Fabrication of $[\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3$ transparent ceramics using conventional sintering technique

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The effect of Bi$_2$O$_3$ content on the crystal structure, microstructure, and optical and electric properties of $[\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3$ ceramics was investigated. These ceramics were fabricated using a conventional pressure-less sintering, and were observed to be opaque at $x = 0$ and 3 but transparent at $x = 5$ and 7. The transmittance at an infrared wavelength of 1310 nm was 68 and 62% at $x = 5$ and 7, respectively. At $x = 5$, a high Curie temperature of 365°C, a ferroelectric polarization-electric field loop with a reduced remanent polarization, and a quadratic electro-optic effect of 3.1 x 10$^{-17}$ m$^2$/V$^2$ were observed. The effective linear electro-optic effect ($\Delta n/E_0$) was calculated by the birefringence ($\Delta n$) divided by a half-wave electric field ($E_0$) of 43.2 kV/cm. This value was equal to 146 pm/V, which was higher than the linear electro-optic effect of previously reported (K,Na)NbO$_3$-based transparent ceramics and a LiNbO$_3$ single crystal. However, it was lower than that of a K(Ta,Nb)O$_3$ single crystal and (Pb,La)(Zr,Ti)O$_3$ transparent ceramics.

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1. Introduction

Electro-optic (EO) materials have been studied for optical devices such as optical modulators, beam deflectors, and optical phased arrays.$^{1,3}$ A currently utilized EO material is a LiNbO$_3$ single crystal. However, its small EO effect requires a large electric field to induce a change in its refractive index. Therefore, EO materials with a great EO effect such as (Pb,La)(Zr,Ti)O$_3$ (PLZT) transparent ceramics and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_5$-PbTiO$_3$ (PMN-PT) single crystals and transparent ceramics have been studied.$^{4-7}$ However, these materials contain toxic lead. Thus, lead-free EO materials have been explored including K(Ta,Nb)O$_3$ single crystals$^{8,9,10}$ and (Sr,Ba)Nb$_2$O$_6$ transparent oriented ceramics.$^{9,10}$ However, K(Ta,Nb)O$_3$ and (Sr,Ba)Nb$_2$O$_6$ need to be in the form of a single crystal or oriented ceramics to show their great EO effect. Recently, Li and Bi co-substituted (K,Na)NbO$_3$, or $[\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]$-(Nb$_{0.95}$Bi$_{0.05}$)$_2$O$_3$, randomly oriented transparent ceramics were fabricated and showed a greater EO effect compared that of the LiNbO$_3$ single crystal.$^{11}$ However, the ceramics required a hot-press technique to remove their pores that reflected light, increasing the manufacturing cost. As reported for $[\text{Li}_{0.1}(\text{K}_{0.5}\text{Na}_{0.5})_{0.9}]$(Nb$_{0.9}$Bi$_{0.1}$)$_2$O$_3$ and Bi content and additional Bi$_2$O$_3$ can improve their transparence without using hot-pressing, which, however, reduces the EO effect.$^{12}$ We previously fabricated PMN-PT-based transparent ceramics using a conventional pressure-less sintering technique rather than a pressure-assisted sintering such as hot-pressing.$^{13-16}$ This was attributed to the use of fine calcined powders and sintering in an oxygen atmosphere to promote densification. In this study, this technique was applied to create $[\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]$NbO$_3$ transparent ceramics with the reduced amounts of Bi$_2$O$_3$ addition. The effect of Bi$_2$O$_3$ sintering aid content on the crystal structure, transparency, microstructure, and electric and EO properties was investigated.

2. Experimental procedure

2.1 Ceramics processing

$[\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]$NbO$_3$ was initially synthesized via a solid-state reaction. Powders of Li$_2$C$_2$O$_4$ (99.0%; Sigma Aldrich), K$_2$C$_2$O$_4$·H$_2$O (99.0%; Sigma Aldrich), Na$_2$C$_2$O$_4$ (99.5%; Kojundo Chemical Laboratory), and Nb$_2$O$_5$ (99.0%; Kojundo Chemical Laboratory) were stoichiometrically weighed, and urea [CO(NH)$_2$]$_2$ (99.9%; Sigma Aldrich) of the same molar amount of $[\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]$NbO$_3$ was added to lower the calcination temperature. These were mixed by a mortar and pestle for 1.5 h. The compact of the ground powders was uniaxially pressed at 40 MPa in a 25-mm-diameter die and calcined at 550°C for 4 h in an open crucible in air. The crystal structure of the ground compact was analyzed by using X-ray diffraction (XRD) with Cu Kα radiation.
(RINT 2500; Rigaku). x (= 0, 3, 5, and 7) wt% Bi$_2$O$_3$ (99.99%; Kojundo Chemical Lab.) was added to the powder and the mixture was pulverized at 500 rpm for 20 min using a planetary ball mill (classic line P-7; Fritsch) with ethanol and stabilized zirconia balls. Here, the 90 wt% of the zirconia balls had a diameter of 0.3 mm and the remainder had a diameter of 3 mm. A 1-wt% polyvinyl alcohol binder was mixed with the powders, and they were passed through 0.8-mm openings. The 10-mm-diameter compacts of the powders were fabricated via uniaxial cold isostatic pressing at 200 MPa. Binder burnout was conducted for the compacts at 700°C for 2 h. Then, the dielectric properties were measured at 1 MHz using an impedance analyzer (IM3570; HIOKI) when samples were cooled from 500°C. Polarization–electric field (P–E) loops were measured at 0.1 Hz using a polarization and strain measuring system (Model JP005-SE; Lead Techno) at room temperature. For EO measurements, the ceramic with x = 5 was cut to a bar with a size of 0.2 × 0.2 × 8 mm$^3$ in volume. A parallel pair of faces with a size of 0.2 × 8 mm$^2$ in area was sputtered using Cr and Au for electrodes. The sample was pole by applying 10 unipolar pulse triangle electric fields with an electric field amplitude of 35 kV/cm at approximately 0.14 Hz at room temperature. Transmitted light intensity I as a function of E was measured with the Senarmont setting with a light wavelength λ of 1310 nm as described elsewhere. The birefringence Δn (= δn/2πL) was determined by measuring the relative light intensity I/I$_0$ (= sin$^2$(φ/2)), where φ is the phase difference between the ordinary and extraordinary light, I$_0$ is the maximum transmitted light intensity, and L is the light path length.

3. Results and discussion

3.1 Crystal structure, optical properties, and microstructure

Figure 1(a) shows the XRD patterns of the [Li$_{0.05}$(K$_{0.5}$Na$_{0.5}$)$_{0.95}$]NbO$_3$ + x wt%Bi$_2$O$_3$ ceramics. For the samples, the crystal structure was perovskite and no secondary phases were observed within the detection limit. The XRD patterns were changed with Bi$_2$O$_3$ content, with x = 3–7 were thinned using a focused ion beam setup which was equipped with an SEM system. Grain size was determined as an average of the diameters of ~60 grains and the error bar was determined as the standard deviation of the diameters. Energy dispersive X-ray spectroscopy (EDS, Voyager 3; Noran Instruments) elemental mapping was performed for the thinned specimen of x = 7 in a TEM chamber (JEM-3000F; JEOL).

For electrical measurements, Ag electrodes were formed by applying Ag paste on ceramic surfaces and heating at 550°C. The dielectric properties were measured at 1 MHz using an impedance analyzer (IM3570; HIOKI) when samples were cooled from 500°C. The XRD patterns were changed with Bi$_2$O$_3$ content, and the XRD parameters of the ceramics were determined by measuring the relative light intensity I/I$_0$ (= sin$^2$(φ/2)), where φ is the phase difference between the ordinary and extraordinary light, I$_0$ is the maximum transmitted light intensity, and L is the light path length.

Figure 1(b) shows the lattice parameter and perovskite cell volume to the one third $t^{1/3}$ and (c) Crystal anisotropy, $|1 - c/a|/(1 - b/a')$ of the ceramics.

![Figure 1](image-url)

(a) XRD patterns of the [Li$_{0.05}$(K$_{0.5}$Na$_{0.5}$)$_{0.95}$]NbO$_3$ + x wt%Bi$_2$O$_3$ ceramics. (b) Lattice parameter and perovskite cell volume to the one third $t^{1/3}$ and (c) Crystal anisotropy, $|1 - c/a|/(1 - b/a')$ of the ceramics.
suggested that Bi ions were partially incorporated into the perovskite cell. In view of the peak splitting at approximately 2θ = 22, 31, and 45°, the crystal system was orthorhombic at x = 0 and tetragonal at x = 3–7. Lattice parameters, perovskite cell volume to the one third \( V^{1/3} \), and crystal anisotropy \( |1 - b/c| \) or \( |1 - c/a| \) are shown in Fig. 1(b). Here, the orthorhombic lattice parameters \( a, b, \) and \( c \) were expressed as the pseudo-tetragonal lattice parameters \( a' = c' = \sqrt{a^2 + c^2/2} \) and \( b \). As \( x \) increased, the \( V^{1/3} \) value decreased. This decrease in the lattice volume is attributed to the smaller ionic radius of Bi3+ with the coordinate number of 12 (1.45 Å) (1Å = 0.1 nm) as compared to that of the averaged ionic radius of \([\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3\) (1.50 Å). As a result of these lattice parameter changes, the crystal anisotropy was decreased with increasing \( x \). In particular, a large decrease was observed at \( x = 5 \).

Figure 2 shows photographs of the \([\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3 + x\%\text{Bi}_2\text{O}_3\) ceramics with a diameter of 8 mm and a thickness of 0.5 mm. Although the ceramics were opaque at \( x = 0 \) and 3, these became transparent at \( x = 5 \) and 7. Figure 3 shows the transmittance spectra of the \([\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3 + x\%\text{Bi}_2\text{O}_3\) ceramics with a thickness of 0.5 mm. At a visible wavelength of 600 nm, the transmittance was nearly zero at \( x = 0 \) and 3; however, it was 15% at \( x = 5 \) and 33% at \( x = 7 \) without a reflectance loss correction. These transmittances were consistent with the appearance. At an infrared wavelength of 1310 nm, which is among the wavelengths used for optical communications, high transmittances of 68% at \( x = 5 \) and 62% at \( x = 7 \) were observed. Notably, at a light wavelength of 900 nm, the transmittance of \([\text{Li}_{0.05}(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_{3.05}\text{Bi}_{0.05}\text{O}_3 + 4\%\text{Bi}_2\text{O}_3\) (10.8 wt % Bi2O3) ceramics prepared via a pressure-less sintering
to the reduction in the crystal anisotropy. In order to understand the stagnant grain growth behavior, EDS elemental mapping was conducted for the ceramics with \( x = 7 \).

**Figure 5** shows the TEM image and EDS elemental mapping of the ceramics with \( x = 7 \). It was found that Bi was partly located at grain boundaries. This confirmed that the addition of Bi\(_2\)O\(_3\) suppressed ceramic grain growth. In addition, it was found that the distribution of K and Na was inhomogeneous; that is, K-rich regions were poor in Na and Na-rich regions were poor in K. Bi was also located at the K-rich regions. A possible reason for this result is the following. During sintering, Bi\(_2\)O\(_3\) was melt (the melting temperature of Bi\(_2\)O\(_3\) is \( \approx 820^\circ\text{C} \)) and \( [\text{Li}0.05(\text{K}0.5\text{Na}0.5)0.95]\text{NbO}_3 \) was partially melt in liquid Bi\(_2\)O\(_3\). The main component of \( [\text{Li}0.05(\text{K}0.5\text{Na}0.5)0.95]\text{NbO}_3 \) is \( (\text{K}0.5\text{Na}0.5)\text{NbO}_3 \) and the KNbO\(_3\)-NaNbO\(_3\) system forms an all-proportional solid-solution.\(^{21}\) When (K,Na)NbO\(_3\) is melt, it separates to K-rich (K,Na)NbO\(_3\) liquid and a Na-rich (K,Na)NbO\(_3\) solid. Thus, Bi- and K-rich and Na-poor regions and Na-rich and Bi- and K-poor regions formed.
These results for the microstructure and the crystal structure suggested that the increase in the transmittance at $x = 5$ and 7 was attributed to the increase in the relative density (a decrease in the number of pores), a grain size smaller than the wavelength of light, and the reduction in the crystal anisotropy.

3.2 Dielectric, ferroelectric, and electro-optic properties

Figure 6 shows the temperature dependence of the dielectric properties of the $[\text{Li}_{0.05}\text{(K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3 + x$ wt % $\text{Bi}_2\text{O}_3$ ceramics. At $x = 0$, a sharp peak and a broad peak were observed at 448 and 80°C, which were associated with the cubic to tetragonal phase transition and the tetragonal to orthorhombic phase transition, respectively. With the addition of $\text{Bi}_2\text{O}_3$, the tetragonal to orthorhombic phase transition temperature was lowered to below room temperature, which was consistent with the change in the crystal system observed in the XRD patterns. With increasing $x$, the cubic to tetragonal (Curie) temperature decreased to 387, 365, and 342°C at $x = 3$, 5, and 7, respectively. The decrease was attributed to the lowered crystal anisotropy with increasing $x$. The increase in the dielectric constant at room temperature was associated with the lowered Curie temperature as well as the increase in the relative density. The sharp dielectric constant peak at the Curie temperature at $x = 0$ was relaxed at $x = 3–7$, which was attributed to the small grain size and weakened ferroelectricity as described in the following paragraph.

Figure 7 shows the $P–E$ loops of the $[\text{Li}_{0.05}\text{(K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3 + x$ wt % $\text{Bi}_2\text{O}_3$ ceramics. At $x = 0$, a ferroelectric hysteresis loop was observed. The loop partly appeared round, which was associated with a space charge contribution possibly obtained from the moisture that resulted from the low density of the ceramics. At $x = 3–7$, ferroelectric hysteresis loops with reduced remanent polarization were observed; these could be associated with disrupted ferroelectric ordering via the $\text{Bi}_2\text{O}_3$ addition. Because the ceramics with $x = 5$ and 7 showed good transparency and ferroelectric responses, they could show EO responses. In this study, the EO response of the ceramics with $x = 5$ was investigated.

Figure 8 shows the EO responses of the $[\text{Li}_{0.05}\text{(K}_{0.5}\text{Na}_{0.5})_{0.95}]\text{NbO}_3 + 5$ wt % $\text{Bi}_2\text{O}_3$ ceramics. An increase in the relative light intensity was observed with the application of electric fields. The birefringence was plotted as a function of an electric field $E$ and the square of electric field $E^2$ and it quadratically increased with respect to $E$ and linearly increased with respect to $E^2$, indicating that the ceramics showed a quadratic EO effect. This result was
different from the linear response of the hot-pressed K0.48Na0.52Nb0.925Bi0.075O3 transparent ceramics and hot-pressed K0.48Na0.52Nb0.925Bi0.075O3 single crystals and lead-based PLZT ceramics.8),24),25) To compare the EO response of the ceramics was 43.2 kV/cm at 146 pm, which was greater than the linear EO response of the hot-pressed (K,Na)-NbO3-based transparent ceramics and a LiNbO3 single crystal. Further improvement in the transmittance may result in this material being a candidate material for EO devices.

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