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Effects of K nonstoichiometry in bismuth layer-structured $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$ ceramics

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Abstract

The effects of K nonstoichiometry on phase formation, grain morphology, dielectric and piezoelectric properties of $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$ (KBT) were studied in the range of excess up to +2 mol% and deficient down to −8 mol% of $K_{0.5}$. The relative densities of the sintered KBT ceramics with various K contents prepared by a solid state reaction method were all higher than 95%. In all samples, a bismuth layer-structured phase was confirmed, although a secondary phase appeared as K deficiency became larger than −6 mol%. Piezoelectric coefficient (d_{33}) increased, showing a high of 16 pC/N at $x = -3$ mol%, and then decreased with further K deficiency while Curie temperature (T_C) decreased showing a low of 540 °C at $x = -8$ mol% from 551 °C at $x = 0$ mol%. Mechanical quality factor (Q_m) of all samples was in the range of 900–1860.

Keywords: C. Piezoelectric properties; Bismuth layer-structured ferroelectrics; KBT; Nonstoichiometry

1. Introduction

Pb containing perovskites such as $PbTiO_3$–$PbZrO_3$ (PZT), $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT), and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN-PT) have been the materials used for various ferroelectric and piezoelectric applications [1]. However, the use of Pb-based ceramics has caused serious human health and environmental problems due to the PbO vaporization during processing and the waste from products containing Pb. Those problems can only be resolved by banning Pb containing ceramics. It is, therefore, necessary to develop health and environment friendly Pb-free piezoelectric materials with compatible properties to those of Pb-based ceramics [2,3].

The Aurivillius family of bismuth (Bi) layer-structured ferroelectrics (BLSF) such as $SrBi_2Ta_2O_9$, $Bi_4Ti_3O_{12}$, $Na_{0.5}Bi_{4.5}Ti_4O_{15}$, $SrBi_4Ti_4O_{15}$, and $CaBi_4Ti_4O_{15}$ has been intensively studied [4–7], because they are potential candidates for piezoelectric and pyroelectric sensor applications requiring large anisotropy and stability at high working temperature. The structural formula of BLSF is generally described as $(Bi_2O_2)^+$ layers and $(A_{m-1}B_mO_{3m+1})^{2-}$ perovskite layers. A is a mono-, di-, or tri-valent cation (Na^+, K^+, Ba^{2+}, Ca^{2+}, Sr^{2+}, Bi^{3+}, etc.) and B is a transition element (Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, etc.). Various combinations of cations are also allowed and m is usually from 1 to 5, indicating a number of perovskite layers sandwiched between the $(Bi_2O_2)^+$ layers.

A well-known merit of BLSF materials over other lead-free materials is that they are suitable for resonators especially at high frequency and temperature utilizing high mechanical quality factor (Q_m) in piezoelectric device applications. However, piezoelectric coefficients (d_{33}) of typical BLSF ceramics are relatively very low, usually under 20 pC/N. To improve piezoelectric d_{33}, various special processing techniques, such as template grain growth (TGG) and hot-forging (HF) have been applied to improve orientation and density. Some improvements have been obtained, but those unconventional processing techniques are not practical for production. Another approach for high d_{33} is a conventional one, controlling composition via extrinsic doping, substitution, and addition [8–11] of foreign components.

$K_{0.5}Bi_{4.5}Ti_4O_{15}$ (KBT) was first fabricated in the 1960s by Subbarao. It was reported to be difficult to achieve dense ceramics by conventional sintering until Wang et al. successfully prepared a dense KBT compound by ordinary firing [12].

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It is still not easy to obtain dense ceramics because of their highly anisotropic crystal shape ($a \sim b \sim 5.4$ Å, $c \sim 41.2$ Å for $m = 4$). In addition, potassium carbonate (K_2CO_3), a typical raw powder for K component, is very hygroscopic and bismuth oxide (Bi_2O_3) is known to be volatile during processing. Therefore, KBT ceramics can easily off-stoichiometric from the beginning of powder processing unless suitably handled. Nevertheless, compositions of KBT ceramics are often assumed to be stoichiometric. In order to clarify any intrinsic effects of compositional variation in K content in KBT ceramics, the effects of K nonstoichiometry on phase formation, grain morphology, dielectric and piezoelectric properties were investigated in this study.

2. Experimental

KBT ceramics with K nonstoichiometry, $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$, were prepared by a conventional solid state reaction method. The starting raw materials used were Bi_2O_3 (Aldrich, 99.9%), K_2CO_3 (Aldrich, 99.995%), and TiO_2 (Aldrich, 99.9%). Hygroscopic K_2CO_3 powder was thoroughly dried at 200 °C for 2 h in a dry oven, and then weighed in a glove box. The compositions of samples were controlled to be $x = -8$ to +2 mol% of $K_{0.5}$. The weighed powders were wet milled with yttria-stabilized zirconia balls in anhydrous ethanol for 2 h. After milling, the powders were calcined first at 780 °C, then 800 °C, for 2 h in air with an intermediate milling and drying to make homogeneous powders. The twice calcined powders were mixed with polyvinylalcohol (PVA) binder, and then pressed to pellets of 10 or 18 mm in diameter and ~1 mm in thickness at a uniaxial pressure of 150 MPa. The pellets were covered with sacrificial powders of the same compositions and sintered in an Al_2O_3 crucible with a lid at 1120 °C for 2 h in air.

The X-ray diffraction (XRD) patterns for the ceramic powders were obtained using an X-ray diffractometer (X'pert MPD 3040 system, Philips, Netherlands) with Cu Kα radiation. It is not easy to take an accurate measurement because diffractometers always have systematic and random errors such as misalignment of the instrument and displacement of the specimen. Therefore, 5 N (99.999%) silicon powder (Alfa Aesar, USA) was used as an internal standard to calibrate XRD patterns from those errors. The microstructure of the sintered ceramics was inspected using a scanning electron microscope (SEM, JMS-5610, Jeol, Japan). For the measurement of dielectric and piezoelectric properties, both sides of pellets were polished down to 0.4 mm in thickness and painted with Ag paste then fired at 650 °C for 0.5 h in air. The specimens were poled in silicone oil at 120 °C under a *dc* field from 7.5 kV/mm and field-cooled to room temperature for 0.5 h. Temperature dependence of dielectric constant (ε) and loss tangent (tan δ) was measured using an impedance analyzer (4192A, Agilent Technologies, USA) in the temperature range from room temperature to 650 °C. Composition dependence of d_{33} was measured at room temperature using a piezo-d_{33} meter (ZJ-6B, IACAS, China). Electromechanical coupling factor (K_p) and mechanical quality factor (Q_m) were calculated from resonant and antiresonant frequencies and capacitances measured at 1 kHz using an impedance analyzer (4194A, Agilent Technologies, USA).

3. Results and discussion

The changes incurred in weight loss by sintering were below 1 wt% in all samples, resulting mostly from PVA burning and moisture evaporation. The relative apparent densities of KBT ceramics were all higher than 95% after sintering. XRD patterns of KBT ceramics are shown in Fig. 1. The formation of a bismuth layer-structured phase with $m = 4$ was identified by analyzing XRD patterns. The intensity of (1 1 9) diffraction peak was the highest among the peaks in the XRD patterns. This is consistent with the report that the most intense reflection of BLSF occurs at the type of $(112m + 1)$ [13]. This bismuth layer-structured phase was maintained at all compositions but a secondary phase started forming in the samples with K deficiency over than −6 mol%. Fig. 2 shows SEM images of the KBT ceramics with various $x = -8$ to +2 mol%. Due to highly anisotropic shape of KBT crystal, grains grew plate-like but grain sizes did not appear to be changed much with *x*. In other words, in terms of grain shape and size, KBT ceramics were not much influenced by K nonstoichiometry within the range of $x = -8$ to +2 mol%.

Fig. 3 shows ε and tan δ of the KBT ceramics measured at 100 kHz as a function of temperature. Dielectric peaks occurring above 540 °C corresponded to the Curie temperature (T_C), which decreased with K deficiency from 551 °C at $x = 0$ mol% to 540 °C at $x = -8$ mol%. Considering dielectric properties of BLSF materials, distortion of oxygen octahedra [14] that could occur by K nonstoichiometry would be a cause for the decrease from the nominally stoichiometric sample. Similar relations between T_C and lattice distortion were observed in PZT [15] and Bi-based titanate ceramics [8,9]. Note tan δ was quite low especially below 350 °C. In other words, there was not much variation in either ε or tan δ in the temperature range of 30–350 °C indicating temperature stability of KBT ceramics.

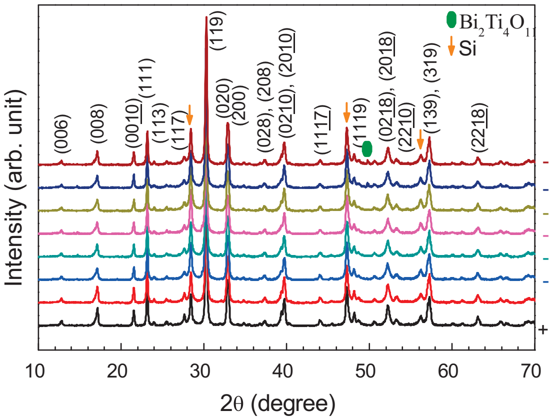

Fig. 1. XRD patterns of $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$ ceramics with various *x* after sintering at 1120 °C for 2 h in air. In all samples, a bismuth layer-structured phase was formed. Indicated as arrows were peaks from 5 N Si used as an internal standard. An impurity phase $Bi_2Ti_4O_{11}$ was also shown.

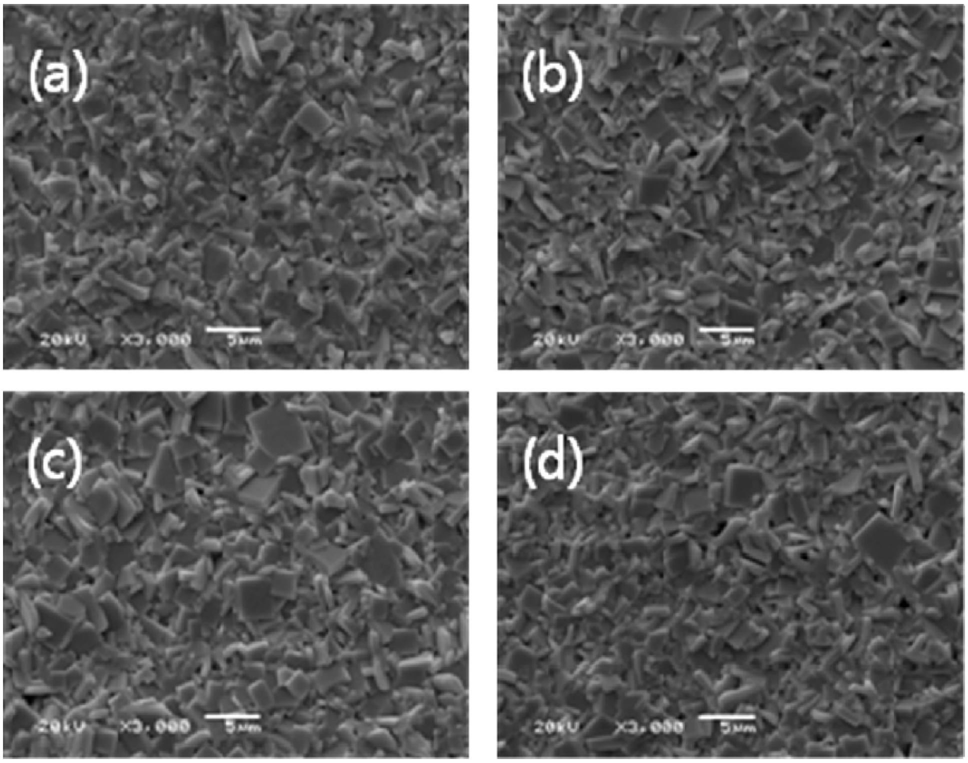

Fig. 2. SEM images taken from the surfaces of $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$ ceramics with various x after sintering at 1120 °C for 2 h in air: (a) +2 mol%; (b) 0 mol%; (c) −3 mol%; and (d) −8 mol%.

Fig. 4 shows composition dependent d_{33}, electromechanical coupling factor (K_p), and mechanical quality factor (Q_m) of KBT ceramics. d_{33} increased showing a peak value 16 pC/N at $x = -3$ mol%, and then decreased with further K deficiency. K_p behaved similarly to d_{33}, showing the highest 4.2% at $x = -3$ mol%, and then decreased with further K deficiency. On the other hand, a high of Q_m obtained was 1860 at $x = -5$ mol%. A-site vacancies formed by K deficiency could be a cause for the increase in d_{33} as they are known to facilitate domain walls movement similar to B-site donor doping in PZT [15,16]. Another possibility could be lattice distortion affected by K nonstoichiometry implying an optimum distortion occurred at $x = -3$ mol% [8]. Further analyses of the detailed XRD patterns are in progress.

After measuring room temperature d_{33}, the specimen with the highest d_{33} at $x = -3$ mol% was chosen to evaluate temperature dependence of piezoelectric properties of KBT ceramics. As shown in Fig. 5, both d_{33} and K_p were stable up to

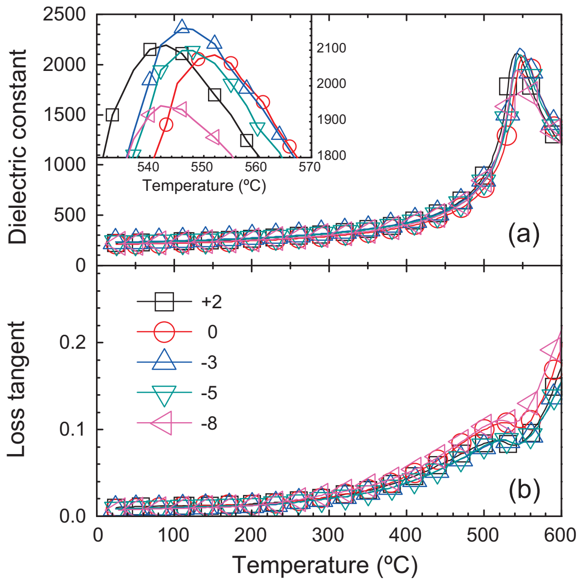

Fig. 3. Temperature dependence of (a) dielectric constant (ε) and (b) loss tangent ($\tan\delta$) of $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$ ceramics with various x at 100 kHz.

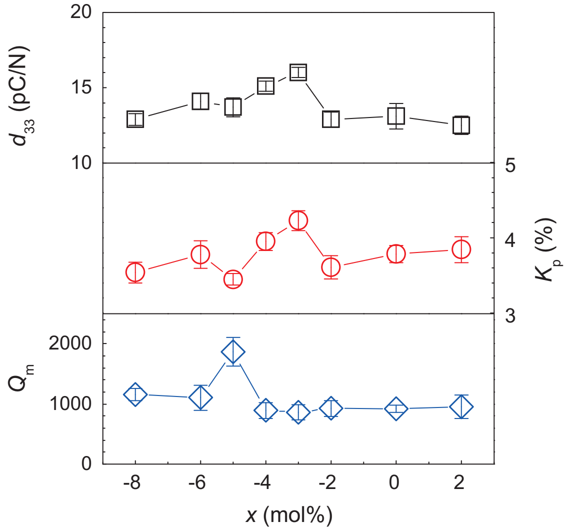

Fig. 4. Piezoelectric coefficient (d_{33}) and electromechanical coupling factor (K_p) of $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$ ceramics with various x at room temperature.

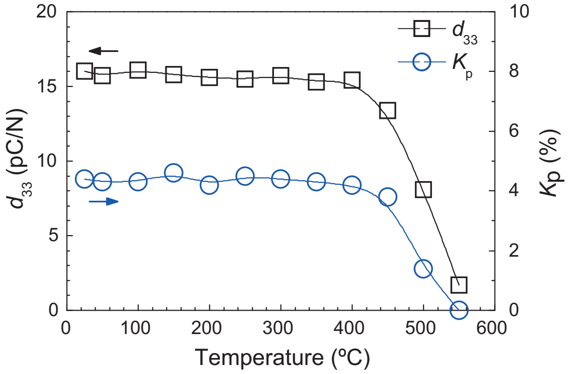

Fig. 5. Temperature dependence of d_{33} and K_p of $K_{0.5+x}Bi_{4.5}Ti_4O_{15}$ ceramics at $x = -3$ mol% in the temperature range from room temperature up to 550 °C.

400 °C, which clearly indicates piezoelectric properties diminish much below T_C in KBT. Nevertheless, temperature stability of KBT is quite high compared with that of other piezoelectric ceramics, including PZT, implying their suitability for high temperature applications with high Q_m. This also explains why KBT possesses high T_C but low d_{33} due to its high anisotropy. It would be possible to have relatively higher d_{33} but lower T_C with less m, and vice versa.

4. Summary

There have been some papers regarding extrinsic doping, substitution, or addition of foreign components. In our understanding, however, the intrinsic effects of compositional variation in K content in KBT ceramics have never been studied. Pb-free KBT ceramics were made by a conventional solid state reaction method and their phase stability, grain morphology, dielectric and piezoelectric properties were investigated in terms of K nonstoichiometry in the range of excess +2 and deficient −8 mol% of $K_{0.5}$. A secondary phase appearing at K deficiency above −6 mol% was observed, but a bismuth layer-structured phase was formed at all compositions. Plate-like grains were observed but grain size was not much changed with K nonstoichiometry. With K deficiency, d_{33} and K_p increased but T_C decreased. Room temperature d_{33} was improved, showing a high of 16 pC/N at $x = -3$ mol% and then decreased. Q_m values of all samples were above 900, showing a peak of 1860 at $x = -5$ mol%. Temperature dependence of d_{33} and K_p of KBT ceramics was found to be stable up to 400 °C.

Acknowledgements

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