J Mater Sci (2007) 42:3276–3279
DOI 10.1007/s10853-007-1669-8

LETTER

The dielectric and ferroelectric properties of tungsten bronze ferroelectric $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ ceramic

X. Hao · Y. F. Yang

Received: 16 February 2007 / Accepted: 6 March 2007 / Published online: 27 March 2007

Introduction

Lead oxide based ferroelectric ceramics, represented by lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT), are widely used for piezoelectric actuators, sensors and transducers due to their excellent ferroelectric properties [1]. However, volatilization of toxic PbO during high-temperature sintering not only causes environmental pollution but also generate instability of composition and electrical properties of products. Therefore, it is necessary to develop environment-friendly lead-free ferroelectric ceramics to replace the PZT-based ceramic, which has become one of the maintrends in present development of ferroelectric materials.

Strontium barium niobate, $Ba_{1-x}Sr_xNb_2O_6$(SBN), one of the lead-free ferroelectric oxides with tungsten bronze (TB) structure have received considerable attention as an excellent candidate of lead-free ferroelectric ceramics because they have large piezoelectric properties and high dielectric constants and the properties of the tungsten–bronze structure which could be modified in a wide scale [2–4]. However, SBN has a drawback of low Curie temperature is about 90 °C [5] and low remnant polarization Pr = 1.7 $\mu c/cm^2$ [6]. Therefore, SBN-based ceramics poled have recently been investigated [7, 8]. Among these investigations, $\alpha(Sr_xBa_{1-x})$ Nb_2O_6:$\beta(K_yNa_{1-y})NbO_3$ systems have large spontaneous polarization, large piezoelectric properties, and high dielectric constants which are very similar to perovskites [9]. In addition, it is in the merits of higher Curie temperature, large electric-optic and strong photorefractive effect and especially no phase transition at room temperature. In this study, the $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ ceramic which has many advantages over single crystals and thin films, such as low cost, ease of fabrication, large size and isotropic properties was prepared. The diffuse phase transition, dielectric and ferroelectric properties of the compound were also reported.

Experiment

The polycrystalline sample of $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}$ Nb_2O_6 was prepared by a low-temperature combustion synthesis process (LCS) [10]. The starting materials were $NbCl_5$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $NaNO_3$, KNO_3, citric acid, ammonia solution and H_2O_2 solution (30%).

The hydrated niobium oxide ($Nb_2O_5 \cdot nH_2O$) was prepared from $NbCl_5$ and H_2O, which was added with citric acid and H_2O_2 solution to get the Nb-citric solution used as the source of niobium. $Ba(NO_3)_2$, $Sr(NO_3)_2$, $NaNO_3$, KNO_3 and citric acid were dissolved in deion water and mixed with the Nb-citric solution. Citric acid was used as an organic fuel because it could not only form stable water-soluble complexes with metal ions but also act as a rich fuel. The required amount of ammonia solution was added to adjust the pH value to 7 to form transparent mixture solution. This mixture solution was evaporated and then ignited at 300 °C at ambient atmosphere, after that the mixtures were calcined at 900 °C for 1 h.

The powder was compacted into pellet at 200 MPa with 10 mm diameter and around 1 mm thickness, which was sintered at 1250 °C for 12 h. X-ray diffraction (XRD)

X. Hao (✉)
China University of Geosciences, Beijing 100083, P.R. China
e-mail: hxian@ciac.jl.cn

Y. F. Yang
Key Laboratory of Rare Earth Chemistry and Physics,
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022 Jilin, P.R. China

patterns were collected on a Rigaku D/Max-IIB diffractometer with Cu Ka radiation ($\lambda = 0.15406$ nm). The fracture morphology of the sintered pellet was studied at room temperature by a scanning electron microscopy (SEM, XL30, ESEM, FEG, FEI). Ag-electrode was screened on both flat surfaces of the pellet to measure the electrical properties of the compound. Temperature-dependence dielectric measurement was made using the Agilent 4294A impedance analyzer equipped with a thermostat from room temperature to 450 °C in frequency range from 100 Hz to 1 MHz. The *P–E* hysteresis loops were measured by a TF analyzer (Model 2000, aixACCT Systems, Germany) at room temperature.

Results and discussion

The XRD pattern of $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ ceramic powder indicates that the sample is of single-phase tetragonal TB structure as shown in Fig. 1. All peaks are indexed according to the standard powder diffraction date (JCPDS file No.38-1255), and there is no evidence for any secondary phase(s) present. The unit cell parameters of this ceramic are as the following: a = 1.24411(5) nm and c = 0.39389(4) nm.

The $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ compound was densified without any additive at 1250 °C for 12 h. The SEM micrograph of the fracture surfaces of the compound at room temperature is shown in Fig. 2. The grain size evaluated from the micrograph is found to be in the range of 3–5 μm. A similar type of microstructure has been found in many materials of this family [11, 12].

The temperature dependence of ε and tan δ for the compound at 100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz were shown in Fig. 3.At 10 kHz the room temperature ε and tan δ are 524 and 0.019, respectively. It was observed that the compound undergone ferroelectric–paraelectric phase transition of diffuse-type. The smooth switch over of ε from low symmetry ferroelectric phase to more symmetry paraelectric phase indicates that the phase transition is of diffuse nature. As expected, the substitution of Na and K, which results in the variation in the tungsten bronze structure, induces significant changes in the dielectric properties. The empty sites in the tungsten bronze structure are decreased for the lower valence conditions of Na^+ and K^+ comparing with that of Sr^{2+} and Ba^{2+}. The substitution of Na and K causes an enhanced structural distortion, resulting in an increase in the Curie point. The Curie temperature of the compound at 10 kHz is 287 °C, which is much higher than about 90 °C of the $Sr_{0.5}Ba_{0.5}Nb_2O_6$ [5]. The variation of tan δ with temperature shows the similar trend. The change in the tan δ values of the compound is

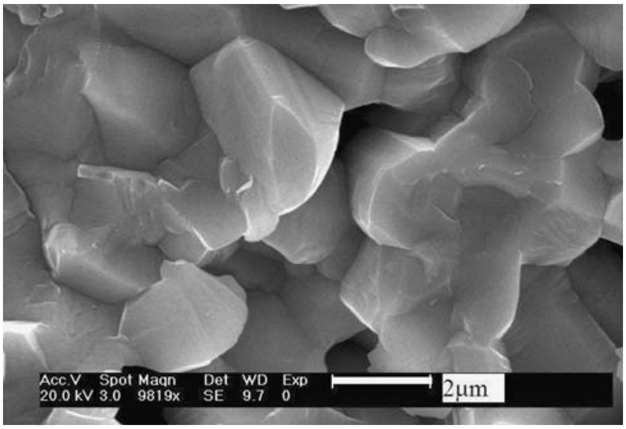

Fig. 2 SEM micrograph of $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$

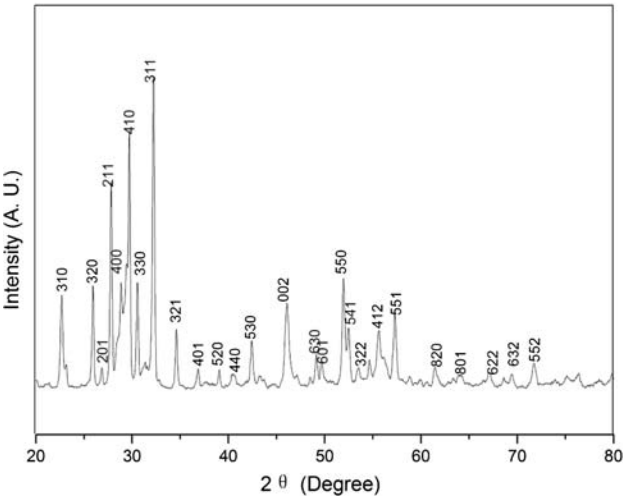

Fig. 1 X-ray diffraction pattern of $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ at room temperature

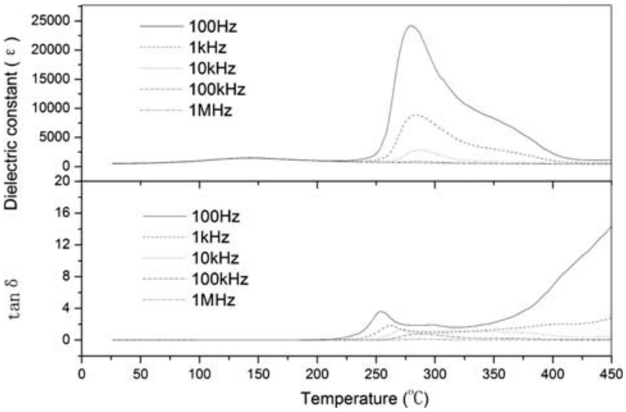

Fig. 3 Temperature dependence of dielectric constant (ε) and dielectric loss (tanδ) of $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ ceramic at 100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz

considerably little at low temperature and increases significantly at high temperature. This increase in tan δ at higher temperature may be due to the enhanced conductivity in the compound and the reduction in ferroelectric domain wall's contribution at high temperature paraelectric phase [13]. It is also observed that the tan δ at high frequencies is much lower compared to that at low frequencies. This kind of dependence of tan δ on frequency is typically associated with loss of energy by conduction process. There are high-temperature anomalies are seen in the temperature range of 350–400 °C for ε and near 300 °C for tan δ in Fig. 3. The presence of the humps is associated with possible relaxation processes. This is attributed to the structural disorder to some degree and results in an increase in spontaneous polarization.

The disorder or diffusivity (γ) degree in the $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ compound has been calculated using a modified empirical relation proposed by S.M. Pilgrim et al., to describe the diffuseness of the ferroelectric phase transition [14].

$$\ln(1/\varepsilon - 1/\varepsilon_{max}) = \ln K + \gamma \ln(T - Tc) \quad (1)$$

Where ε_{max} is the maximum value of ε at T_c, K is an arbitrary constant and γ is the degree of diffuseness. The limiting values 1 and 2 for γ, respectively, reduce the expression to the Curie–Weiss law valid for a normal and the quadratic dependence valid for the ideal relaxor ferroelectric. The value of γ at 10 kHz is 1.81 given by the slope of the $\ln(1/\varepsilon–1/\varepsilon_{max})$ versus $\ln(T–T_c)$ plot (Fig. 4). The values of γ of $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ indicate that the compound exhibits characteristics of diffuse phase transition.

Typical hysteresis loops obtained in $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ has been shown in Fig. 5. It is noticed that the specimen under investigation is saturated hysteresis loops. The remnant polarization (Pr)is 3.5μc/cm^2 and coercive field (E_c) is 16.09 kV/cm. The values which are related to the ferroelectric domain structure [15] are nearly to those of the thin film $(K_{0.5}Na_{0.5})_{0.2}(Sr_{0.5}Ba_{0.5})_{0.9}Nb_2O_6$ reported by Li [16], and higher than that of the $Sr_{0.5}Ba_{0.5}Nb_2O_6$ whose Pr is about 1.7μc/cm^2 and Ec is about 6 kV/cm [6].

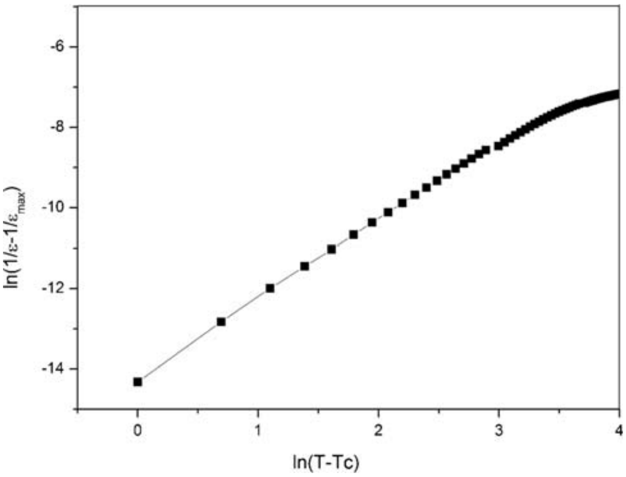

Fig. 4 Variation of $\ln(1/\varepsilon–1/\varepsilon_{max})$ with $\ln(T–T_c)$ at 10 kHz for $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$

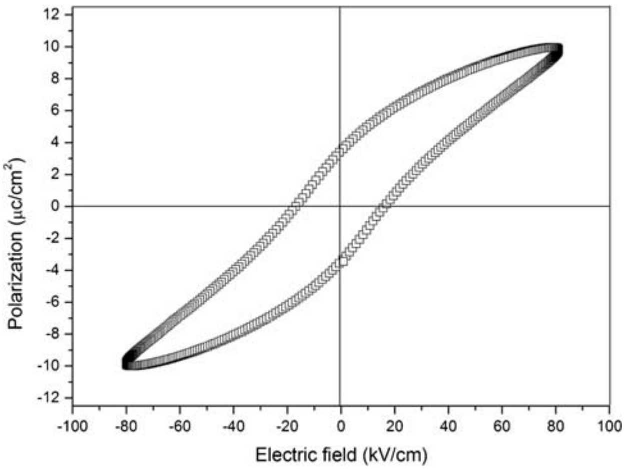

Fig. 5 *P–E* hysteresis loop of $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$

Conclusions

The crystalline phases, dielectric and ferroelectric properties of the $(K_{0.5}Na_{0.5})_{0.1}(Sr_{0.5}Ba_{0.5})_{0.95}Nb_2O_6$ lead-free ferroelectric ceramic were investigated. The results of XRD show that the compound has typical tetragonal structure at room temperature. In summary, the sample has the higher Curie temperature 287 °C than the strontium barium niobate. A diffuse ferroelectric transition behavior occurs in the samples, and the diffusivity is 1.81 for the composition. *P–E* hysteresis loop shows that it has a high polarization remanent Pr and low coercive field E_c than pure SBN ceramic.

References

1. Kumamoto S, Mizumura K, Kurihara Y, Ohhashi H, Okuno K (1991) Jpn J Appl Phys 30:2292
2. Ewbank MD, Neurgaonkar RR, Copy WK, Feinberg J (1987) J Appl Phys 62:374
3. Maciolek RB, Liu ST (1973) J Electron Mater 2:191
4. Neurgaonkar RR, Kalisher MH, Lim TC, Staples EJ, Keester KI (1980) Mater Res Bull 15:1235
5. Patro PK, Kulkarni AR, Harendranath CS (2004) Ceram Int 30:1405
6. Pasricha R, Ravia V (2005) Mater Chem Phys 94:34

7. Sambasiva Rao K, Prasad TNVKV, Subrahmanyam ASV (2003) Mat Sci Eng B 98:279
8. Santos A, Spínola DU, Garcia D, Eiras JA (2002) J Appl Phys 92:3251
9. Xie RJ, Akimune Y, Matsuo K, Sugiyama T (2002) Appl Phys Lett 80:835
10. Yang YF, Liu YY, Meng J, Huan Y, Wu YN (2006) J Alloy Compd (in press)
11. Khachane M, Moure A, Elaatmani M, Zegzouti A, Daoud M, Castro A (2006) Mater Res Bull 41:1798
12. Kakimoto K, Kakemoto H, Baba A, Fujita S, Masuda Y (2001) J Eur Ceram Soc 21:1569
13. Kuharuangrong S (2001) J Mater Sci 36:1727. (DOI: 10.1143/JJAP.45.831)
14. Pilgrim SM, Sutherland AE, Winzer SR (1990) J Am Ceram Soc 73:3122
15. Burfoot JC (1966) Ferroelectrics. Van Norstrand, London
16. Li MY, Wang ZL, Fan SS, Zhao QT, Xiong GC, Chen HC, Liu ZG (1997) Solid State Commun 103:285