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Densification of tungsten-bronze $KBa_2Nb_5O_{15}$ lead-free piezoceramics

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Abstract

Densification of tetragonal tungsten-bronze (TTB) structured $KBa_2Nb_5O_{15}$ ceramics was studied as a function of extra K_2CO_3 amounts (δ) ranging from 0 to 5 mol%. The lattice constant *c*-axis, which corresponds to the spontaneous polarization direction for TTB structure, was remarkably increased compared to *a*-axis, when δ was increased up to 3. In this case, both of the sintered density and tetragonality of $KBa_2Nb_5O_{15}$ ceramics were also enhanced, but were deteriorated in the specimens with higher δ than 3, because of the secondary phase precipitation and inhomogeneous microstructure. The enhanced tetragonality observed in the $\delta = 3$ sample resulted in the increase of the Curie temperature (T_c) *i.e.*, the $\delta = 3$ sample demonstrated the highest T_c (376 °C) which corresponds to about 96% of T_c for the single crystal. Furthermore, diffuse phase transition at T_c was suppressed for the $\delta = 3$ sample, because the optimized amount of excess K_2CO_3 could compensate effectively for the K-loss defect formed in the TTB structure during sintering process.

Keywords: Sintering; Piezoelectric properties; Niobates; Functional applications

1. Introduction

Alkaline-niobate systems based on $KNbO_3$ family has been considered to be the most attractive ceramic system in the research field of lead-free piezoceramics, since the pressure-less sintering finally became possible and excellent piezoelectric properties were reported.[1–3] However, the center of the interest has been paid to perovskite type compounds, while the study on tungsten-bronze type systems has been limited. The most critical reason is that the tungsten-bronze structure is inferior in crystallographic symmetry to perovskite structure, resulting in a difficulty in the domain control of the ceramics only by external electric field in the poling process. Therefore, the available piezoelectric properties are inferior to perovskite type in most cases, and are not good enough to become candidates for lead-free piezoceramics. But, the physical properties of tungsten-bronze type ceramics are possible to be controlled and strengthened by the application of grain orientation techniques using their inherent anisotropic grain shape.

We first reported that alkaline-niobate $KBa_2Nb_5O_{15}$ ceramics, showing single phase tetragonal tungsten-bronze (TTB) structure, could be densified by the careful treatment of powder treatment and its milling procedure under ordinary pressure-less sintering.[4] The derived ceramics demonstrated an anisotropy in the grain orientation against the pressing direction, which resulted in the expected anisotropic electrical properties.[4,5] For this success, the amount of extra K_2CO_3 added to the starting composition played an important role to compensate volatile K_2O loss in the TTB crystal structure without accompanied by the second phase precipitation and abnormal grain growth.

In this paper, the process that decides the optimum quantity of the extra K_2CO_3 content for the crystal structure and property of $KBa_2Nb_5O_{15}$ piezoceramics is reported for the first time.

2. Experimental

High-purity powders of K_2CO_3, $BaCO_3$ and Nb_2O_5 were used as the starting chemicals. These powders were weighed to obtain the compositions according to the formula of $KBa_2Nb_5O_{15} + \delta\ K_2CO_3$, where δ is varied from 0 to 5 mol%. The weighed powders were mixed and crashed by planetary ball-milling with zirconia balls in acetone medium. The dried mixture was calcined at 900 °C for 10 h, then pelletized disk was calcined again at 930 °C for 10 h. The calcined disk was grounded again with planetary ball-milling, followed by sieving and uniaxially forming into a disk with 12 mm in diameter. The disk was further cold-isostatic-pressed under 200 MPa, then

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sintered at 1280 °C for 4 h. All the above heat treatments were carried out under K_2O-riched atmosphere.

The bulk density of the sintered ceramics was measured by the Archimedes method using distilled waster as a medium. Powder X-ray diffraction (XRD) technique was used for phase identification and its accurate lattice parameters were calculated by the whole-powder-pattern decomposition (WPPD) methods[6] based on the step scanning measurement technique using Si as an internal standard. The microstructure was observed by a scanning electron microscope (SEM).

Temperature dependence of the dielectric property was measured for the polished and specimens using an LCR meter at 1 kHz. The electromechanical coupling factor of the electrically poled specimen was evaluated by the resonance-antiresonance method on the basis of IEEE standards using an impedance analyzer. The piezoelectric d_{33} constant was measured by a quasi-static d_{33} meter.

3. Results and discussion

Fig. 1 plots the refined lattice parameters for the sample with different δ. It is possible to estimate the lattice distortion of perovskite subunit in the TTB structure by calculating the axial ratio of $\sqrt{10}c/a$. The lattice constants of $KBa_2Nb_5O_{15}$ slightly increase when δ is increased to 3, and the increase of c-axis is more remarkable than a-axis. As the result, the $\sqrt{10}c/a$ ratio increased to 1.014 at highest for the $\delta = 3$ sample. This fact means that the tetragonality of $KBa_2Nb_5O_{15}$ is enhanced when extra K_2CO_3 amount is fixed to be 3 mol%.

The variation in the sintered density for the samples with different δ is shown in Fig. 2, and demonstrates a close resemblance in shape to the change in the $\sqrt{10}c/a$ ratio as a function of δ. The sintered density increases with increasing δ up to 3, and demonstrated the highest relative density of 93.2%. Powder X-ray diffraction confirmed that a slight amount of secondary phase was formed in the specimens with δ of 4 and 5, although the specimens with δ of 0–3 showed $KBa_2Nb_5O_{15}$ single phase. Fig. 3 presents the microstructures of the samples with different δ. Compared with the sample with δ of 0, grain growth by sintering advances in the sample with δ of 3, but a larger amount of K_2CO_3 ($\delta = 5$) deteriorates its microstructure that contains abnormally grown grains and small particles. Rietveld analysis confirmed that the structural formula of $KBa_2Nb_5O_{15}$ ceramics could be represented as $(K_{1-x/2}\,Ba_{x/4}\square_{x/4})(K_{x/2}\,Ba_{1-x/4})_2\,Nb_5(O_{15-x/2}\square_{x/2})$, when no extra K_2CO_3 ($\delta = 0$) was utilized in the starting composition. It can be therefore considered that excess K_2CO_3 up to 3 mol% seem to have contributed as a defect compensator to the $A1$ site $(K_{1-x/2}\,Ba_{x/4}\square_{x/4})$, in the TTB structure, but more excess K_2CO_3 formed a secondary phase and lowered sintering density finally.

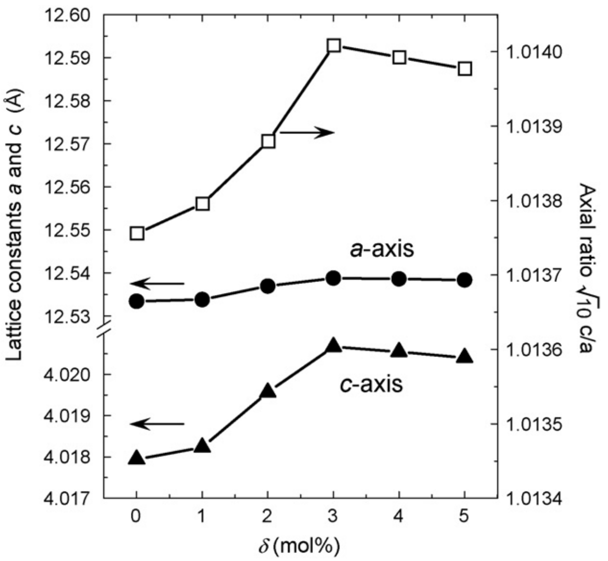

Fig. 1. Lattice constants and their axial ratios measured for $KBa_2Nb_5O_{15} + \delta$ K_2CO_3 ceramics.

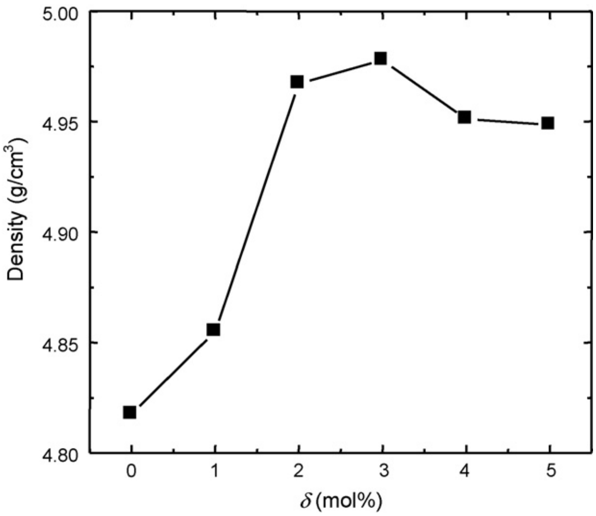

Fig. 2. Sintered density of $KBa_2Nb_5O_{15} + \delta$ K_2CO_3 ceramics.

Fig. 4 presents the temperature dependence of dielectric constant and loss for the sample with δ of 0, 3 and 5. When the Curie temperature (T_c) is roughly estimated as the temperature showing the maximum peak in dielectric constant, the T_c of $KBa_2Nb_5O_{15}$ increases from 365 °C for the $\delta = 0$ sample to 376 °C for the $\delta = 3$ sample, as summarized in Fig. 5. Fig. 5 also shows a linear relationship between T_c and lattice distortion. In general, higher tetragonality induced higher T_c; therefore, the $\delta = 3$ sample demonstrated the highest T_c which corresponds to about 96% of T_c observed in the single crystal. On the other hand, the dielectric loss of $\delta = 3$ and 5 samples is drastically reduced under the half value of the sample with $\delta = 0$ at T_c and above temperatures, indicating that extra amounts of K_2CO_3 could compensate effectively for the K-loss defect in the $A1$ site and reduced ionic conduction in the paraelectric state.

The dielectric anomaly in the paraelectric state above the Curie temperature was evaluated using a modified Curie-Weiss expression $(1/\varepsilon - 1/\varepsilon_{max})$ version $(T - T_c)^{\gamma}/C$, where $1/\varepsilon$ is the dielectric constant inverse, T_c is the temperature at which $\varepsilon(T)$ reaches the maximum value (ε_{max}), γ is the degree of diffuseness of the transition, and C is the Curie-Weiss constant. Table 1 lists the constants derived from the logarithmic plot (Fig. 6) by fit-

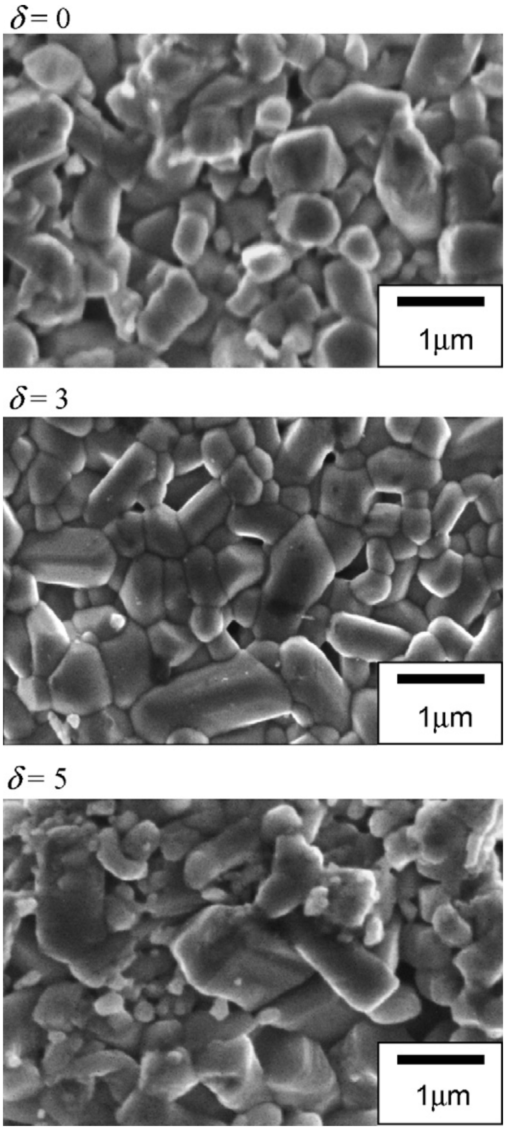

Fig. 3. SEM micrographs of $KBa_2Nb_5O_{15} + \delta\ K_2CO_3$ ceramics.

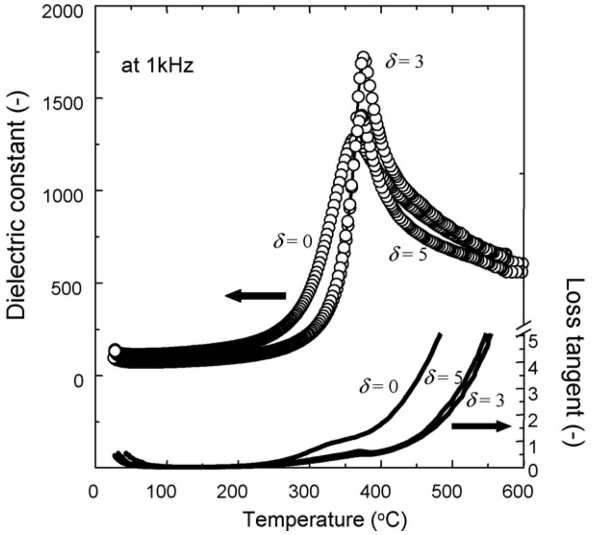

Fig. 4. Temperature dependence of dielectric constant and loss for $KBa_2Nb_5O_{15} + \delta\ K_2CO_3$ ceramics.

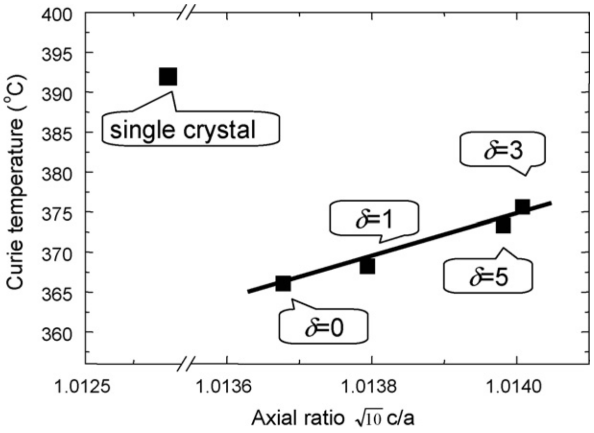

Fig. 5. Relationship between Curie temperature and axial ratio for $KBa_2Nb_5O_{15} + \delta\ K_2CO_3$ ceramics.

Table 1
Diffuse phase transition at Curie temperature for $KBa_2Nb_5O_{15} + \delta\ K_2CO_3$ ceramics

δ (mol%)	$C \times 10^5$	T_c	$T_{cw} - T_c$	γ
0	3.11	366	16	1.29
3	2.06	376	7	1.02
5	2.02	374	9	1.07

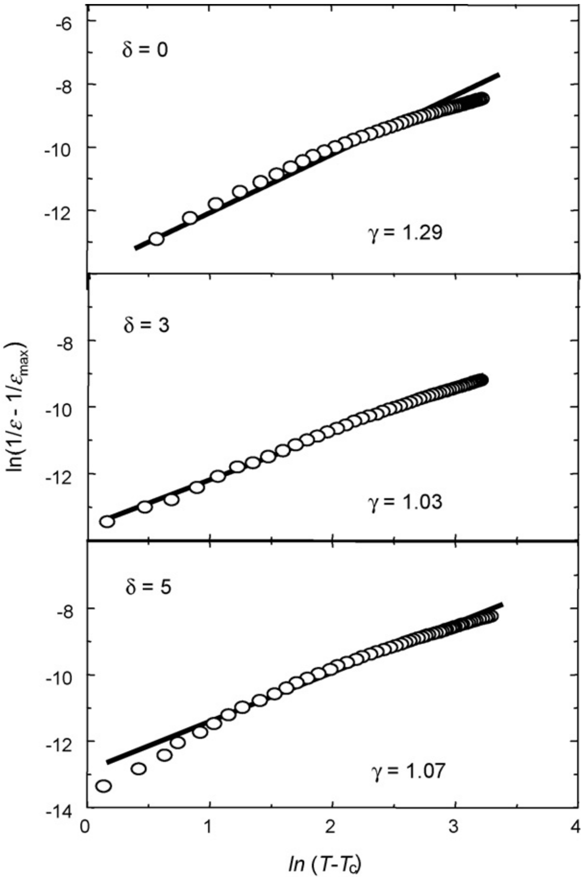

Fig. 6. Linear fitting of logarithmic plots in a modified Curie-Weiss expression $(1/\varepsilon - 1/\varepsilon_{max})$ vs. $(T - T_c)$ for $KBa_2Nb_5O_{15} + \delta\ K_2CO_3$ ceramics.

ting a straight-line equation. When the starting temperature that can follow the linear approximation was defined as T_{cw}, the $\delta = 3$ sample demonstrated the smallest deviation *i.e.*, $T_{\mathrm{cw}} - T_{\mathrm{c}} = 7\,^{\circ}\mathrm{C}$. Furthermore, it is noted that the value of γ for the $\delta = 3$ sample approaches 1.00 which denotes a normal Curie-Weiss behavior. On the other hand, the highest γ equals to 1.29 was calculated for the $\delta = 0$ sample. This seems to have been caused by low sintered density involving inhomogeneous microstructure. Such a diffuse phase transition was also observed in other TTB-structured ferroelectrics including defects or fluctuation in *A*-site cations.[7,8]

The electrical resistivity was much improved by addition of the proper amount ($\delta = 3$) of excess K_2CO_3, and high-voltage external field poling would be possible.[5] As shown in Fig. 3, columnar grains with its longitudinal direction matching to *c*-axis tended to be oriented comparatively easy to the radial direction of the palletized specimen during uniaxial pressing direction. Therefore, a variety of piezoelectric properties, ranging from 32 to 36 pC/N in longitudinal piezoelectric constant (d_{33}) and from 0.27 to 0.43 for thickness-mode electromechanical coupling ratio (k_{t}), were measured for the test pieces prepared from the $\delta = 3$ specimen in which the cutting azimuth from the pellet was controlled among 90 degrees. Especially, the variation of k_{t} is surprisingly wide and therefore its anisotropic piezoelectric properties can be expected to become attractive to a variety of piezoelectric application.

4. Conclusion

The effect of extra K_2CO_3 content for the crystal structure and dielectric property of TTB-structured $KBa_2Nb_5O_{15}$ piezoceramics has been investigated. $KBa_2Nb_5O_{15}$ ceramics is basically difficult in sintering, but the addition of extra amounts (3 wt%) of K_2CO_3 to the stoichiometric starting mixture ratio could work effectively in (1) the K-loss compensation, (2) the increase of sintered density and T_{c} and (3) the stabilization of TTB structure to an ideal tetragonality without secondary phases. These improvements enhanced the dielectric properties of $KBa_2Nb_5O_{15}$ piezoceramics.

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References

1. Kakimoto, K., Masuda, I. and Ohsato, H., Ferroelectric and piezoelectric properties of $KNbO_3$ ceramics containing small amounts of $LaFeO_3$. *Jpn. J. Appl. Phys.*, 2003, **42**, 6102–6105.
2. Guo, Y., Kakimoto, K. and Ohsato, H., Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiNbO_3$ ceramics. *Appl. Phys. Lett.*, 2004, **85**, 4121–4123.
3. Saito, Y., Takao, H., Tani, T., Nonoyama, T., Takatori, K., Homma, T. *et al.*, *Nature*, 2004, **432**, 84–87.
4. Yoshifuji, T., Kakimoto, K. and Ohsato, H., Processing and ferroelectric property of lead-free $KBa_2Nb_5O_{15}$ piezoceramics. *Adv. Mater. Res.*, 2006, 11–12, 113–116.
5. Kakimoto, K., Yoshifuji, T. and Ohsato, H., Anisotropic polarization and piezoelectricity of $KBa_2Nb_5O_{15}$ ceramics derived from pressure-less sintering. *Jpn. J. Appl. Phys.*, 2006, **45**, 7435–7439.
6. Toraya, H., Whole-powder-pattern fitting without reference to a structural model: application to X-ray powder diffraction data. *J. Appl. Cryst.*, 1986, **19**, 440–447.
7. Duran, C., Trolier-McKinstry, S. and Messing, G. L., Fabrication and electrical properties of textured $Sr_{0.53}Ba_{0.47}Nb_2O_6$ ceramics by templated grain growth. *J. Am. Ceram. Soc.*, 2000, **83**, 2203–2213.
8. Santos, I. A., Garcia, D., Eiras, J. A. and Arantes, V. L., Feature of diffuse phase transition in lead barium niobate ferroelectric ceramics. *J. Appl. Phys.*, 2003, **93**, 1701–1706.