Effects of barium substitution on the sintering behavior, dielectric properties of $\text{Ca}_2\text{Nb}_2\text{O}_7$ ferroelectric ceramics

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Barium-doped $\text{Ca}_2\text{Nb}_2\text{O}_7$ ceramics were prepared in the form of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ($0 \leq x \leq 0.6$) by solid-state reaction. The solubility limit of barium in $\text{Ca}_2\text{Nb}_2\text{O}_7$ was found to be $x = 0.4$ based on X-ray diffraction and Raman spectroscopy analysis. When $x \leq 0.4$, $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ solid solutions with a monoclinic perovskites-like layered structure (PLS) were formed, whereas beyond $x = 0.4$, a secondary phase CaNb_2O_6 was detected. The dielectric properties obviously depended on the barium substitution. With increasing barium amount, the dielectric constant increased from 33.5 for pure $\text{Ca}_2\text{Nb}_2\text{O}_7$ to 38.6 for $x = 0.4$ ($f = 1$ MHz). The Curie temperature (T_c) of the $x = 0.1$ sample was $1280 \pm 5^\circ\text{C}$. The phase transition was confirmed to be the second order.

Keywords: Dielectric properties; perovskites-like layered structure; barium substitution.

1. Introduction

In recent years, the perovskite-like layer structured (PLS) ferroelectrics with a formula of $\text{A}_n\text{B}_n\text{O}_{3n+2}$ ($n = 2 \sim 7$) have received considerable attention in view of their wide ranging properties such as dielectric, ferroelectric, piezoelectric, magnetic, electro-optic, microwave dielectric properties and superconducting properties.^{1–10} The diverse properties of $\text{A}_n\text{B}_n\text{O}_{3n+2}$ are related to their unique structure composed of corner-shared BO_6 octahedra with A cations within the perovskite-like layers, where n is the number of octahedral layers in the perovskite slab.^{1,2,5} In the PLS structure, A sites can accommodate large cations, e.g., alkali metals, alkaline-earth metals, and rare earths metals, and B sites (A and B) are available for a wide variety of small cations with high ionic polarizability, such as Ti, Nb, Ta, W, etc.

In the previous reports, the formation and physical properties of the PLS-ed $\text{A}_n\text{B}_n\text{O}_{3n+2}$ compounds with $n = 2\text{--}6$ have been especially emphasized.^{1–4,7–10} Particularly, much attention has been focused on the $n = 4$ series ($\text{A}_2\text{B}_2\text{O}_7$) for their potential use in high-temperature piezoelectric applications because of their super-high Curie points, such as $\text{La}_2\text{Ti}_2\text{O}_7$ ($T_c \sim 1482^\circ\text{C}$),^{1,11} $\text{Nd}_2\text{Ti}_2\text{O}_7$ ($T_c \sim 1482^\circ\text{C}$),^{1,12} $\text{Sr}_2\text{Nb}_2\text{O}_7$ ($T_c \sim 1482^\circ\text{C}$),^{2,13} etc. In addition, efforts have

been made to improve the piezoelectric activity of $\text{A}_2\text{B}_2\text{O}_7$ through compositional modifications and texturing technologies, such as hot-forging, spark plasma sintering (SPS).^{14–16}

$\text{Ca}_2\text{Nb}_2\text{O}_7$ is a member of the family of PLS $\text{A}_n\text{B}_n\text{O}_{3n+2}$ -type compounds with $n = 4$. Single-crystal $\text{Ca}_2\text{Nb}_2\text{O}_7$ was found to be ferroelectric with extremely high Curie point ($T_c > 1500^\circ\text{C}$) in 1970s. More recently, Ning *et al.*¹² have given a reasonable prediction for the Curie point of $\text{Ca}_2\text{Nb}_2\text{O}_7$ to be about 1525°C , based on the temperature dependence of dielectric spectroscopy. The purpose of the present paper was to study the effects of barium doping on the crystal structure, dielectric properties of $\text{Ca}_2\text{Nb}_2\text{O}_7$.

2. Experimental

$\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ($0 \leq x \leq 0.6$, abbreviated as CBN), were prepared by high temperature solid state reactions of high purity raw powders CaCO_3 (99.9%), BaCO_3 (99.9%), and Nb_2O_5 (99.95%). The raw powders were weighed and fully mixed in stoichiometric amounts and ball milled for 4 h. The mixtures were dried and calcined at 1250°C for 4 h. After calcining, the samples were thoroughly reground and mixed with a 3 wt.% solution of polyvinyl alcohol (PVA) as a

binder. The resultant slurries were then dried and pressed into cylindrical compacts of different thickness in the range 1–3 mm and 11 mm in diameter under a pressure of 100 MPa. The samples were fired at 600°C for 2 h to remove the organic binder and then sintered in the range 1300–1350°C for 4 h.

The phase constitutions of the samples were examined using a Rigaku DMAX-RB X-ray diffractometer (XRD) using CuK α radiation ($\lambda = 0.15406$ nm) in a 2θ range from 10° to 70°. The microstructures were studied using a JSM-5610LV scanning electron microscopy (SEM). The densities of the compacts were measured by the Archimedes method. To study the relative density of the samples, the theoretical density was obtained from the crystal structure based on the XRD data.

Prior to dielectric measurements, Pt pastes were applied to the circular faces, then dried at 900°C for 1 h. Temperature-dependent dielectric measurements were made using an HP4294A LCR meter equipped with a thermostat from room temperature (20°C) to 1400°C at 100 kHz, 500 kHz and 1 MHz.

3. Results and Discussion

The room temperature XRD patterns performed on the $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ($0 \leq x \leq 0.6$) powders calcined at 1250 °C are shown in Fig. 1. Within the limitation of XRD, when $x \leq 0.4$, all the observed diffraction peaks could be indexed based on the standard JCPDF cards (No. 23-0122) for $\text{Ca}_2\text{Nb}_2\text{O}_7$ with a space group $P2_1$, suggesting that barium dissolved into the lattice structure of $\text{Ca}_2\text{Nb}_2\text{O}_7$ to form solid solutions. Nevertheless, the trace amount of a second phase detected as CaNb_2O_6 (JCPDF cards No. 39-1392) was observed in CBN ceramics with $x > 0.4$. Additionally, it is observed that XRD peaks shifted to lower angles as x increased from 0 to 0.3, indicating lattice expansion because of

Fig. 1. Room temperature XRD patterns of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ powders calcined at 1250°C (Peaks of second phases are marked with triangles).

the larger effective ionic radius of Ba^{2+} (1.61 Å) than that of Ca^{2+} (1.34 Å). The peak shifting terminated with further increase in Ba content. The unit cell parameters (a , b , c , V) refined by the least square method are shown in Fig. 2 as well as the linear fitting based on Vegard's law. As observed, the lattice parameters generally increased as Ba content increased with a nearly linear variation in the range of 0.1–0.3, which is in well agreement with the lower angle shifting of XRD peaks due to the lattice expansion caused by the larger Ba substitution. Beyond $x = 0.3$, a deviation from the Vegard's law was detected. These results indicate that the solid solubility limit of Ba in $\text{Ca}_2\text{Nb}_2\text{O}_7$ lattice is less than $x = 0.4$.

It is well known that Raman spectroscopy is a helpful tool to understand the local vibrational characteristics and is sensitive to the structure evolution of materials. Thus, Raman spectroscopy was employed to further confirm the phase purity and solution limit of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$. Figure 3 shows the room temperature Raman spectra of all the $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics in the range 100–1000 cm^{-1} . Similar Raman spectroscopy was observed for the samples with $x = 0.1$ –0.3. On the other hand, the modes at 120.6 cm^{-1} , 280 cm^{-1} and 779 cm^{-1} appeared at $x = 0.4$ and the intensity increased with x value, along with gradually depressed modes around 132 cm^{-1} , 160 cm^{-1} , and 178 cm^{-1} . The modes at 120.6 cm^{-1} , 280 cm^{-1} , and 779 cm^{-1} were attribute to the appearance of CaNb_2O_6 phase, which is consistent with the previous report.¹⁷ Although XRD data showed no diffraction peaks from CaNb_2O_6 in the $x = 0.4$ sample, the Raman peaks of CaNb_2O_6 were detected. The Raman analysis further confirmed that the upper limitation for Ba substitution in $\text{Ca}_2\text{Nb}_2\text{O}_7$ is less than $x = 0.4$. For this reason, only the results from the samples with $x \leq 0.4$ were reported hereafter.

Figure 4 shows the variation of the bulk densities of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics as a function of sintering temperature. A similar variation tendency with sintering temperature is observed for all samples. The bulk density increased to a maximum value at a critical temperature, and further increase in sintering temperature decreased the density. The optimum sintering temperature was obtained at which the maximum density was achieved and shown in the inset of Fig. 4 as well as the corresponding density maxima. It is found that barium doping significantly lowered the sintering temperature from 1375°C for $x = 0$ to 1275°C for $x = 0.4$, indicating an effective improvement in the sinterability of $\text{Ca}_2\text{Nb}_2\text{O}_7$ ceramics. The increasing density is due to the heavier mass of Ba atom (137.33 g/mol) than that of Ca atom (40.08 g/mol). In addition, the relative densities of all the sintered samples were higher than 95% of the theoretical densities. Scanning electron microscope (SEM) images of the as-prepared ceramics ($x = 0.1, 0.2, 0.3$, and 0.4) are shown in Fig. 5. These ceramics have a close microstructure with low porosity. And the grains are homogeneously distributed with average grain size in the range of 2–15 μm , suggesting that they are suitable for subsequent characterization.

Fig. 2. Unit cell parameters (a , b , c , V) of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ (the linear fitting based on Vegard's law).

The room temperature dielectric properties are listed in Table 1. With increasing barium doping amount, the room temperature dielectric constant is found to increase from 33.5 for CBN to 38.6 for CBN-0.4, whereas the loss tangent drops almost an order of magnitude.

Figure 6 shows the temperature dependent dielectric properties measured at four fixed frequencies (100 kHz, 500 kHz, and 1 MHz) for the $x = 0.1$ sample. As seen, sharp

dielectric constant peaks together with loss peaks on the $\tan\delta$ - T curves were observed for all frequencies. The characteristic temperature corresponding to the dielectric constant peaks was the Curie temperature (T_c) for the $x = 0.1$ sample with a value of 1280 ± 5 °C. Compared with the pure $\text{Ca}_2\text{Nb}_2\text{O}_7$, the barium doping in CBN materials markedly decreases the Curie temperature. Similar behaviors have been reported for the barium-doped $\text{Sr}_2\text{Nb}_2\text{O}_7$. It should be noted

Fig. 3. The room temperature Raman spectra of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ samples.

Fig. 4. Variation in bulk densities of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics as a function of sintering temperature.

Fig. 5. Backscattered electron image of as-fired surface of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics sintered at 1350°C : (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, and (d) $x = 0.4$.

Table 1. Sintering temperature, densities and the room temperature dielectric properties of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics.

x	Sintering temperature ($^\circ\text{C}$)	ρ_{th} (g/cm^3)	ρ_d (g/cm^3)	ρ_{rd} (%)	ε_r (1 MHz)	$\tan\delta$ (1 MHz)
0	1375	4.52	4.42	97.8	33.5	1.1×10^{-3}
0.1	1350	4.61	4.48	97.2	34.4	8.6×10^{-4}
0.2	1300	4.65	4.53	97.5	35.2	5.6×10^{-4}
0.3	1300	4.71	4.65	98.6	36.9	4.2×10^{-4}
0.4	1275	4.78	4.69	98.0	38.3	2.8×10^{-3}

Fig. 6. The temperature dependent dielectric properties measured at four fixed frequencies (10 kHz, 100 kHz, 500 kHz, and 1 MHz) for the $x = 0.1$ sample.

that for the other samples with $x > 0.1$, it is impossible to get the T_c values directly from the temperature dependence of dielectric properties because the ceramics began to melt at the temperature prior to the T_c values. This also corresponds well with the lower sintering temperatures in the barium-doped $\text{Ca}_2\text{Nb}_2\text{O}_7$.

From Fig. 6, it is observed that no frequency shift on the T_c value was detected, suggesting no relaxation phenomenon in the $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics. In order to clarify the phase transition order of $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics, the heating and cooling ε_r - T curves at 1 MHz of the CBN-0.1 are shown in Fig. 7. Obviously, the heating and cooling curves yield almost the same T_c values, suggesting no thermal hysteresis. This is a common feature for the second-order phase transition. Moreover, Draegert and Singh¹⁸ proposed that the ferroelectric phase transition can be evaluated by the slopes of

Fig. 7. The heating and cooling ε_r - T curves at 1 MHz of the CBN-0.1 ceramic.

the reciprocal dielectric constant versus temperature below and above T_c (denotes as S^- and S^+ , respectively). Simply, the ratio S^-/S^+ is in the range $(-4, -2)$ the phase transition is identified as a second order type, whereas for a first order transition, the ratio S^-/S^+ is < -4 . As shown in the inset of Fig. 7, the ratio S^-/S^+ in the present ceramic was -2.49 , which is close to -2 . Thus, coupling with the Fig. 7, it is reasonable to deduce a second-order transition for the $\text{Ca}_{2-x}\text{Ba}_x\text{Nb}_2\text{O}_7$ ceramics.

4. Conclusions

Investigations on the dielectric properties of the barium-doped $\text{Ca}_2\text{Nb}_2\text{O}_7$ ceramics were carried out. The solubility of Ba^{2+} into Ca^{2+} lattice was found to be limited to ~ 30 mol% on the basis of XRD and Raman results. It is also found that the barium doping slightly increased the dielectric constant of $\text{Ca}_2\text{Nb}_2\text{O}_7$ and decreased the Curie temperature (T_c) obviously. The phase transition was confirmed to be of second order based on the slopes of the reciprocal dielectric constant versus temperature below and above T_c .

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