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Short communication

Orthorhombic to tetragonal phase transition due to stress release in (Li,Ta)-doped(K,Na)NbO_3 lead-free piezoceramics

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Abstract

XRD and Raman scattering experiments revealed an interesting finding that phase structure changed from orthorhombic to tetragonal symmetry when pulverizing (Li,Ta)-doped (K,Na)NbO_3 lead-free piezoelectric ceramics (sintered body) to powder. Both orthorhombic and tetragonal phases coexist in the $Li_{0.05}(Na_{0.51}K_{0.49})_{0.95}Nb_{0.80}Ta_{0.20}O_{3.00}$ (LKNNT) sintered bulk sample at room temperature, but almost only the tetragonal phase is observed in the ground powder. In addition, annealing experiment enhanced the formation of tetragonal phase and improved the temperature stability of piezoelectricity. It is revealed that the internal stress existing in the LKNNT ceramics favors the formation of orthorhombic phase, which transfers to tetragonal phase when the stress was released.

Keywords: C. Piezoelectric properties; D. Niobates; D. Perovskites

1. Introduction

Lead zirconate titanate (PZT)-based piezoceramics have been widely used in actuators, sensors, ultrasonic transducers and other important fields for many years due to its excellent piezoelectric and ferroelectric properties. Because of the toxicity of lead and the increasing concern on environment, lead-free piezoceramics are gaining more and more attention in recent years.[1,2] Among several lead-free piezoceramics, (K,Na)NbO_3 (KNN)-based ceramics are considered as the promising substitutes for PZT-based piezoceramics since a breakthrough made by Saito et al.[3–5] Because of the poor piezoelectric properties of pure KNN ceramics, recently much effort have been taken to improve the piezoelectric properties of KNN ceramics by doping Li and/or Ta.[6–12] The mechanism of the improvement of piezoelectric properties is that doping Li and/or Ta in KNN ceramics can greatly decrease the tetragonal to orthorhombic transition point ($T_{T\text{–}O}$) from about 200 °C to room temperature, so the doped ceramics show higher piezoelectric properties at room temperature due to the coexistence of two phases.[13] However, for such a modified KNN composition with the $T_{T\text{–}O}$ close to room temperature, the state of two-phase coexistence will disappear even for a slight temperature increasing and the dominate phase will be tetragonal, at the same time the piezoelectric property decreasing obviously.

In addition to the temperature effect, this study revealed an interesting phenomenon related to stress effect on the phase structure of (Li,Ta)-doped KNN ceramics. It was found that orthorhombic to tetragonal phase transition occurred when the bulk material was pulverized to powder. Similarly, the same phenomenon was confirmed even in the bulk material after being annealed at sufficiently high temperatures for a long time.

2. Experimental

KNN-based lead-free ceramics with a nominal composition of $Li_{0.05}(Na_{0.51}K_{0.49})_{0.95}Nb_{0.80}Ta_{0.20}O_{3.00}$ (abbreviated as LKNNT) were prepared by a conventional method. Commercially available oxides and carbonate powders, Nb_2O_5 (99.95 wt%), Ta_2O_5 (99.0 wt%), Li_2CO_3 (97.0 wt%), K_2CO_3 (99.0 wt%), Na_2CO_3 (99.8 wt%), were used as raw materials. According to the above composition, these powders were weighted after correcting their purity and mixed by ball milling in ethanol using ZrO_2 balls for 24 h, and then the slurry was dried and calcined at 850 °C for 5 h. The synthesized powder was ball milled again for 24 h also in ethanol and dried, after that the

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powders were pressed into small disks of 10 mm in diameter, followed by cold isostatic pressing at 200 MPa. Finally, these pellets were sintered in air at 1120 °C for 2 h.

The crystal structure of sintered bulk and ground powder samples was determined by X-ray diffraction (XRD) with monochromatic Cu $\mathrm{K}_{\alpha 1}$ radiation (Rigaku, D/Max 2500, Tokyo, Japan). The Raman spectrum was measured by the LabRAM HR800 (France). The electric-field-induced strains were measured by using an attachment onto the TF ANALYZER 1000 ferroelectric measuring system (aixACCT Systems GmbH, Germany).

3. Results and discussion

Fig. 1 compares the XRD patterns of sintered bulk and ground powders. It is clear that the XRD pattern of LKNNT ground powders is quite different from that of LKNNT as-sintered bulk sample. The (0 0 1) and (0 0 2) peaks became significantly weak when the as-sintered sample were pulverized to powder. In KNN-based ceramics, the analysis of the relative intensity of two peaks around $2\theta = 45°$ in XRD patterns is an effective method to distinguish the phase structure of ceramics that usually show orthorhombic and/or tetragonal symmetry at room temperature.[14] It is well known that when the KNN-based ceramics is of orthorhombic phase, $a = c > b$, $I_{(0\,0\,2)}/I_{(0\,2\,0)}$ equals 2 and the (0 0 2) line has a smaller Bragg angle. But $a = b < c$, the $I_{(0\,0\,2)}/I_{(0\,2\,0)}$ equals 0.5 and the (0 0 2) line is located at a smaller Bragg angle for KNN-based ceramics of tetragonal phase.[14,15] When the sintered bulk sample are ground into powder, the $I_{(0\,0\,2)}/I_{(0\,2\,0)}$ as included in Fig. 1 becomes smaller, which indicates that a phase transition occurs. In addition, it was confirmed that the peak position of (0 0 2) also changed. It is clear that phase transformation occurs from orthorhombic to tetragonal symmetry when grinding the LKNNT ceramic bulk sample to powder. It seems that tetragonal phase becomes thermodynamically stable in the powder form at a state free of internal stress existing in polycrystalline materials. In other words, the orthorhombic phase can remain in the ceramic pellets due to

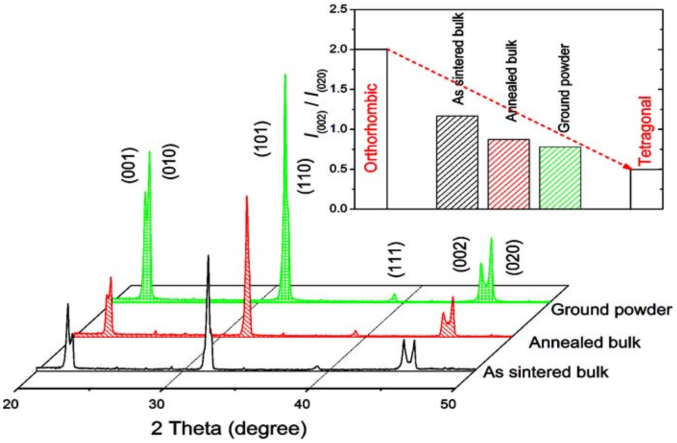

Fig. 1. XRD patterns of $\mathrm{Li}_{0.05}(\mathrm{Na}_{0.51}\mathrm{K}_{0.49})_{0.95}\mathrm{Nb}_{0.80}\mathrm{Ta}_{0.20}\mathrm{O}_{3.00}$ ceramic samples.

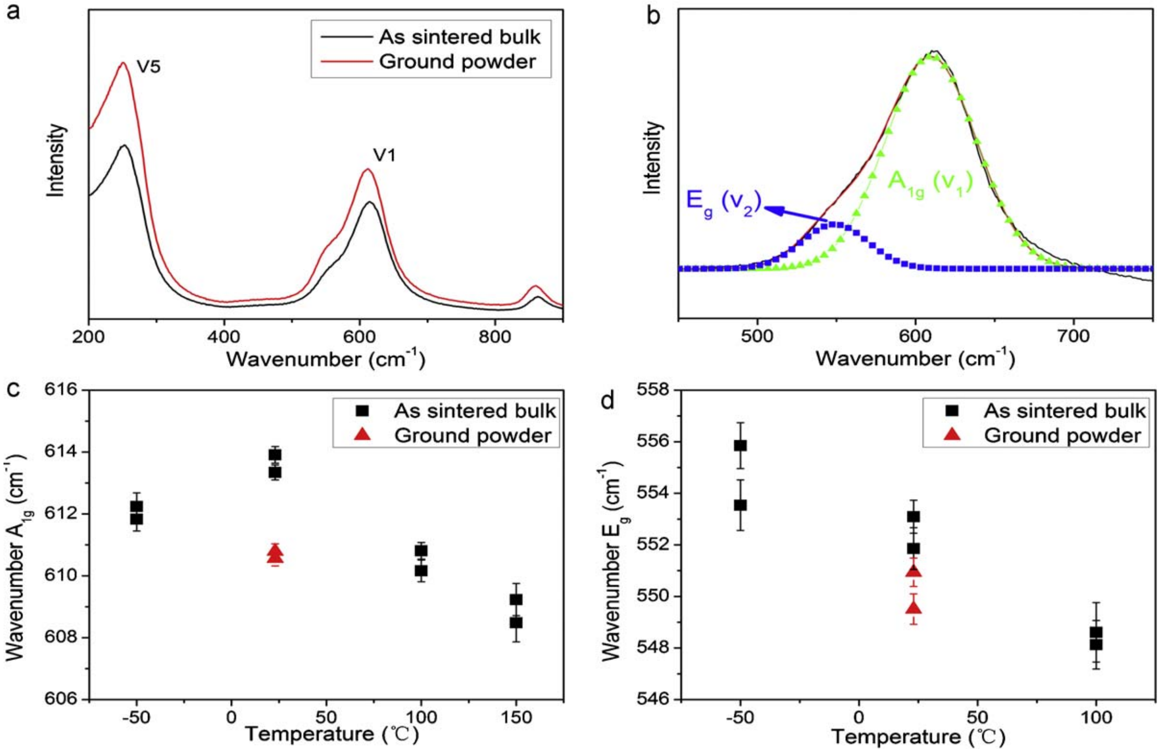

Fig. 2. The analyzing procedure of phase structure of $\mathrm{Li}_{0.05}(\mathrm{Na}_{0.51}\mathrm{K}_{0.49})_{0.95}\mathrm{Nb}_{0.80}\mathrm{Ta}_{0.20}\mathrm{O}_{3.00}$ ceramics by Raman spectroscopy: (a) Raman spectra of LKNNT bulk sample and its ground powder at room temperature, (b) fitted Raman spectrum between 450 and 700 cm^{-1}, (c) A_{1g} peak position of ground powder at room temperature and that of bulk sample at different temperatures, and (d) E_g peak position of ground powder at room temperature and that of bulk sample at different temperatures.

an additional effect. It was reported that the phase structure is affected by the existence of internal stress in PZT films and bulk samples.[16,17] Recently, Kakimoto et al. investigated the pressure-dependent Raman scattering spectra of Li-doped KNN (LKNN) ceramics and found that hydrostatic compressive favors the orthorhombic phase rather than tetragonal phase.[18] As shown in Fig. 1, after being annealed at 900 °C for 24 h, the tetragonal phase became dominant even in the ceramic bulk sample whose $I_{(0\,0\,2)}/I_{(0\,2\,0)}$ ratio is close to that obtained in the ground powders, which again confirmed the orthorhombic to tetragonal phase transition when the internal stress is weaken. Such a phase transition was further proved by the following Raman spectroscopy experiments.

Raman spectroscopy is used as a powerful tool to analyze the phase structure of KNN-based ceramics.[13,19,20] Fig. 2(a) shows the different Raman spectra of LKNNT bulk sample and ground powder of the sintered sample. Fig. 2(b) shows the sketch of analysis of Raman spectrum in which the part between 450 and 700 cm^{-1} can be fitted using a sum of Gaussian lines. The fitted line corresponds well to the original data with $R^2 > 0.99$. The peak positions of Gaussian lines at ~550 cm^{-1} and ~610 cm^{-1} are ascribed to E_g ($\nu 2$) and A_{1g} ($\nu 1$), respectively. E_g ($\nu 2$) and A_{1g} ($\nu 1$) are stretching modes of the vibrations of the BO$_6$ octahedron and are sensitive to the change of phase structure.[13,20] The Raman spectra of LKNNT bulk sample were measured at different temperatures, whereas its corresponding ground powder was measured at room temperature only. Considering the ingredient inhomogeneity in KNN-based ceramics, each sample was measured twice at two different regions to gain two spectra. As shown in Fig. 2(c), the wavenumber A_{1g} of the bulk sample decreases with increasing temperature due to its intrinsic phase transition from orthorhombic to tetragonal symmetry, and the wavenumber A_{1g} of the ground powder at room temperature is close to that of the as-sintered bulk sample at elevated temperature. In addition, as shown in Fig. 2(d), the same result was obtained as for the case of E_g ($\nu 2$) mode. Both results in Fig. 2(c) and (d) showed that the phase structure of the LKNNT ground powder is more similar to that of LKNNT bulk sample at elevated temperature where the tetragonal phase will become dominant. Therefore, the Raman experiments also confirmed that there existed a phase transition during the process pulverizing the LKNNT bulk sample into powder, which is consistent with the above XRD results. We observed that the volume of the annealed bulk sample was a little larger than that prior to annealing treatment, suggesting that the internal stress existing in the bulk sample is compressive stress, which favors the existence of orthorhombic phase rather than tetragonal phase in LKNN piezoceramics.[18] On the contrary, when pulverizing the bulk sample into powder, the tetragonal phase appeared without the effect of internal compressive stress existing in LKNNT bulk sample. This phenomenon can be explained by the principle of thermodynamics, as shown schematically in Fig. 3. For both bulk and powder samples, with decreasing temperature the orthorhombic phase become more thermodynamically stable than tetragonal one, resulting in an intersection corresponding to $T_{T\text{–}O}$ where two phases co-exist. As shown by the dash lines, the ground powder should have lower Gibbs free energy than the bulk materials with the same composition. The reason is described in the following. The Gibbs free energy (G) is defined as the following thermodynamics equation:

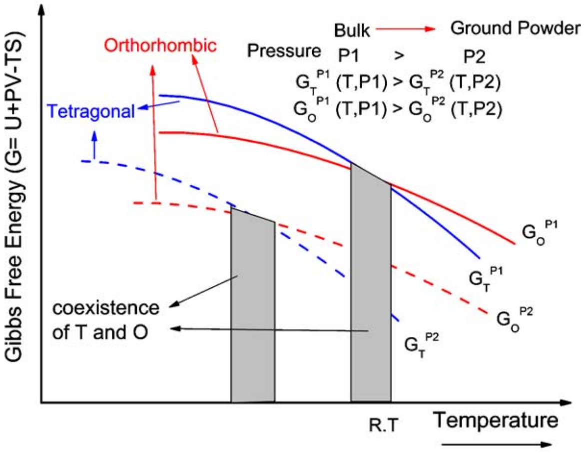

Fig. 3. Sketch of thermodynamic analysis of the phase transition caused by the release of internal stress, the solid lines and dash lines denote the Gibbs free energy of bulk sample and ground powder, respectively.

$$G = U + PV - TS \tag{1}$$

$$dG = -SdT + VdP \tag{2}$$

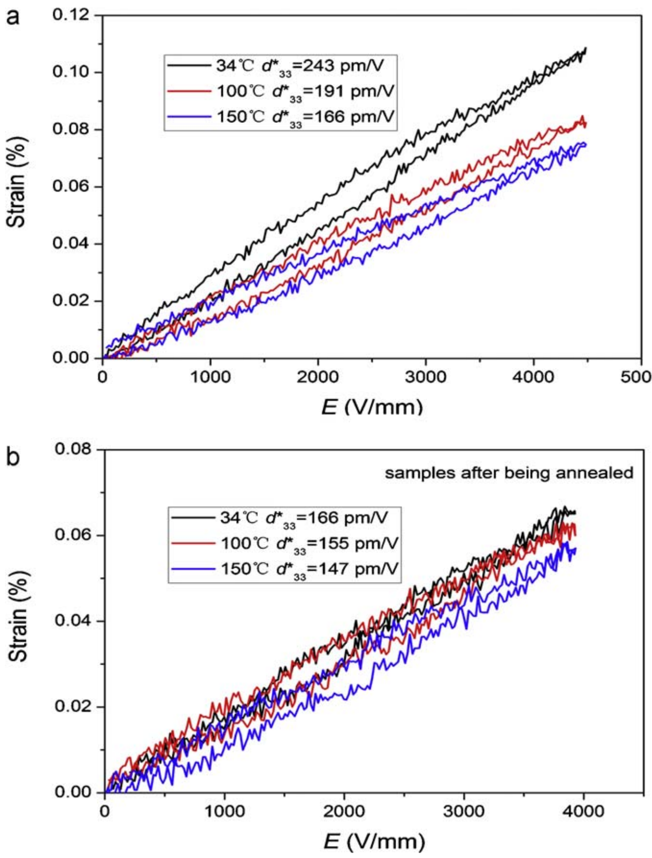

Fig. 4. Piezoelectric constant d_{33}* of LKNNT ceramics at different temperatures: (a) as-sintered sample and (b) annealed sample.

where U, P, V, T and S denotes internal energy, pressure, volume, temperature and entropy, respectively. It is clear that Gibbs free energy (G) increases when the pressure is increased or the temperature is reduced. The Gibbs free energy is lowered when grinding the bulk to powder as a consequence of the release of the internal compressive stress. Therefore, as shown in Fig. 3, at room temperature the tetragonal phase has the lowest free energy, which can qualitatively explain why the dominate phase in the ground powder is tetragonal.

Fig. 4 shows curves of electric-field-induced strains at different temperatures for LKNNT ceramic bulk sample before and after annealing. It is clear that even for the same material the piezoelectric responses became different after annealing at 900 °C. Such differences were not related to any possible composition change (e.g. the evaporation of alkali oxide Na_2O and K_2O) during annealing at the low temperature (900 °C). Because the annealing process can eliminate the internal stress which leads to the formation of the main tetragonal phase in the ceramic pellets, the annealed piezoceramics sample shows higher temperature-stable piezoelectricity than those without annealing treatment. At the same time, the annealed ceramic sample shows a d_{33}* of 166 pm/V at 34 °C, which is the same as the result measured at 150 °C in as-sintered sample. This further proved that the phase structure of the annealed sample is similar to that of un-annealed samples at a higher temperature where the tetragonal phase appears.

4. Conclusions

We have found an interesting phenomenon in $Li_{0.05}(Na_{0.51}K_{0.49})_{0.95}Nb_{0.80}Ta_{0.20}O_{3.00}$ piezoceramics that the phase structure of the ceramics changes when the sintered pellets are ground to powder. We confirmed that the release of internal stress in ceramics pellets leads to the phase transition from orthorhombic to tetragonal phase. Annealing was applied to the sintered piezoceramics pellets to eliminate the internal stress and the tetragonal phase becomes dominant, which caused the improvement of temperature dependence of piezoelectric property of the ceramics. This result reveals that the internal stress also plays a very important role in the phase transition in KNN-based piezoceramics.

Acknowledgements

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References

1. Cross E. Lead-free at last. *Nature* 2004;**432**:24–5.
2. Ringgaard E, Wurlitzer T. Lead-free piezoceramics based on alkali niobates. *J Eur Ceram Soc* 2005;**25**:2701–6.
3. Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, et al. Lead-free piezoceramics. *Nature* 2004;**432**:84–7.
4. Rodel J, Jo W, Seifert KTP, Anton EM, Granzow T, Damjanovic D. Perspective on the development of lead-free piezoceramics. *J Am Ceram Soc* 2009;**92**:1153–77.
5. Shrout TR, Zhang SJ. Lead-free piezoelectric ceramics: alternatives for PZT? *J Electroceram* 2007;**19**:111–24.
6. Hollenstein E, Davis M, Damjanovic D, Setter N. Piezoelectric properties of Li- and Ta-modified $(K_{0.5}Na_{0.5})NbO_3$ ceramics. *Appl Phys Lett* 2005;**87**:182905.
7. Wu J, Xiao D, Wang Y, Wu L, Jiang Y, Zhu J. K/Na ratio dependence of the electrical properties of $[(K_xNa_{1-x})_{0.95}Li_{0.05}](Nb_{0.95}Ta_{0.05})O_3$ lead-free ceramics. *J Am Ceram Soc* 2008;**91**:2385–7.
8. Wang K, Li JF. Domain engineering of lead-free Li-modified $(K,Na)NbO_3$ polycrystals with highly enhanced piezoelectricity. *Adv Funct Mater* 2010;**20**:1924–9.
9. Song HC, Cho KH, Park HY, Ahn CW, Nahm S, Uchino K, et al. Microstructure piezoelectric properties of $(1-x)(Na_{0.5}K_{0.5})NbO_{3-x}LiNbO_3$ Ceramics. *J Am Ceram Soc* 2007;**90**:1812–6.
10. Azough F, Wegrzyn M, Freer R, Sharma S, Hall D. Microstructure and piezoelectric properties of CuO added (K, Na, Li)NbO_3 lead-free piezoelectric ceramics. *J Eur Ceram Soc* 2010;**31**:569–76.
11. Lin D, Kwok KW, Chan HLW. Microstructure phase transition, and electrical properties of $(K_{0.5}Na_{0.5})_{1-x}Li_x(Nb_{1-y}Ta_y)O_3$ lead-free piezoelectric ceramics. *J Appl Phys* 2007;**102**:034102.
12. Zhao P, Zhang BP, Li JF. Enhanced dielectric piezoelectric properties in $LiTaO_3$-doped lead-free $(K,Na)NbO_3$ ceramics by optimizing sintering temperature. *Scripta Mater* 2008;**58**:429–32.
13. Wang C, Hou YD, Ge HY, Zhu MK, Yan H. Crystal structure and orthorhombic–tetragonal phase transition of nanoscale $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$. *J Eur Ceram Soc* 2009;**29**:2589–94.
14. Guo Y, Kakimoto K, 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.
15. Wang K, Li JF. Analysis of crystallographic evolution in $(Na,K)NbO_3$-based lead-free piezoceramics by x-ray diffraction. *Appl Phys Lett* 2007;**91**:262902.
16. Wu C, Duan W, Zhang XW, Liu Z. Effects of hydrostatic pressure on $Pb(Zr_{1-x}Ti_x)O_3$ near the morphotropic phase boundary. *J Appl Phys* 2010;**108**:124102.
17. Li JF, Zhu ZX, Lai FP. Thickness-dependent phase transition and piezoelectric response in textured Nb-doped $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films. *J Phys Chem C* 2010;**114**:17796–801.
18. Kakimoto K, Sumi T, Kagomiya I. Pressure-dependent raman scattering spectrum of piezoelectric $(Li,Na,K)NbO_3$ lead-free ceramics. *Jpn J Appl Phys* 2010;**49**:09DM10.
19. Rubio-Marcos F, Romero JJ, Ochoa DA, Garcıa JE, Perez R, Fernandez JF. Effects of poling process on KNN-modified piezoceramic properties. *J Am Ceram Soc* 2010;**93**:318–21.
20. Klein N, Hollenstein E, Damjanovic D, Trodahl HJ, Setter N, Kuball M. A study of the phase diagram of $(K,Na,Li)NbO_3$ determined by dielectric and piezoelectric measurements, and Raman spectroscopy. *J Appl Lett* 2007;**102**:014112.