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Ferroelectric perovskite-type barium copper niobate: $BaCu_{1/3}Nb_{2/3}O_3$

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Abstract

A perovskite-type $BaCu_{1/3}Nb_{2/3}O_3$ was prepared by high temperature reaction using $BaCO_3$, CuO and Nb_2O_5. The X-ray powder diffraction pattern of this compound was indexed with the tetragonal cell with the lattice parameters of $a = 4.0464(4)$ and $c = 4.1807(4)$ Å ($c/a = 1.033$). This compound had the tetragonal perovskite-type structure in which the *B* site was occupied statistically by Nb and Cu atoms. From high temperature X-ray powder diffraction patterns this compound had a phase transition from the tetragonal to cubic symmetry in the temperature range of 500–600 °C. The *P–E* and *S–E* hysteresis loops occurred at room temperature and the apparent maximum in the temperature dependence of the dielectric constant was observed at 520 °C. The temperature dependence of the inverse of magnetic susceptibility exhibited paramagnetic behavior.

Keywords: Ferroelectric; Perovskite-type; Oxide

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1. Introduction

The family of perovskite-type oxides has various electrical properties such as ferroelectricity, piezoelectricity, semiconductivity, superconductivity and ion-conductivity [1]. In particular ferroelectric and piezoelectric perovskite-type oxides as represented in $BaTiO_3$ and $Pb(Zr,Ti)O_3$ are very important electric materials. However, $Pb(Zr,Ti)O_3$ having excellent piezoelectric property is one of unfavorable compounds for environmental issues because of containing a large amount of toxic Pb atom. Various substitutive materials for $Pb(Zr,Ti)O_3$ have been proposed, for example $Na_{0.5}Bi_{0.5}TiO_3$ [2,3] and $KNbO_3$ [4] with the perovskite-type structure or the tetragonal tungsten bronze-type oxides [5], however, no compound superior to $Pb(Zr,Ti)O_3$ has appeared yet. Recently it was reported that ceramics with controlled texture which was based on multi-component perovskite-type niobates exhibited excellent piezoelectric property [6]. This result suggested another way of developing lead-free piezoelectric materials. On the contrary we pursue to discover a new lead-free piezoelectric compound in niobates containing barium [7,8] and found that a perovskite-type barium copper niobate, $BaCu_{1/3}Nb_{2/3}O_3$ was a ferroelectric compound.

The barium transition metal niobates, $Ba_3M^{2+}Nb_2O_9$ (M^{2+} = Mn, Co, Ni, Zn) were reported to have the cubic and hexagonal perovskite-type structures [9], and for M^{2+} = Cu stoichiometric perovskite-type niobate could not be prepared but oxygen deficient one, $Ba_{2.5}CuNb_{1.5}O_{7.25}$ [10] or $Ba_3Cu_{1+x}Nb_{2-x}O_{9-1.5x}$ [11] was obtained. However, in 1967 Venevtsev et al. reported that $BaCu_{1/3}Nb_{2/3}O_3$ had the tetragonal perovskite-type structure and was a ferroelectric compound with $T_c = 370$ °C from high temperature X-ray diffraction and measurement of dielectric constant [12]. Kapyshev et al. [13] and Fesenko et al. [14] reported synthesis and the lattice parameters of tetragonal perovskite-type $BaCu_{1/3}Nb_{2/3}O_3$. In any event,

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there has been no report for the details of electrical property of $BaCu_{1/3}Nb_{2/3}O_3$. Here we will describe the electrical property of the perovskite-type $BaCu_{1/3}Nb_{2/3}O_3$.

2. Experimental

The mixtures of $BaCO_3$ (99.0%), Nb_2O_5 (99.95%) and CuO (98.0%) with a molar ratio of 3:1:1.2 were calcined at 800 °C for 6 h in air. The calcined powder samples were well ground and then heated three times at 1200 °C in air. The reaction durations were 48, 36 and 36 h. The product was identified by X-ray powder diffraction using monochoromated Cu*K*α radiation. High temperature X-ray powder diffraction data were carried out from room temperature to 1000 °C.

The sintered body was prepared by treating the powders at 4.5 GPa and 1000 °C for 0.5 h in a cubic-anvil-type high-pressure apparatus. The diameter and thickness of the pellet were 3 and 0.4 mm, respectively. The surface of the pellet was polished with emery paper and then was painted with Ag paste as an electrode. Temperature dependence of dielectric constant was measured at 1.0 kHz from room temperature to 600 °C. The *P* (polarization)–*E* (electric field) hysteresis loop was measured by a charge-amplifier circuit at 50 Hz and and *S* (strain)–*E* (electric field) hysteresis loop was measured using a contact-type displacement sensor at 0.1 Hz at room temperature. The magnetic susceptibility was measured by using SQUID from 2 to 300 K.

3. Results and discussion

According to Ono [10] and Langbein et al. [11] a stoichiometric perovskite-type $Ba_3Cu^{2+}Nb_2O_9$ could not be prepared but $Ba_{2.5}CuNb_{1.5}O_{7.25}$ and $Ba_3Cu_{1+x}Nb_{2-x}O_{9-1.5x}$ were obtained. Venevtsev et al. [12], Kapyshev et al. [13] and Fesenko et al. [14] reported only the lattice parameters of tetragonal perovskite-type $Ba_3CuNb_2O_9$ ($= BaCu_{1/3}Nb_{2/3}O_3$), but purity of their samples was ambiguous. We prepared successfully a perovskite-type $BaCu_{1/3}Nb_{2/3}O_3$ by repeating the reaction with the mixture containing excess CuO at 1200 °C. When a stoichiometric mixture was used or the reaction was not repeated at lower temperature, the X-ray powder diffraction patterns of the products showed the diffraction peak at $2\theta = 29.35°$ which could not be indexed with the tetragonal cell. This peak was considered to come from an impurity phase because using excess CuO and repeating the reaction at higher temperature made it disappeared. As shown in Fig. 1, the X-ray powder diffraction of the product synthesized as the single phase could be indexed with the tetragonal cell of the lattice parameters; $a = 4.0464(4)$ and $c = 4.1807(4)$ Å ($c/a = 1.033$) and these values were compared with the published data ($a = 4.048$ and $c = 4.174$ Å [12,13] and $a = 4.041$ and $c = 4.193$ Å [14]).

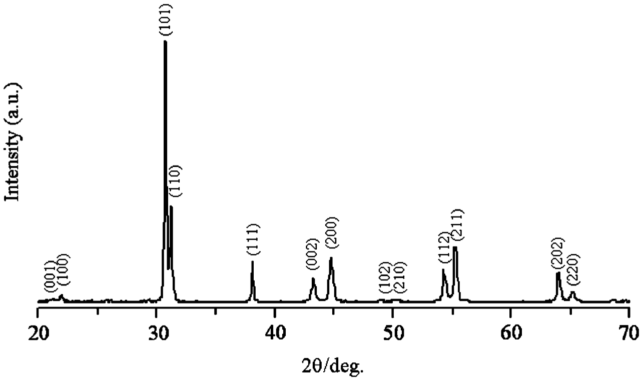

Fig. 1. The X-ray powder diffraction pattern for $BaCu_{1/3}Nb_{2/3}O_3$.

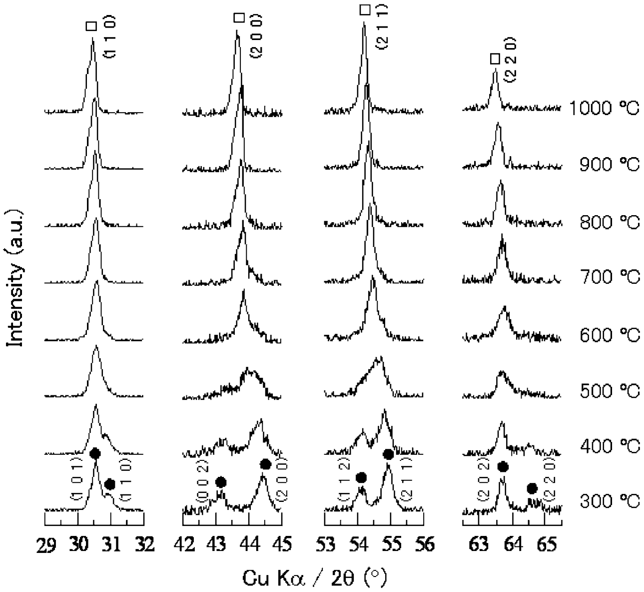

Fig. 2. The high temperature X-ray powder diffraction patterns for $BaCu_{1/3}Nb_{2/3}O_3$ from room temperature to 1000 °C in air.

The crystal structure refinements with Rietveld method [15] were carried out for five possible space groups: the non-centrosymmetrical ones *P*422 (#89), *P*4*mm* (#99), $P\bar{4}2m$ (#111), $P\bar{4}m2$ (#115) and the centrosymmetrical one *P*4/*mmm* (#123). Although they were all successful ($R_{wp} = 9.33$–9.37%) with the assumption that the occupancy of Nb and Cu atoms was fixed to be 0.667 and 0.333, respectively, the fact that Curie temperature was observed at 520 °C indicates that this compound should have a non-centrosymmetrical space group at room temperature. The crystal structure refinement of $BaCu_{1/3}Nb_{2/3}O_3$ obtained using X-ray powder diffraction data with the space group *P*4*mm* (#99) in four non-centrosymmetrical ones was smallest, and led to $R_{wp} = 9.33\%$ and $R_p = 6.67\%$. However, this result remained obscure because the differences of the *R*-values among these refinements were very small, and therefore we are preparing to collect neutron powder diffraction data in order to confirm the precise crystal structure of this compound. Anyway from the X-ray powder diffraction pattern it was clarified that this compound had the tetragonal perovskite-type

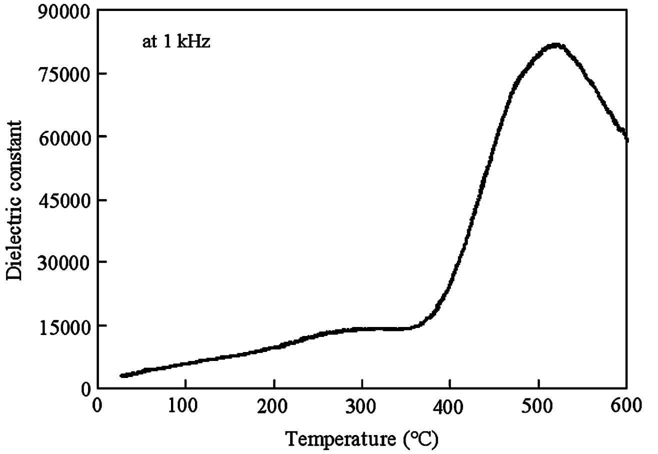

Fig. 3. The temperature dependence of dielectric constant for $BaCu_{1/3}Nb_{2/3}O_3$.

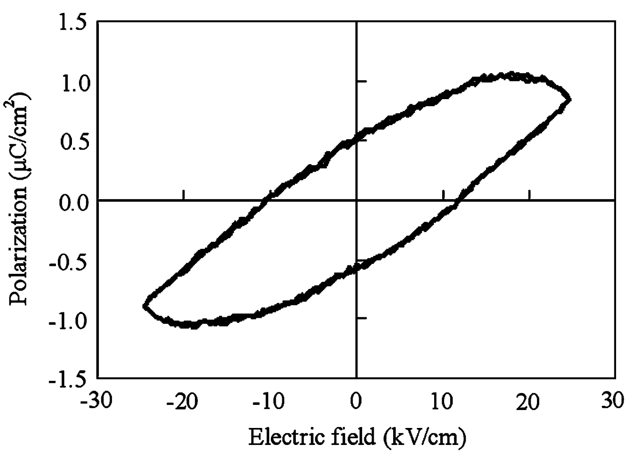

Fig. 4. The *P*–*E* hysteresis loop for $BaCu_{1/3}Nb_{2/3}O_3$.

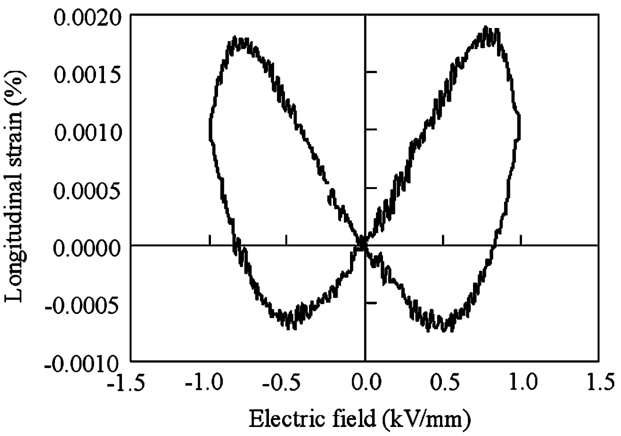

Fig. 5. The *S*–*E* hysteresis loop for $BaCu_{1/3}Nb_{2/3}O_3$.

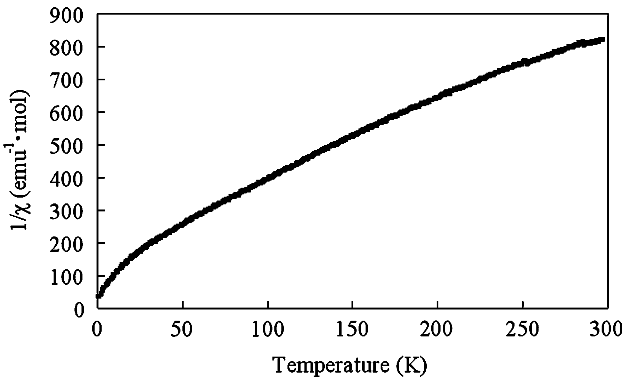

Fig. 6. The temperature dependence of the inverse of magnetic susceptibility for $BaCu_{1/3}Nb_{2/3}O_3$.

structure. Although the crystal structures of $Ba_3Nb_2MO_9$ (M = Mn, Co, Ni, Zn) have been reported to have the cubic perovskite-type structure (space group $Pm\bar{3}m$) in which niobium and M metals are occupied statistically at the B site [9], $BaCu_{1/3}Nb_{2/3}O_3$ has a tetragonal one.

Fig. 2 shows the results of high temperature X-ray powder diffraction for $BaCu_{1/3}Nb_{2/3}O_3$ measured from room temperature to 1000 °C in air. This compound had a phase transition from the tetragonal to cubic symmetry in the temperature range of 500–600 °C. The X-ray powder diffraction patterns at $\geqslant 600\,^{\circ}\mathrm{C}$ could be indexed as the cubic cell and the lattice parameter was $a = 4.1246(8)$ Å at 600 °C. The X-ray powder diffraction pattern of the sample after cooling was identical with that before heating. This fact suggests that this transition is reversible. The phase transition temperature was much higher than the previously published one ($T_c = 370\,^{\circ}\mathrm{C}$) [12] and this difference may be caused by the deviation of the chemical composition.

The temperature dependence of specific dielectric constant shows the peak at 520 °C which corresponded to the phase transition as shown in Fig. 3. Also both the *P* (polarization)–*E* (electric field) and *S* (strain)–*E* (electric field) hysteresis loops are observed at room temperature as shown in Figs. 4 and 5, respectively. From these results it may be concluded that $BaCu_{1/3}Nb_{2/3}O_3$ is a ferroelectric compound with $T_c = 520\,^{\circ}\mathrm{C}$. However, high dielectric loss was observed, especially in high temperature region and the *P*–*E* hysteresis loop was strongly deformed when compared with that for a typical ferroelectric compound. These may be caused by a small amount of impurity phase such as CuO which cannot be detected by X-ray powder diffraction. The temperature dependence of the inverse of magnetic susceptibility exhibits paramagnetic behavior as shown in Fig. 6.

4. Conclusions

It was confirmed that a perovskite-type barium copper niobate, $BaCu_{1/3}Nb_{2/3}O_3$ was a ferroelectric compound with $T_c = 520\,^{\circ}\mathrm{C}$. The crystal structure at room temperature was refined by Rietveld method using X-ray powder diffraction pattern and the phase transition from tetragonal to cubic phases was confirmed by high temperature X-ray powder diffraction patterns.

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