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Low temperature fabrication of lead-free KNN-LS-BS ceramics via the combustion method

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Abstract

Lead-free piezoelectric 0.992(0.95$K_{0.5}Na_{0.5}NbO_3$–0.05$LiSbO_3$)–0.008$BiScO_3$; KNN-LS-BS ceramics were successfully prepared using the combustion method. The highest % perovskite phase was found in the sample calcined at 700 °C for 1 h. The structural phase of orthorhombic structure was also detected in this sample. For the sintered ceramics, a pure tetragonal perovskite phase was observed in the samples sintered between 1025 and 1100 °C. The microstructure of ceramics showed a square or rectangular shape and the average grain size increased with increasing of sintering temperature. The density of the ceramics increased with increasing of sintered temperature up to 1075 °C, were it reached 97.5% of theoretical density and then dropped in value when the sintered temperature further increased. The excellent electrical properties of ε_r at $T_c=6600$, tanδ at $T_c=0.04$, P_r (at 40 kV/cm) = 19.4 μC/cm^2 and E_c (at 40 kV/cm) = 24.1 kV/cm were obtained in the most dense ceramic. The results indicate that the KNN-LS-BS ceramics are promising lead-free piezoelectric materials.

Keywords: A. Sintering; C. Dielectric properties; D. Perovskites; KNN-LS-BS ceramics

1. Introduction

In recent years, the most widely used piezoelectric materials are lead-base PZT ceramics due to their excellent electrical properties [1–3]. The use of lead-base ceramics can cause a serious threat to human health and create environmental problems. As a consequence, much of the current research is oriented toward more environmentally friendly lead-free materials [4–6]. An alternative group of lead-free piezoelectric materials are those based on a KNN solid solution which have a high Curie temperature ($T_c \sim 420$ °C) and high piezoelectric constant ($d_{33} \sim 100$ pC/N) [7–10]. Nevertheless, it is extremely difficult for pure KNN to achieve high density by using ordinary sintering methods because their phase stability is limited to 1140 °C for potassium sodium niobate [9]. In order to solve the above problem, additives of $LiAO_3$ ($A=$ Na. Ta, Sb) and $BiBO_3$ ($B=$ Fe, Sc, Al) were added into the KNN ceramics to form a new solid solution, which enhanced the density, dielectric, and piezoelectric properties [11–16]. Among these materials, 0.992(0.95$K_{0.5}Na_{0.5}NbO_3$–0.05$LiSbO_3$)–0.008$BiScO_3$; KNN-LS-BS has been considered a good candidate for lead-free piezoelectric ceramics because its high piezoelectric constant d_{33} of 305 pC/N, high dielectric constant of ~6100, and favorable electromechanical planar k_p of 0.54. Minhong et al. [15] fabricated the KNN-LS-BS via the solid state reaction method. The KNN-LS-BS were calcined at 900 °C for 6 h and sintered at 1090 °C for 3 h. The results suggested that LS-BS can be diffused into a KNN lattice to form a new solid solution in which the KNN-LS-BS ceramics exhibited a structural phase indexed in the tetragonal perovskite ferroelectric phase and whose maximum density was ~96%.

It is well known that the solid state reaction method is relatively simple, yet it is time consuming, needing high firing temperatures, is energy intensive, and the calcined powders are often of a large particle size [17]. Recently, interest has been shown in the combustion method as a

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mean of preparing ferroelectric ceramics. It is not a complicated method, which produces ultra-fine powders, with a high density, and excellent electrical properties, which use lower firing temperatures and have a lower soak time compared to other methods [18–20]. This because the combustion reaction provides heat that can be effectively applied to the starting materials. This energy speeds up the chemical reaction of the materials. In addition, from the literature survey, the ferroelectric properties of KNN-LS-BS ceramics have not been studied. Therefore, the purposes of this paper are to synthesize of KNN-LS-BS ceramics via the combustion method and to investigate the effect of firing temperatures on phase structure, microstructure, density and electrical properties of KNN-LS-BS ceramics.

2. Experimental

The raw materials of $0.992(0.95K_{0.5}Na_{0.5}NbO_3$–$0.05LiSbO_3)$–$0.008BiScO_3$ samples processed by the combustion method were pure reagent K_2CO_3, Na_2CO_3, Nb_2O_5, Li_2O_3, Sb_2O_3, Bi_2O_3 and Sc_2O_3. They were weighed and milled for 24 h using planetary milling with a zirconia ball media and ethanol. They were then dried and sieved. The powders were mixed with glycine in a ratio of 1:2. These powders were calcined at 650–750 °C for 0.5–2 h. The calcined powders, milled with 3 wt% PVA aqueous, were uniaxially pressed into discs with a diameter of 15 mm under 80 mPa pressures and subsequently sintered between 1000 and 1100 °C for 3 h. The phase structure and microstructure were studied by the X-ray diffraction (XRD) and scanning electron microscope (SEM). Bulk densities were measured by Archimedes method using distilled water as a medium. The dielectric properties (measured from 30 to 400 °C), and ferroelectric properties were determined by a LCR meter and a ferroelectric test system, respectively.

3. Results and discussion

The XRD patterns of KNN-LS-BS powders calcined at 650–750 °C for 0.5–2 h are displayed in Fig. 1(a). The phase structure in all samples is an orthorhombic perovskite structure. The impurity phases of $NaSbO_3$ and $LiSbO_3$ were detected. At the calcination temperature of 650, 700 and 750 °C, using a dwell time of 1 h, the %perovskite phases were 91.4, 94.3 and 92.2%, respectively. To improve the %perovskite phase, shorter and longer dwell times (0.5 and 2 h) were adopted using a calcination temperature of 700 °C. The sample exhibited a %perovskite of 93.2 and 93.0% when the dwell time was 0.5 and 2 h, which is lower than the powders calcined at 700 °C for 1 h. Therefore, the calcination temperature of 700 °C for 1 h was used for the preparation of the KNN-LS-BS ceramics.

The XRD patterns of KNN-LS-BS ceramics sintered at 1000–1100 °C for 2 h is shown in Fig. 1(b). The structural phase indexed in the tetragonal perovskite phase in all samples. The impurity phase was found in the sample sintered at 1000 °C. While, the pure perovskite structure

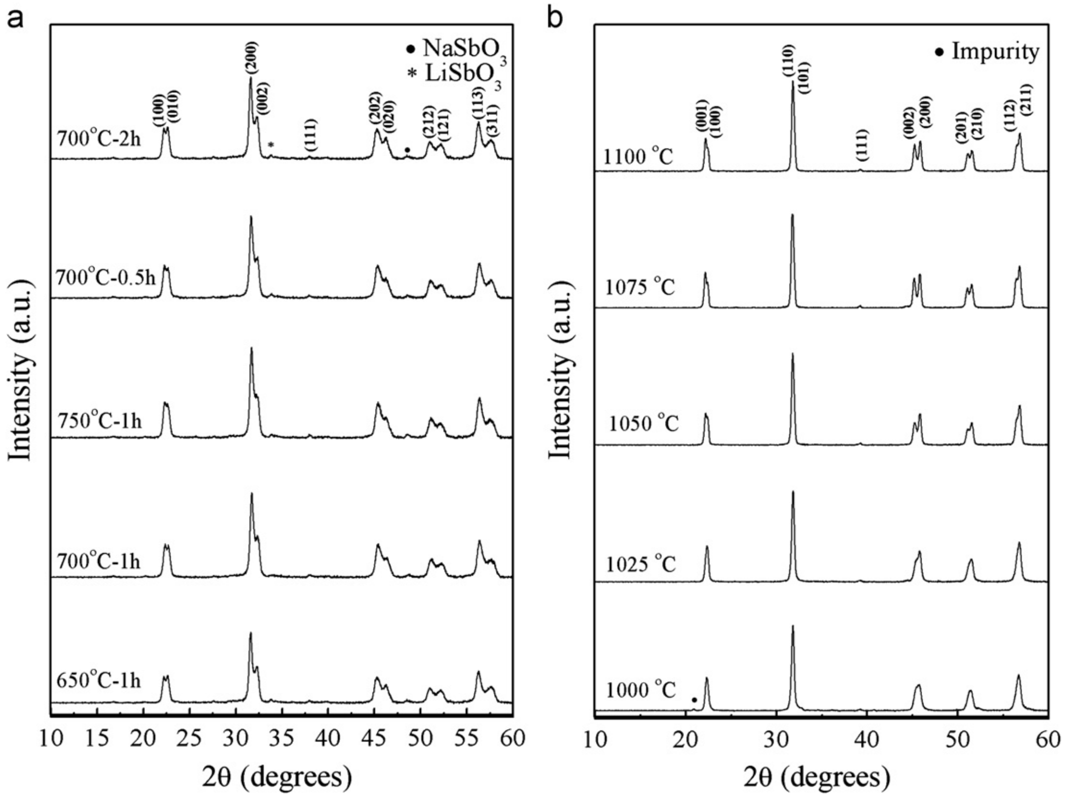

Fig. 1. XRD patterns of (a) KNN-LS-BS powders calcined at 650–750 °C and (b) KNN-LS-BS ceramics sintered at 1000–1100 °C for 2 h.

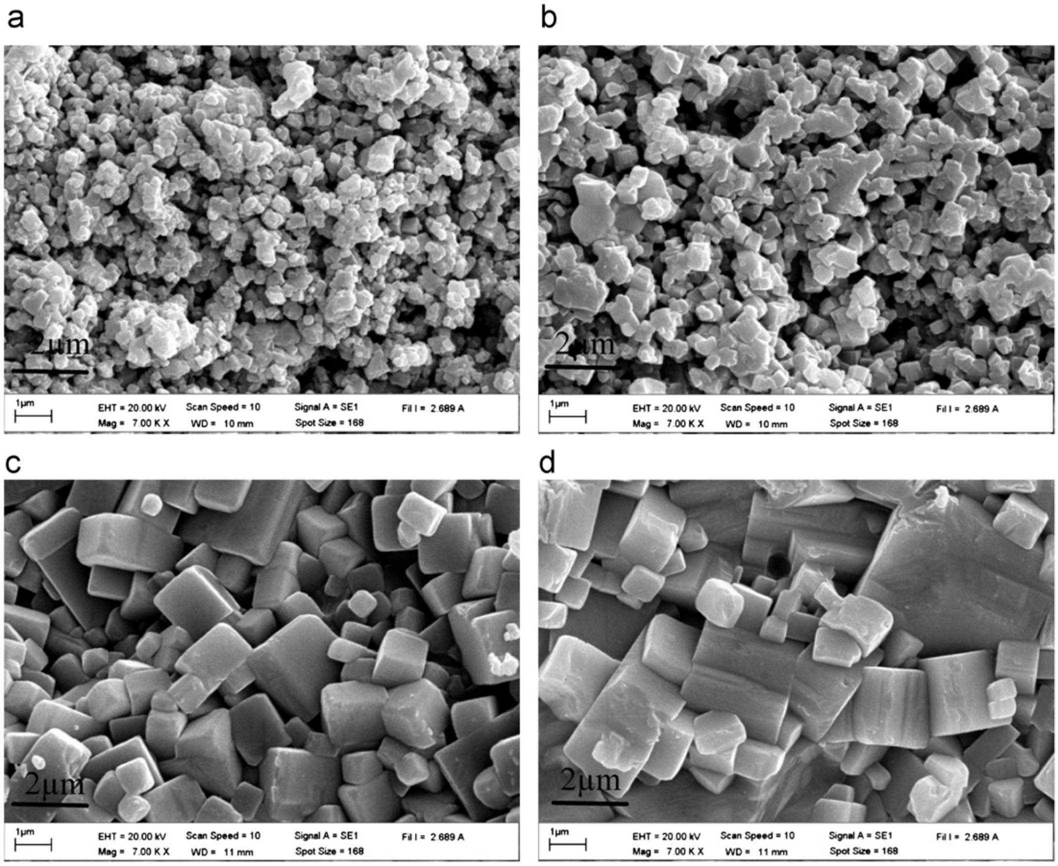

Fig. 2. The natural surface SEM micrographs of KNN-LS-BS ceramics sintered at (a) 1000 °C, (b) 1050 °C, (c) 1075 °C and (d) 1100 °C [15].

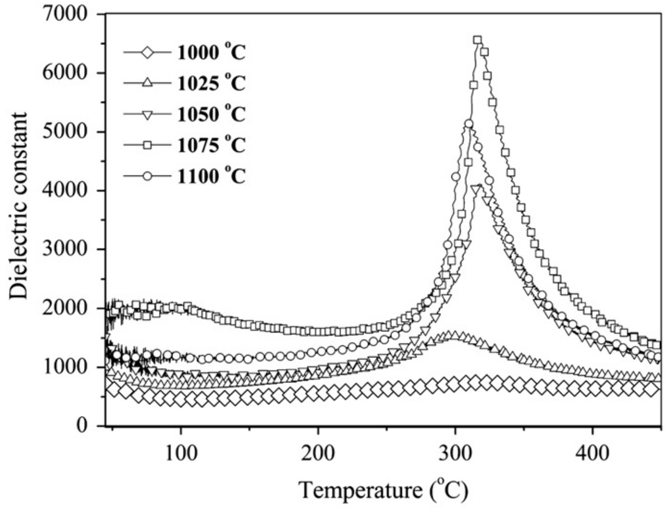

Fig. 3. Temperature dependence of dielectric constant of KNN-LS-BS ceramics sintered at 1000–1100 °C for 2 h.

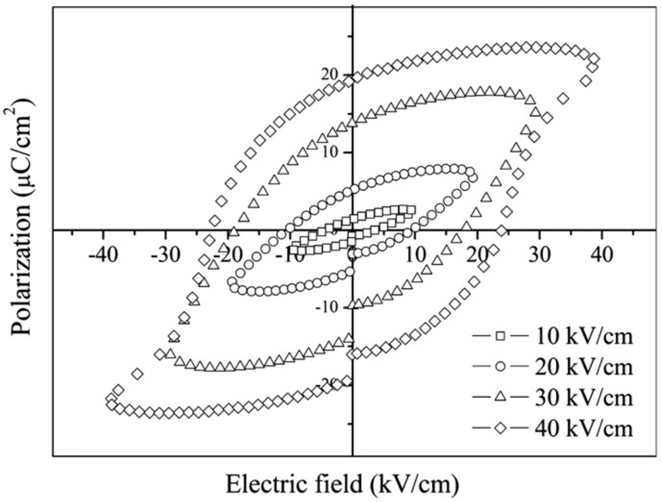

Fig. 4. *P*–*E* hysteresis loops of KNN-LS-BS ceramics sintered at 1075 °C.

was obtained in samples sintered at 1025–1100 °C. Moreover, it can be seen that at sintering temperatures of 1050–1100 °C, the obviously separated XRD peaks (such as 0 0 2 and 2 0 0) were observed. These represent the higher crystallinity of ceramics. The lattice parameter *a*, *c* and *c*/*a* ratio were calculated and are listed in Table 1. The lattice parameter *a* decreased, while the lattice parameter *c* and *c*/*a* ratio increased with increasing of sintered temperatures.

Fig. 2 shows the natural surface SEM micrograph of KNN-LS-BS pellets sintered at 1000–1100 °C for 2 h. A characteristic square or rectangular morphology of the grain were obtained in all samples. At a low sintering temperature of 1000–1050 °C, in Fig. 2(a) and (b), many distinct pores occurred. At a higher sintering temperature of 1075 °C, in Fig. 2(c), the porosity decreased and the average grain size extremes increased. When the sintering temperature increased to 1100 °C, in Fig. 2(d), grain boundaries began to melt and the small grains merge together to produce a larger grain. The average value of grain size, as measured by the linear intercept method, increased from 0.32 to 1.32 μm with increasing of sintering temperature from 1000 to 1100 °C, as shown in Table 1.

The linear shrinkage, bulk density (ρ) and theoretical density (%T.D.) of KNN-LS-BS ceramics sintered between 1000 and 1100 °C for 2 h are shown in Table 1. The linear shrinkage of ceramics increased from 4.0 to 15.9% when the sintered temperature increased. The density of sintered pellets increased to a maximum of 1075 °C, with a value of 4.56 g/cm^3 or 97.5% of theoretical density. A further increase in the sintering temperature resulted in a drop in value. This may be due to distending from the trapped gas in the pores. The gas-filled pores combined and grew because the grains growth [15]. The density corresponded to the microstructure results. Moreover, the density in this study was higher than the density of ceramics prepared via solid state reaction method [15].

The temperature dependence of the dielectric constant of KNN-LS-BS ceramics under 1 kHz is shown in Fig. 3. For the pellets sintered at 1050–1100 °C, the result exhibited a sharp phase transition peak at around 320 °C representing the ferroelectric tetragonal phase to paraelectric cubic phase transition. This agrees with previous work by Minhong et al. [15]. At 1025 °C, a broad peak of dielectric constant was found. The peak was not clearly observed in the samples sintered at 1000 °C. The Curie temperatures (T_c) of ceramics are in a range of 293–320 °C, as seen in Table 1. The dielectric constant at T_c first increased and reached its highest at 1075 °C, and then dropped as a sintering temperature increased above 1075 °C. The highest dielectric constant (at T_c) of 6600 and lowest dielectric loss (at T_c) of 0.04 of the KNN-LS-BS ceramics were obtained from the samples sintered at 1075 °C for 2 h, as shown in Table 1. The dielectric properties were in a good agreement with the phase structure, microstructure and density results. This indicated that high quality KNN ceramics could be prepared via the combustion method. In addition, the dielectric constants observed in this study were higher than the ceramics prepared by the solid state reaction method [15].

In order to characterize the ferroelectric properties of KNN-LS-BS ceramics, the room temperature P–E hysteresis loops of the densest pellets were measured at different electric field strengths as shown in Fig. 4. It can be seen that the shape of the hysteresis loops differed greatly with different electric field strengths. A loop pinching was observed at lower electric fields (10–30 kV/cm), which is linked to a preferred orientation of defect dipole in the materials [15]. At electric fields higher than 30 kV/cm,

Table 1
Lattice parameters, c/a ratio, average grain size, linear shrinkage, density, Curie temperature and dielectric properties of KNN-LS-BS ceramics.

Sintered temperature (°C)	Lattice parameters (Å)		c/a ratio	Average grain size (μm)	Linear shrinkage (%)	Density		T_c(°C)	ε_r at T_c	tanδ at T_c
	a	C				ρ (g/cm^3)	%T.D.			
1000	–	–	–	0.32	4.0	4.20	89.7	–	–	–
1025	–	–	–	0.44	6.6	4.22	90.2	293	1550	0.08
1050	3.9639	4.0080	1.01	0.50	11.3	4.25	90.5	320	4120	0.08
1075	3.9622	4.0151	1.03	1.11	15.6	4.56	97.5	317	6600	0.04
1100	3.9602	4.0206	1.06	1.32	15.9	4.50	96.2	310	5170	0.05

pinching loops vanished and well formed symmetric loops were observed.

At the maximum electric fields of 40 kV/cm, the coercive field (E_c) and remnant polarization (P_r) of 24.1 kV/cm and 19.4 μC/cm^2 existed.

4. Conclusions

Lead-free KNN-LS-BS ceramics were successfully prepared by the combustion method. The calcination and sintering conditions influenced the phase structure, microstructure, density and dielectric properties of KNN-LS-BS ceramics. The highest % peroskite phase of the calcined powders was detected in samples calcined at 700 °C for 1 h. The tetragonality of the sintered pellets increased with increasing sintering temperature from 1050 to 1100 °C. The microstructure of the ceramics exhibited distinct porosity when the samples were sintered at low temperatures (1000–1050 °C). The melting of the grain boundary was observed in the pellets sintered higher than the appropriate temperature of 1075 °C. The outstanding density and electrical properties of %T.D. = 97.5%, ε_r at T_c = 6600, tanδ at T_c = 0.04, P_r (at 40 kV/cm) = 19.4 μC/cm^2 and E_c (at 40 kV/cm) = 24.1 kV/cm were obtained from the samples sintered at 1075 °C for 2 h. These had superior density and better electrical properties than those obtained by using the solid state reaction method.

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