in the range of 300-900 nm are shown in Figure 5.2. As shown in Figure 5.2, the transmittance T of the KNN-La ceramics remains at a low value in the whole range of the measurement, while the observed T for the KNN-La-xBi ceramics start to increase from about 400 nm and reach their high values at 900 nm. In general, the



observed T for the ceramics prepared by the hot-press sintering is higher than those prepared by the two-step sintering technique (Fig. 4.5). The observed T of the KNN-La ceramics prepared by the two-step sintering technique is almost zero at 900 nm while the observed T of the ceramics prepared by hot-press sintering technique reaches 2% at 900 nm. Also, the observed T for the KNN-La-1Bi ceramics prepared by the hot-press sintering technique is about 100% larger than that prepared by the two-step sintering technique. On the other hand, the observed T for the KNN-La-2Bi ceramic is about 50% lower than that prepared by the two-step sintering.

The SEM micrographs of the fracture and thermally etched surfaces of the KNN-La-xBi ceramics are shown in Figures 5.3 and 5.4, respectively. As shown in Figure 5.3, there are no obvious pores and cracks being observed in the ceramics. So the improvement in the optical properties of the ceramics should be attributed to the elimination of the pores which can also be evidenced by the decrease in the white spots on the ceramics (Figure 5.1). As the reduction in the number of pores, the light scattering by them is reduced and thus resulting in the improvement in the optical properties of the ceramics of the ceramical properties of the properties of the ceramical properties of the ceramical properties of the ceramical properties of the properties of the ceramical properties of the propertie



the optical properties of the ceramics should be partly attributed to the reduced scattering of visible and IR lights by the smaller grains. The lower transmittance of the KNN-La-2Bi ceramic should be partly resulted from the "un-optimized" fabrication processing.



Figure 5.2 Optical transmittance spectra for the KNN-La and KNN-La-xBi ceramics.




Figure 5.3 SEM micrographs of the fracture surfaces of ceramics: (a) KNN-La-0.5Bi (b)



KNN-La-1Bi (c) KNN-La-2Bi





Figure 5.4 SEM micrographs of the thermally etched surfaces of ceramics: (a) KNN-La-0.5Bi (b) KNN-La-1Bi (c) KNN-La-2Bi

The plots of $(\alpha hv)^2$ versus hv for the KNN-La-xBi ceramics are shown in Figure 5.5. The observed E_g of the KNN-La-0.5Bi, KNN-La-1Bi and KNN-La-2Bi ceramics are 3.02, 3.12 and 3.03 eV, respectively. As shown in Figure 5.5 (b), because of the higher transmittance, the linear portion of the curve for the KNN-La-1Bi ceramic is longer and hence the E_g determined from it may have a higher accuracy. The observed E_g for the KNN-La-1Bi ceramic is 3.12 eV which is the same as the observed E_g for the KNN-La-2Bi ceramic prepared by the two-step sintering technique. Similarly, probaby due to low transmittance, the observed E_g for the KNN-La-0.5Bi and KNN-La-1Bi ceramics may have a large experimental error.



Figure 5.5 Plots of $(\alpha hv)^2$ versus hv for the KNN-La-xBi ceramics. The optical band

gap energy E_g is obtained by extrapolating the linear portion of the curve to zero.



5.3 Conclusions

In this chapter, the KNN-La-xBi ceramics have been prepared by the hot-press sintering technique. The pressure applied during the sintering is effective in promoting uniform densification but does not have significant effects on the grain size. Although the pores cannot be completely eliminated after the hot-press sintering, the number of them is decreased considerably and hence the optical transmittance of the ceramics is increased by more than 100%. For the KNN-La-1Bi ceramics, the observed transmittance reaches a high value of 55% in the near-IR region. The improvement in the optical properties should be attributed to the reduced light scattering by the pores. However, the ceramics prepared by the hot-press sintering technique become brittle.



THE HONG KONG POLYTECHNIC UNIVERSITY Chapter 6 Conclusions

In this work, new lead-free KNN-La-xBi, i.e., $(K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO_3 + x$ mol% Bi₂O₃, electro-optic ceramics have been successfully fabricated by both the twostep sintering technique and hot-press sintering technique. Although the hot-press sintering technique is more effective in improving the optical properties of the ceramics, the ceramics prepared by the two-step sintering technique also exhibit good optical transparency, showing a transmittance of ~50% in the near-IR region. The ceramics also exhibit strong linear electro-optic responses, giving an effective linear electro-optic coefficient of 120-145 pm/V.

The two-step sintering technique has been evaluated as effective in suppressing the grain growth the KNN and KNN-La, i.e., $K_{0.5}Na_{0.5}NbO_3$ of and (K_{0.5}Na_{0.5})_{0.9475}La_{0.0175}NbO₃, respectively, ceramics. Our results reveal that the grain growth of the ceramics is mainly affected by the first-step sintering temperature T_1 and sintering time t₁ while the densification is controlled by the second-step sintering temperature T_2 and the dwelling time t_2 . The grain sizes of the KNN ceramics are reduced significantly from ~16 to ~3 μ m by using the two-step sintering technique. Probably due to the limitation of the grain size for ceramics prepared by the mixed-



oxide method, the two-step sintering technique only reduces the grain sizes of the KNN-La ceramics slightly from 0.8 to 0.5 μ m. Although the grain size of the KNN-La ceramics is reduced to ~ 0.5 μ m, the ceramics only become translucent. This should be due to the significant light scattering partly by the large and non-uniform grains and partly by the pores or cracks resulted from non-uniform densification. Our results also demonstrate that despite the decrease in the grain size, the dielectric and piezoelectric properties of the ceramics are not deteriorated.

Excess Bi₂O₃ has been shown effective in promoting uniform densification as well as suppressing the grain growth of the KNN-La ceramics. The grains of the KNN-La-xBi are smaller and more uniform, and hence their optical properties are improved significantly. For the KNN-La-2Bi ceramic, the transmittance reaches a high value of 50% in the near-IR region. Our results also reveal that the ceramics possess a cubic-like crystal structure and hence minimal optical anisotropy. A diffuse phase transformation is also induced in the ceramics, causing them to become more relaxor-like and contain more polar nano-regions. As a result, the light scattering at the grain boundaries as well as the domain walls are reduced significantly, and then the optical properties of the ceramics are improved. Although a relaxor-like behaviour is induced, the ceramics



exhibit strong linear electro-optic response, giving a high effective linear EO coefficient of 120-145 pm/V.

Transparent KNN-La and KNN-La-xBi ceramics have also been successfully fabricated by hot-press sintering technique. The hot-press sintering technique is effective in promoting uniform densification and hence reducing the pores in the ceramics. As a result, the optical properties of the ceramic are improved significantly. For the KNN-La-1Bi ceramic prepared by hot-press sintering technique, the observed transmittance is increased by more than 100%, reaching a high value of 55% in the near-IR region. However, probably due to non-uniform shrinkage of the ceramics, the ceramics become easily broken during the sintering process.



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