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Preparation and characterization of lead-free $(K_{0.47}Na_{0.51}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ piezoceramic/epoxy composites with 0–3 connectivity

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Abstract

Lead-free $(K_{0.47}Na_{0.51}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ (KNLNT) piezoceramic/epoxy composites with 0–3 connectivity were prepared using cold-pressing. The dielectric and piezoelectric properties of the composites were examined as a function of mean particle size (D) within the range of 27–174 μm at a fixed ceramic content of 85 vol%. The dielectric constant increased with D by the combined effects of increased connectivity and decreased surface-to-volume ratio of ceramics. When $D = 125$ μm, the piezoelectric constant showed a highest value of 44 pC/N that is much greater than those of previous reports on lead-free piezoelectric 0–3 ceramic/polymer composites.

Keywords: B. Composites; C. Piezoelectric properties; C. Dielectric properties; D. Niobates

1. Introduction

Piezoelectric ceramic–polymer composites attract great attention because the importance of biomedical and piezoelectric energy harvesting applications using piezoelectric composites is rapidly increasing [1–3]. The simplest structure of ceramic-polymer composites is the 0–3 type connectivity in which ceramic particles are randomly dispersed in a polymer matrix, whose primary benefit is the simplicity in fabrication of products with various shapes. There have been lots of reports on 0–3 piezoelectric ceramic-polymer composites [4–8], however, most employed Pb-based piezoelectric materials because of their excellent electromechanical properties.

Recently lead-free piezoelectric ceramics are intensively explored for repelling Pb-based ceramics because many countries started to ban harmful elements including Pb in electronic products. Meanwhile there have been limited works on lead-free piezoceramic/polymer composites [9,10] even though intensive and extensive studies have been carried out on the development of new lead-free piezoceramics. Therefore this study investigates lead-free piezoceramic/epoxy composites using a $(K,Na)NbO_3$-based ceramic that is one of the most widely investigated lead-free piezoelectric materials. In particular the effect of particle size on the ferroelectric, dielectric and piezoelectric properties of lead-free piezoceramic/epoxy composites is examined. For comparison, Pb-based piezoceramic/epoxy composites are also prepared and characterized.

2. Experimental

A conventional solid state reaction route was applied to prepare the powders with a composition of $(K_{0.47}Na_{0.51}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ (hereinafter abbreviated as KNLNT). Powders of K_2CO_3 (99.0%), Na_2CO_3 (99.9%), Nb_2O_5 (99.95%), Li_2CO_3 (99.9%), and Ta_2O_5 (99.9%) supplied by Kojundo Chemical, Japan were used as raw materials. The powders were weighed according to the chemical formula, ball-milled for 24 h in anhydrous ethanol, and calcined at 850 °C for 2 h. The calcined powder was added with polyvinyl alcohol as a binder and pressed into circular disks with a diameter of 12 mm at 100 MPa. The green compacts were sintered in a covered alumina crucibles at 1100 °C for 4 h in air. After then the pellets were softly crushed using a mortar and pestle. Crushed powder was classified using stacked standard sieves with apertures of 38, 53, 75, 106, 150, and 180 μm.

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The 0–3 composite was prepared by dispersing 85 vol% KNLNT powder into epoxy resin supplied by Kukdo Chemical, Korea. KNLNT particles, epoxy, and its hardener were blended in methyl-ethyl-ketone (MEK) using a magnetic stirrer until gel-like paste was obtained. After aging, the paste was pressed into circular pellets at 150 MPa. The samples were then lapped to 0.8 mm in thickness and electroded by applying silver paste on both surfaces. The polarization–electric field (*P*–*E*) hysteresis loops were measured using a modified Sawyer–Tower circuit at a frequency of 30 Hz. After poling under a dc field of 5 kV/mm in silicone oil kept at 80 °C for 30 min, the piezoelectric coefficient (d_{33}) was characterized using a Berlincourt d_{33}-meter (IAAS ZJ-2, Beijing, China). The surface microstructure was observed using a field-emission scanning electron microscope (FE-SEM), JEOL, JSM-65OFF, Japan and the crystal structure was analyzed with using an X-ray diffractometer (XRD), RAD III, Rigaku, Japan.

3. Results and discussion

The polished surface FE-SEM micrographs of KNLNT/epoxy composites as a function of aperture size of standard sieves that had been used for classifying the crushed KNLNT powder are displayed in Fig. 1. It is seen that KNLNT particles are uniformly dispersed in epoxy matrix, demonstrating 0–3 connectivity. However, many pores are also observed between ceramic particles and epoxy, which are presumed to correspond to trapped air during the pressing stage because the pore size increases with KNLNT particle size. In case of coarse particles, their rearrangement during pressing seems more difficult, leading to lower densities in green compacts. According to the linear intercept method [11], the average particle size (*D*) of KNLNT ceramics was determined using cross-sectional FE-SEM images with a magnification of 200, in which 89–212 particles were included. The *D* was characterized as (a) 27 μm,

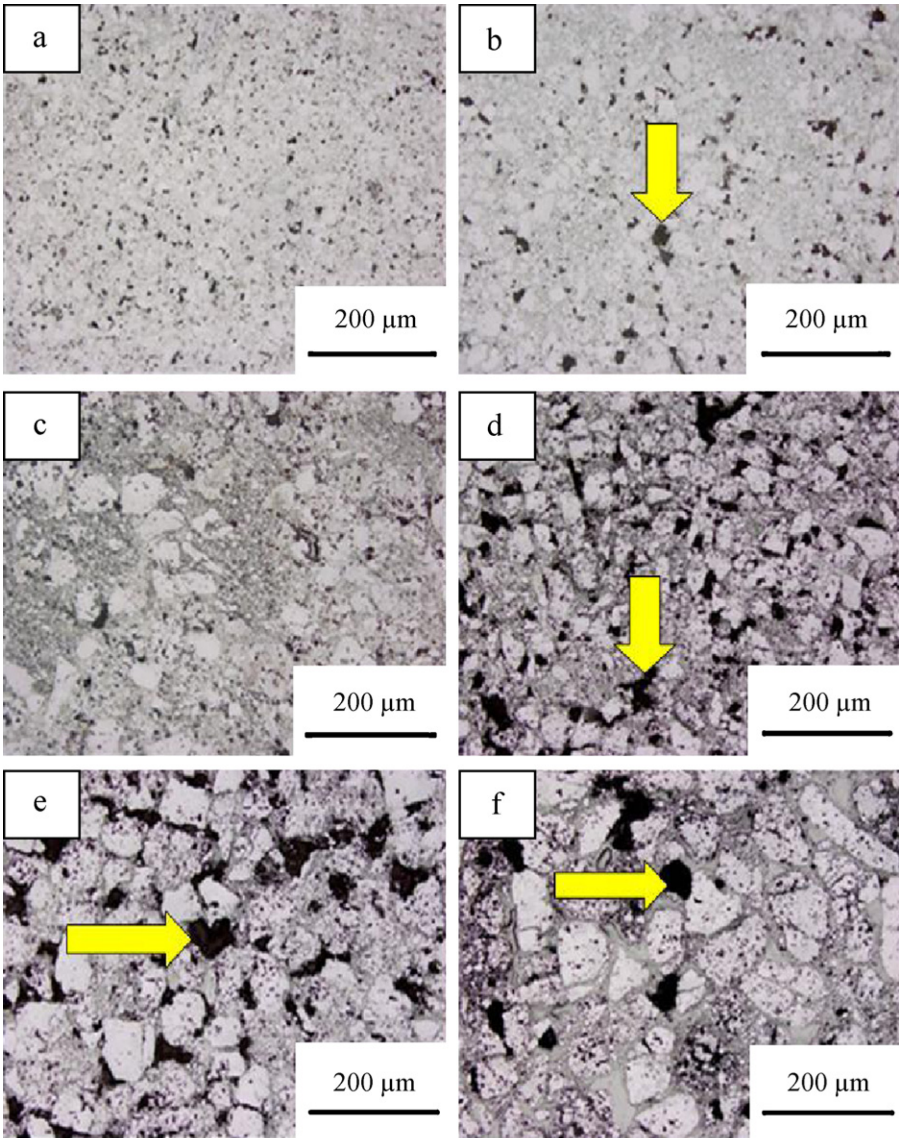

Fig. 1. The polished surface FE-SEM micrographs of KNLNT/epoxy composites. The KNLNT particles were classified using stacked standard sieves with apertures of (a) 38 μm, (b) 53 μm, (c) 75 μm, (d) 106 μm, (e) 150 μm, and (f) 180 μm, respectively.

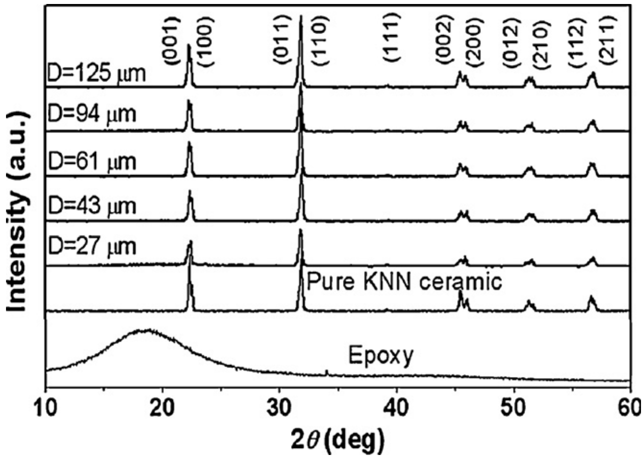

Fig. 2. X-ray diffraction patterns of KNLNT/epoxy composites for different mean particle sizes.

(b) 43 µm, (c) 61 µm, (d) 94 µm, (e) 125 µm and (f) 174 µm, respectively, in the order of photos arranged in Fig. 1.

XRD patterns of a KNLNT ceramic disk, an epoxy pellet, and KNLNT/epoxy composites are shown in Fig. 2. KNLNT ceramics correspond to a tetragonal perovskite structure like a previous report [12] while epoxy turns out amorphous. All composites reveal a crystalline tetragonal phase without any secondary phase, indicating that there has been little chemical reaction between KNLNT and epoxy matrix.

Fig. 3 represents P–E hysteresis loops of KNLNT/epoxy composites for different ceramic particle sizes. When $D = 27$ µm, the remnant polarization (P_r) and coercive field (E_c) is 9.7 µC/cm^2 and 18.9 kV/cm, respectively. As the D increases up to 125 µm, the P_r reaches a highest value of 12.1 µC/cm^2 while the E_c gradually decreases down to 17.6 kV/cm. This tendency is similar to the following D dependence of d_{33} and will be discussed later again.

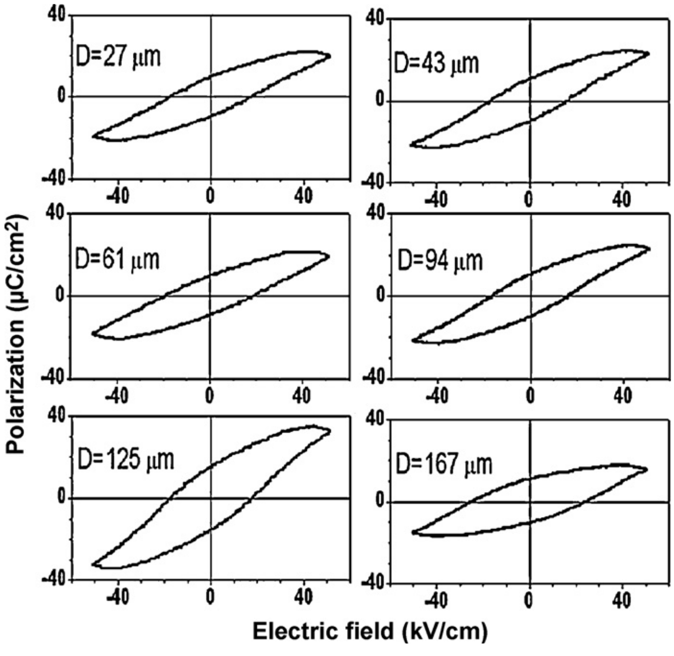

Fig. 3. P–E loops of KNLNT/epoxy composites for different mean particle sizes.

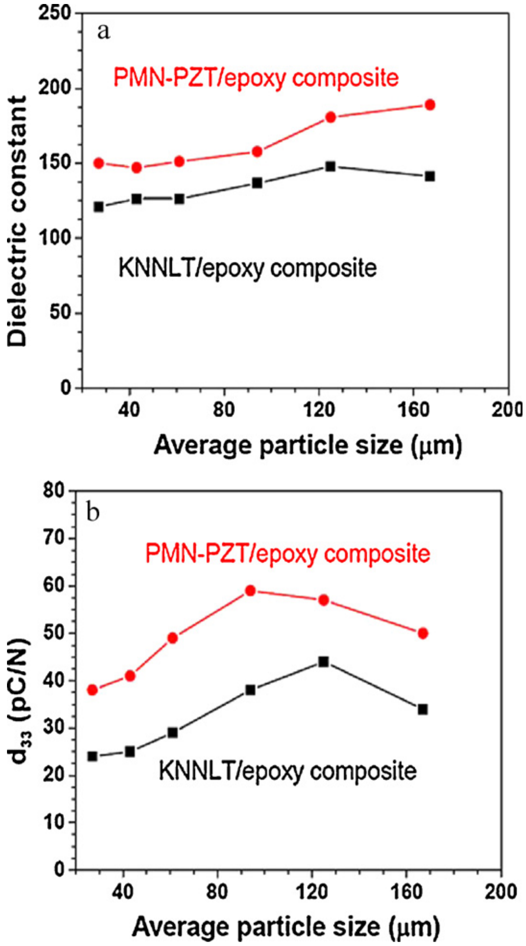

Fig. 4. Particle size dependence of (a) relative dielectric constant and (b) piezoelectric constant d_{33} of KNLNT/epoxy composites.

Fig. 4 reveals the dielectric and piezoelectric constants, ε_r and d_{33}, of KNLNT/epoxy composites as a function of D of KNLNT particles, whose ε_r and d_{33} are measured as 545 and 135 pC/N, respectively. For comparison, the data for Pb-based piezoceramic/epoxy composites are displayed together, which were prepared using Li-doped $0.2Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.8Pb(Zr_{0.475}Ti_{0.525})O_3$ (PMN–PZT) whose detailed properties were reported in a previous article [13]. The ε_r and d_{33} of PMN–PZT ceramics are 1520 and 450 pC/N, respectively. It can be seen that the ε_r increases with the ceramic particle size for both lead-based and lead-free composites similarly to other previous reports on 0–3 piezoelectric composites [8,14,15]. This phenomenon can be explained by the decreased surface-to-volume ratio and/or the increased connectivity between ceramics with increasing particle size. A very recent theoretical approach [16] also demonstrated that ε_r increases with ceramic connectivity in a piezoelectric ceramic–polymer composite. In our system, the enhancement in the connectivity with D was also observed in the FE-SEM micrographs given in Fig. 1.

On the other hand, the particle size dependence of d_{33} shows a peak like P_r when $D = 94$–125 µm for both lead-free and Pb-based particles, as can be seen in Fig. 4(b). The d_{33} was also reported to be improved by increasing particle size at a given volume fraction of ceramic fillers within $D < 130$ μm for both $BaTiO_3$ [14] and $PbTiO_3$ [15] ceramics. In addition it is generally known that both the piezoelectric constants and P_r are strongly dependent on the domain reorientation during poling. In our case, the domain reorientation in piezoelectric particles at the poling step appears to be also enhanced with an increase in D because of the improved connectivity. When $D > 125$ μm, however, the poling field cannot be sufficiently elevated because of the reduced breakdown voltage that is probably due to the pores [17,18] trapped between larger particles as represented in Fig. 1. It should be mentioned that the highest d_{33} value of 44 pC/N obtained in this work for KNN-based piezoelectric composites is quite higher than those reported on other lead-free piezoelectric ones [9,14], which all are lower than 32 pC/N although a recent work reported a very high d_{33} of 155 pC/N in 1–3 lead-free composites. [10]

4. Conclusions

Lead-free KNLNT ceramic/epoxy composites with 0–3 connectivity were successfully prepared using cold-pressing. It was found that the mean particle size of piezoelectric ceramics greatly influence on their dielectric and piezoelectric properties. When $D = 125$ μm, the piezoelectric constant showed a maximum value of 44 pC/N, which is much higher than those previously reported on lead-free piezoelectric 0–3 ceramic/polymer composites.

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