Microstructural, Raman and dielectric properties of 
\((1-x)\)NaNbO\(_3\)–\(x\)BiCrO\(_3\) biphase ceramics

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Abstract

The phase, microstructural and dielectric properties of \((1-x)\)NaNbO\(_3\)–\(x\)BiCrO\(_3\) \((x = 0.1, 0.2, 0.3, 0.4\) and 0.5\) ceramics with perovskite–pyrochlore mixed-phase were investigated. A single-phase solid solution in the sintered specimens was identified as observed perovskite phase for \(x = 0.1\) and pyrochlore for \(x = 0.5\). The results indicate that the microstructure has mixed large and small grains. Dielectric constants and dielectric loss were measured as functions of temperatures \((-15\) to 200 °C\) at 1 kHz. Complex impedance spectroscopy shows the presence of barrier layers in biphase ceramics. The Raman spectra and porosity percentage in the biphase system were also measured.

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1. Introduction

Sodium niobate (NaNbO\(_3\)) exhibits a remarkably large number of successive phase transitions and is one of the most complex perovskite ferroelectric materials [1,2]. The dielectric behavior of the NaNbO\(_3\) may be modified by the addition of Li\(^+\) [3] or K\(^+\) [4] cations which induce a ferroelectric phase at room temperature. Sodium niobate is of particular interest [5] because the antiferroelectric phase is based on some solid solutions with good ferroelectric and piezoelectric properties [6,7].

Most studies have focused on doped sodium niobate. Replacing Na\(^+\) with high-valence ions creates additional positive charges, which are compensated for by negative charges created by replacing Nb\(^{5+}\) with low-valence ions. The electrical properties are affected by oxygen non-stoichiometry, doping, stress and electric fields [6]. Therefore, the participation of oxygen vacancies in the conduction process raises a question about partial ionic and partial electronic conduction. Materials with such mixed characteristics are interesting due to their potential applications in electrochemical devices [8].

BiCrO\(_3\) is a multiferroic material [9], which is responsible for the high dielectric permittivity of perovskite ceramics when doped into them [10]. The family of perovskite-structure ABO\(_3\) compounds has attracted considerable attention over the past half-century. However, to our knowledge, A\(^1+\)B\(^{3+}\)O\(_3\)–A\(^3+\)B\(^{5+}\)O\(_3\) perovskite-structure compounds such as the \((1-x)\)NaNbO\(_3\)–\(x\)BiCrO\(_3\) system have not been observed and this fact motivates this research, which studies the stability of the single perovskite phase and the pyrochlore second phase, mixed in a \((1-x)\)NaNbO\(_3\)–\(x\)BiCrO\(_3\) system. Therefore, this work attempts to systematize the effect of this mixed-phase on the phase relations, Raman spectra and dielectric properties of the BiCrO\(_3\)-doped NaNbO\(_3\) ceramics.

2. Experiments

The compounds used in this investigation were formed in a conventional solid-state reaction. Solid solution oxides with the formula \((1-x)\)NaNbO\(_3\)–\(x\)BiCrO\(_3\) \((x = 0.1, 0.2, 0.3, 0.4\) and 0.5\) were prepared. The starting materials Na\(_2\)CO\(_3\), Nb\(_2\)O\(_5\), Bi\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) had a purity of at least 99.9%. The powders were mixed and ground with acetone in zirconium oxide ball mill for 12 h. The mixed powders were dried and calcined at 950 °C for 5 h. Finally, the calcined powders were reground and pressed into disks at 200 MPa with diameters of 10–11 mm and thicknesses of 2–3 mm. The disks were sintered in air at 1250 °C for 3 h, followed by cooling at a rate of 3 °C/min, to 800 °C, cool.

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Sintered discs were cleaned by N₂ gas and gold was deposited on the surfaces for microstructural observation. The electrodes used to make measurements were deposited on the surface of ground disk by rubbing on an In–Ga alloy.

The phase-purity, structure and the lattice parameters of the samples were determined by X-ray powder diffraction (Rigaku D/max) with Cu-Kα radiation at room temperature. Next, the grain morphology and grain size were characterized by scanning electron microscopy (SEM, Hitachi S-3000N, Japan). The SEM equipped with an energy dispersive spectrometer (EDS) detector was used to do chemical analysis for sintered discs. The Raman spectra were obtained using a Dilor RTI instrument and excitation wavelengths were provided by an Ar⁺ Spectra-Physics laser with an exciting wavelength of 514.5 nm. The open porosity of the sintered (1−x)NaNbO₃–xBiCrO₃ in de-ionized water was calculated using the Archimedes’ method using the equation [11].

\[
\text{Open porosity} = \frac{W - D}{W - B} \times 100\%
\]

where \( B \) is the weight of the samples measured in water, \( D \) the weight of the samples measured after drying at 100 °C for 24 h, and \( W \) is the weight measured after the water has been removed from the surfaces of the samples. The dielectric constants and dielectric loss were measured at temperatures from −15 to 200 °C using an LCR meter (HP4284A).

3. Results and discussion

Fig. 1(a) presents the XRD patterns of the powders that were calcined at 950 °C for 5 h. The undoped NaNbO₃ had an orthorhombic structure. Mixed phases of cubic perovskite and pyrochlore were observed in (1−x)NaNbO₃–xBiCrO₃ with \( x = 0.1–0.4 \) and single pyrochlore phase was present at \( x = 0.5 \). However, in Fig. 1(b), the crystal structures of the samples sintered at 1250 °C for 3 h were characterized as cubic perovskite–pyrochlore and mixed-phases. Sintering at high temperature reduced the pyrochlore content in the mixed-phases. The relative amounts of perovskite and pyrochlore phases were obtained from XRD patterns of the sintered samples by measuring the major peak intensities for the perovskite (1 1 0) and pyrochlore (2 2 2) phases. The following relationship was used [12]

\[
\text{Pyrochlore (\%)} = \frac{I_{\text{pyro.(2 2 2)}}}{I_{\text{pyro.(2 2 2)}} + I_{\text{perov.(1 1 0)}}} \times 100\%
\]

The phase structure gradually changed from perovskite to pyrochlore as \( x \) increased. The relative amounts of the pyrochlore phase were obtained from the XRD patterns. The relative amounts of pyrochlore at \( x = 0.1, 0.2, 0.3, 0.4 \) and 0.5 were 0, 25.4, 56.1, 73.7 and 100%, respectively. The pyrochlore phase content increased linearly with the increase of the BiCrO₃ content and the system was pure pyrochlore phase at \( x = 0.5 \). The transformation of NaNbO₃ from an orthorhombic structure to a cubic perovskite-structure is complex and may be caused by a change in the angles of rotation of the BO₆ framework [13]. In this work, a generally observed (1 1 1) peak is too weak to be noticed as belonging to the cubic perovskite. A similar phenomenon was also observed from the mixed oxide.

![Fig. 1. X-ray diffraction patterns of compositions of (1−x)NaNbO₃–xBiCrO₃ (a) the powders calcined at 950 °C for 5 h and (b) the samples sintered at 1250 °C for 3 h.](image-url)
system NaNbO₃–BaSnO₃ [14]. The formula for the pyrochlore phase can be regarded as (Bi₃⁺Na₄⁺)(Cr₄⁺Nb₄⁺O₈⁻), in which Bi³⁺ (1.20 Å) or Na⁺ (1.18 Å) ions occupy the A-sites of A₂B₂O₆O’⁻ type pyrochlores and Cr⁴⁺ (0.62 Å) and Nb⁵⁺ (0.64 Å) ions occupy the B-sites. Additionally, δ > γ and y < 0.5 are assumed and pyrochlore ceramics are assumed to be deficient in oxygen. The lattice constants were determined from the diffraction patterns using a computer program called Unit Cell. The d-values of the phases are almost constant at x = 0.2–0.4. Therefore, the biphase ceramics can be indexed by the lattice parameter a = 3.92 Å for cubic perovskite and a = 10.49 Å for cubic pyrochlore.

**Fig. 2 (a–e)** presents microstructures of surfaces of uniform, large-small mixed, and liquid-phase sintering surfaces of biphase ceramics. This figure shows SEM photographs of the ceramics sintered at 1250 °C for 3 h. Large grains and small grains are observed in Fig. 2(b–d). The mean grain sizes of the large grains and small grains are 8–10 and 2–3 μm, respectively. The grains were small and uniform at x = 0.1 in Fig. 2(a). As x increased (pyrochlore phase content increased), the number of large grains gradually increased, until no small grain remained. The pure pyrochlore ceramic in Fig. 2(e) underwent liquid-phase sintering, perhaps because the sintering temperature was high or soaking time was long [15].

**Fig. 2.** SEM photographs of the as-fired (1−x)NaNbO₃–xBiCrO₃ ceramics with (a) x = 0.1, (b) x = 0.2, (c) x = 0.3, (d) x = 0.4 and (e) x = 0.5 sintered at 1250 °C for 3 h (with a magnification value of 3000).
The energy dispersive spectroscopy analysis is conducted for that $x = 0.1, x = 0.5$ and the results compared with those obtained at $x = 0.3$, as presented in Fig. 3(a–d). The results indicate that the energy dispersive spectrometer peak at $x = 0.1$ is similar to the peak of the small grains at $x = 0.3$. That at $x = 0.5$ is similar to the large grains at $x = 0.3$ with a high peak of Bi atom content. Therefore, the small grains were of the perovskite phase and the large grains were of the pyrochlore phase. Chen et al. [16] also indicated that the large grains in perovskite–pyrochlore mixed lead-based ceramics were pyrochlore. Quantifying the elemental composition of selected grains is difficult because Na or O atoms have very small atomic numbers and are very light. However, the liquid-phase sintering changed the composition for Na and O atoms at the surface of the sample, according to EDS in Fig. 3(b).

Fig. 4 presents the shrinkage and percentage open porosity of the pellets sintered at $1250^\circ$C for 3 h. The lowest shrinkage percentage was around 14% at $x = 0.2$, at which the porosity percentage was high, about 6%. This result shows that biphasic ceramics with big–small mixed grains were difficult to sinter. Mechanical stress arose in the grain boundary during sintering, because the thermal expansions of the structures differed. Wang et al. [17] also determined that the samples of various pyrochlore-fluorite biphasic ceramics exhibited various thermal expansion coefficients. However, the sintering density increased...
with $x$, because bismuth-based pyrochlore was sintered at lower temperatures.

Fig. 5a plots the dielectric constant $\varepsilon_r$ as a function of temperature for all samples at 1 kHz. The peak at the transition temperature ($T_m$) of 59°C is clearly the highest at $x=0.4$. For $x=0.3$, the highest peak is at $\sim 62°C$ ($T_m$). However, no peak is present and the dielectric constant is low at $x=0.1$, 0.2 and 0.5 at various temperatures from $-15$ to $200°C$. The dielectric constant of around 260 at $x=0.2$ is slightly less than that of around 530 for $x=0.1$ at room temperature. A well-defined single perovskite phase was observed in the sample with $x=0.1$, and some pyrochlore phases were present in the sample with $x=0.2$. Sample $x=0.2$ had a greater open porosity percentage than other materials and so had a lower dielectric constant. Additionally, the presence of pyrochlores is believed to reduce the optimum dielectric permittivity of perovskites [16]. The dielectric constant at $x=0.5$ has a low value of around 220, slightly increased with the temperature, and the structure is single cubic pyrochlore structure at room temperature. In Fig. 5b, the dissipation factors ($D$) for $x=0.3$ exhibit two peaks at 55 and $85°C$, because two phase are mixed. Therefore, two peaks seem to be combined into a wider peak for the pyrochlore-rich sample with $x=0.4$. When the temperature exceeds $130°C$, all of the curves of dielectric loss against temperature are warped upwards by the effect of leakage conductivity since the oxygen vacancies migrate at elevated temperatures [18].

Following sintering and during cooling, reoxidation occurs, but only in the grain boundaries and the surface, because the temperature decreases rapidly and insufficient time is available for equilibrium to be reached. Therefore, the grain boundaries and surfaces become relatively insulating. The grain–grain boundary interface layer is typically called a “barrier layer” [19]. The complex impedance was analyzed using Cole–Cole impedance plots, to verify the presence of barrier layers in the biphase ceramics. Fig. 6a and b show the Cole–Cole impedance plots for $x=0.2, 0.3$ and 0.4 at temperatures of 16 and $63°C$. The complex impedance diagrams of some samples measured at $16°C$ lack a proper semicircle, so distinguishing the grain contribution from those of the boundary is difficult. Therefore, measurements were made at a temperature of $63°C$, and two well-resolved semicircles were clearly visible at $x=0.3$. The first semicircle, at high frequency above 5 kHz for $x=0.3$, corresponds to a particular behavior exhibited by the material or the bulk characteristics. The second semicircle represents the contribution of grain boundaries at low frequencies, and verifies the presence of barrier layers in perovskite–pyrochlore biphase ceramics for $x=0.3$ at $63°C$.

CaCu$_3$Ti$_4$O$_{12}$ ceramics exhibited a similar dielectric mechanism. Sinclair et al. [20] have adopted impedance spectroscopy (IS) to establish the electrical microstructure of CaCu$_3$Ti$_4$O$_{12}$ ceramics and found them to be electrically inhomogeneous, containing semiconducting grains with insulating grain boundary regions. This characteristic has potential application for internal barrier layer capacitors (IBLCs) [21]. Much fundamental science, ceramic processing and development must be conducted before biphase ceramics may be regarded as a new class of materials that is suitable for applications in ceramic-based capacitors.

Before the characteristics of the (1-$x$)NaNbO$_3$–$x$BiCrO$_3$ ceramics in relation to the composition can be considered in detail, the Raman spectra of the end members (NaNbO$_3$) must be first obtained. Fig. 7 presents the Raman spectrum of the pure NaNbO$_3$ at room temperature. It agrees well with the results in previous work [22]. The dark doped NaNbO$_3$ samples have a lower intensity than the light single phase NaNbO$_3$. Since the Raman spectra of doped-NaNbO$_3$ and pure NaNbO$_3$ differ noticeably, the evolution of the structural changes of (1-$x$)NaNbO$_3$–$x$BiCrO$_3$ biphase ceramics, which depend on composition, can be followed using XRD, SEM and permittivity data. According to the literature, $x=0.1$ corresponds to the cubic perovskite-structure presented in Fig. 7, which shows that scattering effect occurs at six wavenumbers, roughly 120, 217, 422, 571, 861 and 874 cm$^{-1}$. The sharp peaks observed at low frequency (about 120 cm$^{-1}$) are artifacts of the electronic of the Raman spectra apparatus. The $x=0.2$ sample had four bands,
$F_1$, $F_2$, $F_3$ and $F_4$. These bands appear at frequencies that do not differ much from those of the parent NaNbO$_3$. The Raman bands are quite broad, which in fact is associated with the disorder of cations at the coordinated site, and to some overlapping Raman modes. As mentioned above, the Raman spectra of the biphase system clearly show that the $x=0.2$ spectrum is similar to the $x=0.1$ one, whereas all the other spectra present the essential features of the $x=0.5$ spectrum; the evolution associated with the composition is undetectable. In the NaNbO$_3$-rich biphase ceramics, the line at the $F_1$ site is shifted a slightly downward. This band is assigned to vibration of specifically the (Na/Bi)–O bonds [23]. When the Bi content is increased, the frequency of this vibration decreases, as the Bi mass significantly exceeds the Na mass. However, the peak $F_3$ for pure NaNbO$_3$ is observed at 602 cm$^{-1}$, but for $x=0.3$ is at 571 cm$^{-1}$. When the BiCrO$_3$ content increases with $x$ until $x=0.5$, rather major changes occurs, all of the bands show marked broadening, and many are shifted downwards or upwards from their original frequencies at $x=0.1$.

In relation to the band at $F_4$, the peak from pyrochlore is not only broadened (associated with combined two peaks for $x=0.1$) but also shifted slightly downwards. Additionally, the Raman band at $F_2$ disappeared slowly as the BiCrO$_3$ content increased. The band profiles must be associated with the disorder at the A-sites and B-sites, and the phase substitution broadens the Raman bands.

4. Conclusions

Solid solution oxides with the formula of $(1-x)$NaNbO$_3$–$x$BiCrO$_3$ were successfully synthesized by a conventional solid-state reaction. Based on the X-ray investigation the material is crystallized with a mixed biphase structure. The results show that the small grains were the perovskite phase and the large grains were the grain of pyrochlore phase. The sintered sample $x=0.2$ had a lower shrinkage percentage and a higher porosity percentage than other compositions. The highest dielectric constant peak was measured at around 59 °C for $x=0.4$ and at 62 °C for $x=0.3$. Barrier layers are also present in biphase ceramics, as determined by complex impedance spectroscopy. The Raman spectra of the biphase system showed significant broadening of bands as the BiCrO$_3$ content increased, and many of these bands are shifted downwards or upwards from their original frequencies at $x=0.1$. 

Fig. 6. Complex impedance plots ($Z''$ vs. $Z'$) of $(1-x)$NaNbO$_3$–$x$BiCrO$_3$ with $x=0.2$, 0.3 and 0.4 at (a) 16 °C and (b) 63 °C.

Fig. 7. Raman spectra of several compositions of the $(1-x)$NaNbO$_3$–$x$BiCrO$_3$ system at $x=0.1$, 0.2, 0.3, 0.4 and 0.5.
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