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Investigation of nano particle additives on lithium doped KNN lead free piezoelectric ceramics

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Abstract

Lead free potassium sodium niobate modified piezoelectric ceramics were synthesized through conventional mixed oxide method. Crystal structure and microstructure were analyzed by X-ray diffraction and scanning electron microscopy (SEM). The effects of nano ZnO, CuO and SnO_2 additives as the nano scale sintering aids, on microstructure and electrical properties of $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ (KNNL-6) ceramics were investigated. The optimum dielectric and piezoelectric properties of $\varepsilon_r = 560$, $d_{33} = 215$ pC/N and tan $\delta = 0.008$ were obtained for pure KNNL-6 that sintered at 1000 °C for 2 h. The results show that with addition of nano particle sintering aids, the piezoelectric coefficient d_{33} of $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ ceramics was decreased. The decrease in piezoelectric charge coefficient could be due to the hardening effect, which lowers the piezoelectric charge.

Keywords: Lead-free ceramics; KNNL-6; Nano particles; Piezoelectric; Microstructure

1. Introduction

Lead based ceramics such as PZT with exceptional piezoelectric properties have been widely used in piezoelectric devices [1]. However, the environmental and health hazards of lead are well-known, and recycling and disposal of devices containing lead-based piezoelectric materials is of great concern. Throughout the world, demand is growing for materials that are benign to the environment and human health. The among of lead free piezoceramics, (K,Na)NbO3 (KNN) ceramics that have good piezoelectric properties and a high curie temperature get more attention [2,3]. However, it is very difficult to obtain dense and well-sintered KNN ceramics using ordinary sintering process because of the high volatility of alkaline elements at high temperatures [4–6]. Its processing difficulties have led to divergences in reported electrical properties and resulting in apparently poor piezoelectric properties of pure KNN ceramics [5]. These difficulties are concerned with a narrow sintering window, the volatilization of K and Na in high sintering temperature, a poling barrier owing to high loss tangent and the evolution of secondary phases. In order to resolve this problem, different methods have been performed. At present, there are several methods to improve densification and piezoelectric properties of KNN ceramics. One is to use new processing techniques such as hot press, spark plasma sintering, and reactive template grain growth technique [6–9], the cost of which, however, is relatively high compared to normal oxide sintering method. The other one is to modify $(Na,K)NbO_3$ ceramics using dopants to form solid solutions [10–13], or using sintering aids such as, CuO and ZnO [14–18]. In the later technique, the novel sintering aids such as $K_4CuNb_8O_{23}$, $K_{5.4}CuTa_{10}O_{29}$, CuO and ZnO were introduced to KNN ceramics to decrease sintering temperature. Decreasing sintering temperature will help to prevent loss of volatile elements such as sodium [14–17].

In this work, $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ (KNNL-6) piezoelectric ceramics were synthesized by traditional solid state sintering and then the effects of the nano particle additives as the nano scale sintering aids, on the structure and electrical properties were investigated.

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2. Experimental procedure

High purity oxide and carbonate powders of Nb_2O_5 (99.9%, Merck, ≤250 μm), nano scale ZnO (99.5%, ≤50 nm, Noavaran Catalist, Iran), nano scale CuO (99.5%, ≤50 nm, Advanced Materials US), nano scale SnO_2 (99.5%, ≤50 nm, Advanced Materials US), K_2CO_3 (99.9%, Merck, ~1 mm) and Na_2CO_3 (99.9%, Merck, ~1 mm) and Li_2CO_3(99.9%, Merck, ~1 mm) were used as the starting materials. Polyvinyl pyrrolidone (PVP K-15, Sigma–Aldrich) with molecular mass of 10,000 g mol^{-1} was used as dispersant. Powders with stoichiometric weights were mixed for 6 h in a plastic jar containing zirconia balls at isopropyl alcohol media. The slurry was dried in oven and then the calcinations were carried out at 850 °C for 4 h. In order to enhance the compositional uniformity, the calcined powders were ground by attrition milling and then calcined under the same conditions. Nano particle powders were dispersed with the aid of PVP K-15 solution. Required amounts of nano additives (0.4 mol%) were mixed with KNNL-6 powder by attrition milling for 1 h. The powders were dried and pressed into disks of 10 mm in diameter under a pressure of 250 MPa and sintered at temperature range of 980–1080 °C for 2 h. The density of the sintered samples was measured by the Archimedes method. The microstructure was investigated by a ZEISS S-360 scanning electron microscopy (SEM) and crystal structure was identified by using X-ray diffraction (XRD) with Cu Kα radiation utilizing a Bruker AXS D8 ADVANCE diffractometer. To measure the electrical properties, all the samples were carefully polished to reach parallel surfaces and then electroded by silver paste and gold. The samples for the measurement of piezoelectric properties were polled by applying dc fields of 3 kV/mm for 30 min in a silicon oil bath maintained at 100 °C. Capacitance and tan δ were measured at 1 kHz before and after poling by a LCR meter. The piezoelectric coefficient was measured by a Berlincourt-type quasi-static d_{33} meter at 100 Hz in samples with proper aspect ratio. The dielectric constant was obtained as a function of temperature using LCR meter with a temperature-controlled furnace.

3. Results and discussions

Fig. 1 shows the size distribution of nano ZnO particles measured by particle size analyzer. The average particle size of nano ZnO is about 50 nm, which was in agreement with SEM photographs. The results of sedimentation test shows that adding PVP K-15 as dispersing agent has hindered the sedimentation of nano particles. Actually, PVP K-15 has impeded the agglomeration of nano particles. In contrast, the sample without dispersing agent precipitated immediately after beginning the test.

Fig. 2 shows the XRD patterns of the calcined powder. A single-phase perovskite structure and no secondary phase were observed. With addition of nano particles, because of the small amount (0.4 mol%), secondary phases were not observed [19]. The SEM images of fracture surfaces of $(K_{0.5}Na_{0.5})_{0.94}Li_{0.06}NbO_3$ + 0.4 mol% nano particles ceramics sintered at 1060 °C for 2 h are shown in Fig. 3. With the co-addition of nano ZnO and nano CuO, grain growth was observed. While with addition of nano ZnO and SnO_2, along with decreasing the grain size, the dense and uniform microstructures were observed. A liquid phase, which may be formed in the grain boundary of the ceramics with addition of nano ZnO and nano CuO, results in the increase of grain size of the ceramics. The addition of SnO_2 could further decrease the melting point of liquid phases, leading to a relatively low sintering temperature, and increase the quantity of liquid phases, thus more effectively promoting densification [20]. The KNNL-6 ceramics which sintered at 980–1080 °C for 2 h had relatively high densities (>94% of theoretical density). Fig. 4 shows the dependences of piezoelectric coefficient d_{33} on sintering temperature for $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ ceramics with 0.4 mol% nano additives sintered at 980–1080 °C for 2 h. The piezoelectric coefficient d_{33} of all samples increased with sintering temperature and then decreased at high temperatures. The evaporation of potassium oxide at high temperature was possibly the origin of such behaviour. The sintering temperature that piezoelectric coefficient d_{33} became maximum, was defined the optimum sintering temperature. The maximum value of d_{33} 215 pC/N was achieved for pure KNNL-6 ceramics at sintering temperature of 1000 °C for 2 h. From Fig. 4, with addition of nano particle sintering aids, the piezoelectric coefficient d_{33} of pure $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ ceramics

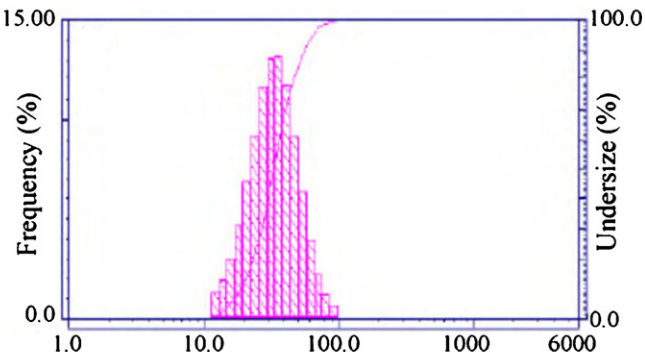

Fig. 1. Particle size distribution of nano size ZnO powder.

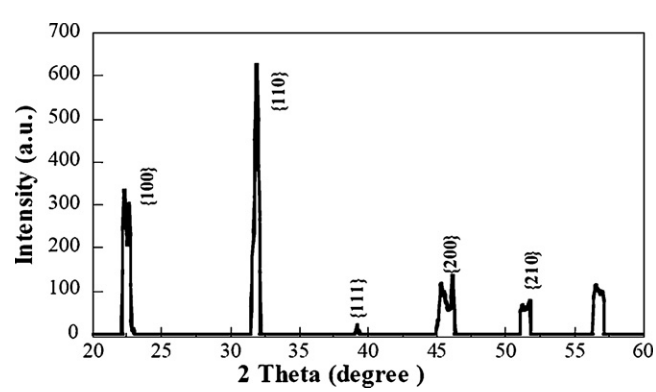

Fig. 2. X-ray diffraction pattern of $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ calcined powder at 850 °C for 4 h.

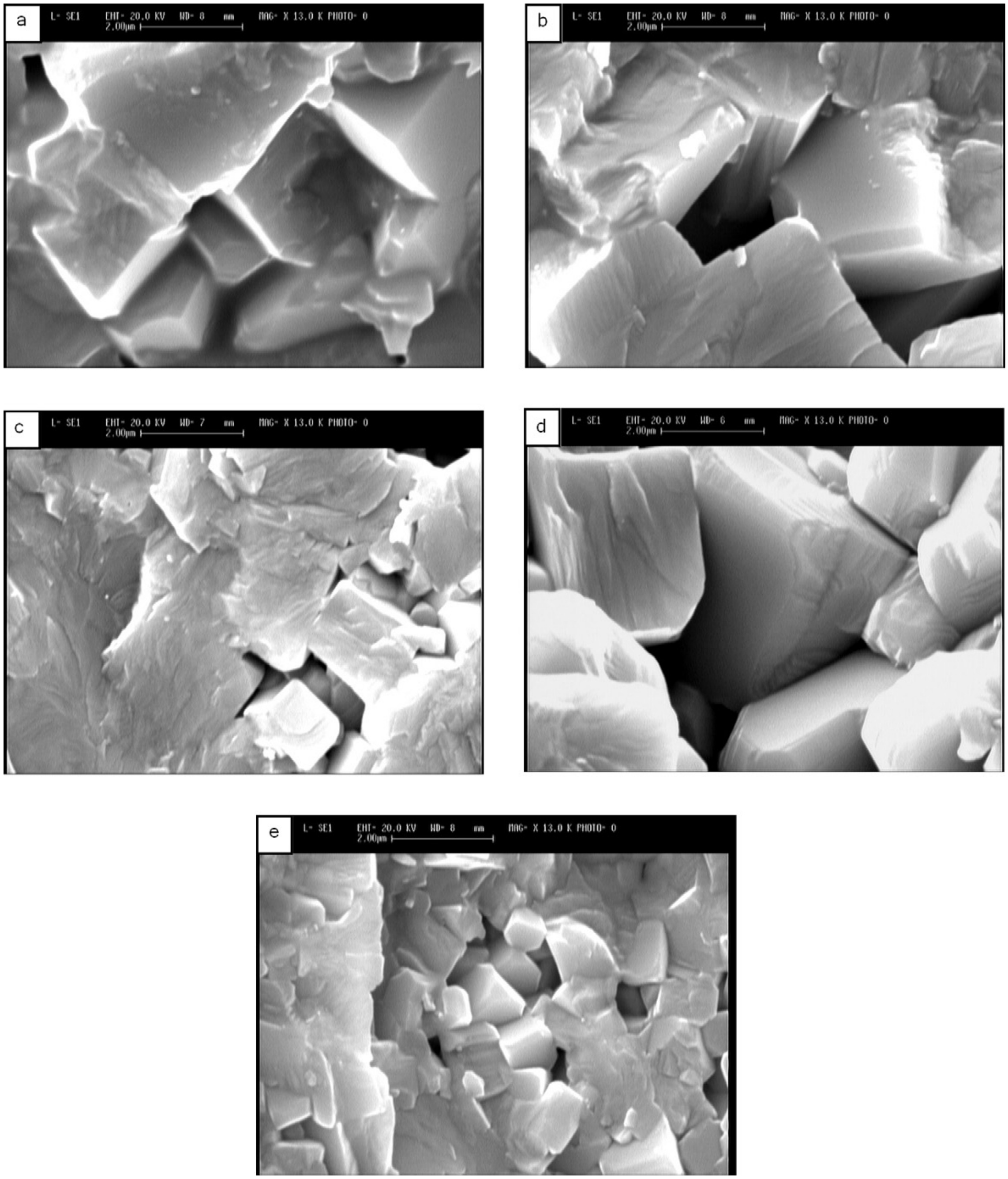

Fig. 3. SEM images of fracture surface of $(K_{0.5}Na_{0.5})_{0.94}Li_{0.06}NbO_3$ + 0.4 mol% nano particles ceramics sintered at 1060 °C for 2 h: (a) pure, (b) nano CuO, (c) nano SnO_2, (d) nano ZnO, (e) nano ZnO + nano SnO_2.

decreased. The nano particles-added to KNN would not only act as a sintering aid, but some of the ions will enter into the ABO_3 perovskite structure. Because the ionic size of Sn^{4+} (0.71 Å), Zn^{2+} (0.74 Å) and Cu^{2+} (0.73 Å) are similar to that of Nb^{5+} (0.69 Å), this implies that Sn^{4+} should occupy B-site to substitute for Nb^{5+}, which resulted in the formation of oxygen vacancies. The oxygen vacancy may form a defect dipole that can provide a domain pinning effect transforming KNN into a

Table 1
Summary of dielectric and piezoelectric properties of KNNL-6 with 0.4 mol% nano additives sintered at optimum sintering temperature for 2 h.

	Pure @1000 °C	ZnO @1060 °C	CuO @1020 °C	SnO_2 @1000 °C	ZnO + SnO_2 @1000 °C
ε_r (1 kHz)	560	550	578	628	688
tanδ (1 kHz)	0.008	0.013	0.021	0.024	0.018
d_{33} (pC/N)	215	168	152	130	178

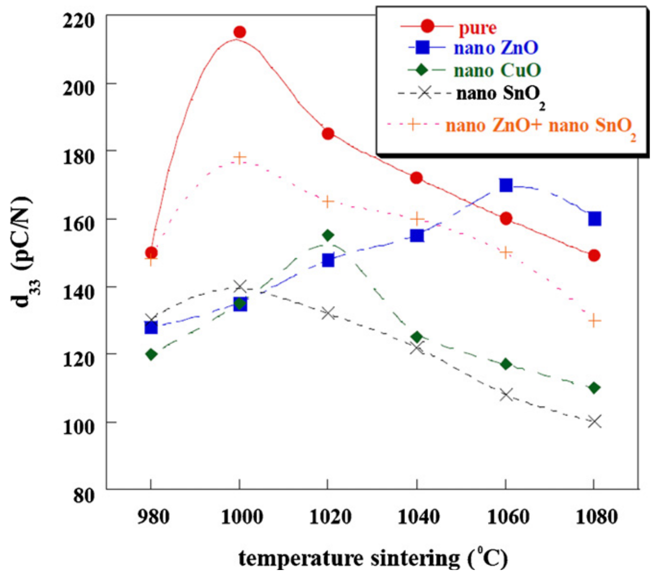

Fig. 4. Dependences of piezoelectric coefficient d_{33} on sintering temperature for $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ ceramics with 0.4 mol% nano additives.

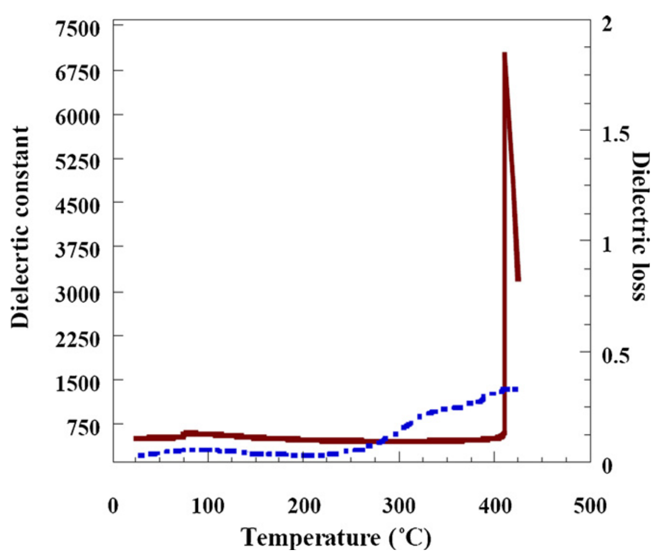

Fig. 5. Dielectric constant and loss tangent at 1 kHz as a function of temperature for KNNL-6 ceramics sintered at 1000 °C for 2 h.

hard piezoelectric ceramic.

$$Nb_{Nb} + 3/2O_o + ZnO \rightarrow Zn_{Nb}''' + 1/2Nb_2O_5 + 1/2V_o^{\bullet\bullet}$$

Table 1 summarizes the data of dielectric and piezoelectric properties of KNNL-6 with 0.4 mol% nano additives ceramics sintered at optimum sintering temperatures for 2 h. Dielectric constant and loss tangent as a function of temperature for the KNNL-6 with 0.4 mol% nano ZnO and 0.4 mol% nano SnO_2 ceramics sintered at 1000 °C for 2 h are shown in Fig. 5. The Curie temperature and phase transition orthorhombic to tetragonal are about 410 °C and 75 °C respectively.

4. Conclusion

$(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ (KNNL-6) piezoelectric ceramics were synthesized by traditional solid state sintering and then the effects of the nano particle additives as the nano scale sintering aids, on the structure and electrical properties were investigated. The optimum dielectric and piezoelectric properties of $\varepsilon_r = 560$, $d_{33} = 215$ pC/N, $\tan\delta = 0.008$ and $T_c = 410$ °C were obtained for pure KNNL-6 that sintered at 1000 °C for 2 h. The results show that with addition of nano particle sintering aids, the piezoelectric coefficient d_{33} of $(K_{050}Na_{0.50})_{0.94}Li_{0.06}NbO_3$ ceramics was decreased. The decrease in piezoelectric charge coefficient could be due to the hardening effect, which lowers the piezoelectric charge.

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