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Piezoelectric and dielectric properties of $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$–PVDF composites

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Abstract

(Li, Ta, Sb) modified sodium potassium niobate/poly(vinylidene fluoride) [$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$–PVDF] 0-3 composites were prepared by a cold press technique, and their piezoelectric and dielectric properties were characterized. All composites exhibited good dispersion of ceramic particles in the polymer matrix. The piezoelectric and dielectric constants were found to be enhanced as the concentration of sodium potassium niobate increases. Even though the process is simple, the composite prepared in this study showed better piezoelectric and dielectric properties than PZT–polymer composites. At room temperature, a $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$–PVDF (7:3) composite revealed a relative dielectric constant, $\varepsilon_r = 166$, piezoelectric constant, $d_{33} = 33$ pC/N and coercive field, $E_c = 5$ kV/cm.

Keywords: A. Pressing; B. Composites; C. Piezoelectric properties; D. Niobates

1. Introduction

Piezoelectric ceramic–polymer composites are promising materials for transducer applications, and they are widely used in high-pressure sensors, energy harvesting device, underwater hydrophones, biomedical imaging with ultrasound, and nondestructive testing applications [1–10]. The study of $Pb(Zr,Ti)O_3$ (PZT) ferroelectric ceramics and the ferroelectric polymer(such as PVDF (polyvinylidene fluoride)) were much reported on their piezoelectric, dielectric and pyroelectric properties [11–18]. However, the high volatilization of PbO as a main component of PZT ceramics during firing and disposal of PbO contaminating materials cause severe environmental pollution. Therefore, it is desired to use lead-free materials for environmental and safety concerns with respect to the utilization, recycling, and disposal of lead-based piezoelectric ceramics. Among various materials, $(K_{1-x}Na_x)NbO_3$ (KNN) has been considered as one of the most promising candidates for lead-free piezoelectric ceramics since Saito et al. [19] obtained remarkably high d_{33} values of about 300 and 416 pC/N with a $(Na_{0.52}K_{0.44}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ (abbreviated as KNNLST) ceramic and textured one, respectively [19].

The simplest ceramic–polymer composite is a structure in which ceramic particles randomly dispersed in a polymer matrix, which is well known as 0-3 connectivity. The critical factor in the 0-3 composite is to ensure homogeneous distribution of the filler in the matrix. In this study, we prepared piezoelectric polymer–ceramic composites using KNN ceramics modified with Li, Ta, and Sb in order to examine their feasibility for energy harvesting applications. In particular, their figure of merit as an energy harvesting device was studied as a function of the volume fraction of ceramics in the composite.

2. Experimental

$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ ceramic powder was synthesized using conventional solid-state reaction. The starting materials were powders of Na_2CO_3 (99.0%), K_2CO_3 (99.0%), Ta_2O_5 (99.9%), Nb_2O_5 (99.9%), Li_2CO_3 (99.0%) and Sb_2O_5 (99.9%) supplied by Kojundo Chemical, Japan. The mixed powder was weighed according to the chemical formula

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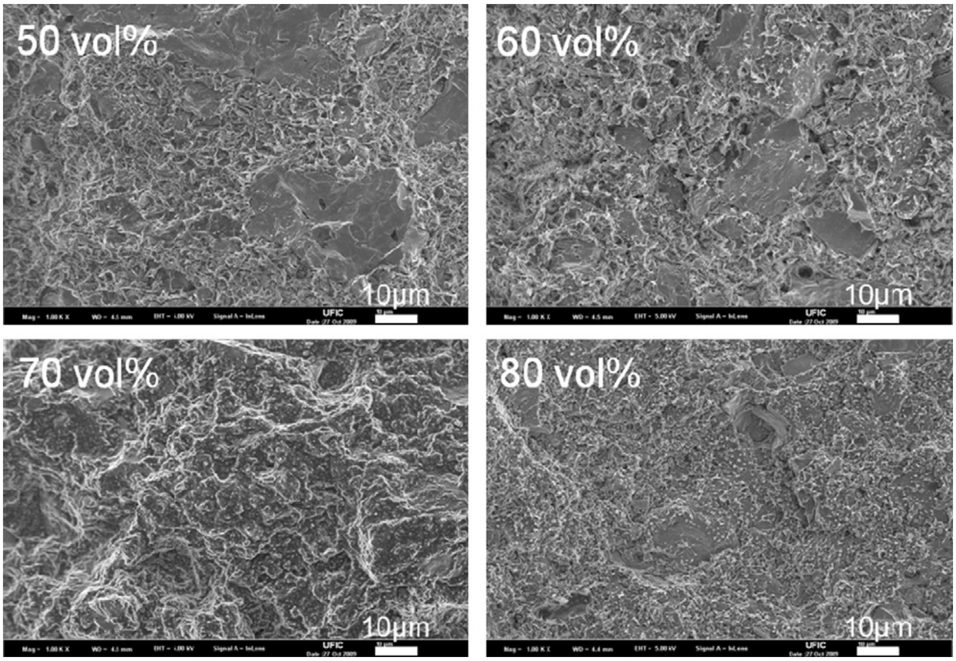

Fig. 1. SEM micrographs of KNNLST–PVDF composite for different volume fractions of ceramics.

and calcined at 850 °C for 5 h in air. After calcinations, the calcined powder was sintered at 1090 °C for 3 h. PVDF of average molecular weight 534,000 was used in this study. Fine PVDF powder and piezoelectric ceramic particles added 3-aminopropyltriethoxysilane as a coupling agent was blended using a planetary mill at 300 rpm for 3 h. At this step, the volume fraction of ceramics was varied from 40 vol.% to 80 vol.%. The mixture powder was cold-pressed to disk pellets at 100 MPa and fired at 200 °C for 2 h. Sliver paste was applied on both sides of a specimen as electrodes and dried at 100 °C for 1 h. The samples were poled in a silicon oil bath kept at 120 °C under a DC electric field of 5 kV/mm for 30 min. After aging for 24 h, the bulk density was measured according to the Archimedes principle. The dielectric properties were examined using an Agilent 4294A impedance analyzer and the piezoelectric constant d_{33} was measured with a quasi-static d_{33}-meter (PM-100, Piezotest, UK). The crystal structure and microstructure were analyzed with an X-ray diffractometer (XRD, D/MAX 2500-V/PC, Rigaku, Japan) and a field emission scanning electron microscope (FE-SEM, Supra 40, Zeiss, Germany).

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the SEM micrographs of fractured surface of KNNLST–PVDF composites with various ceramic volume fractions. All the micrographs reveal that the ceramic powders are well dispersed in the polymer matrix without obvious agglomeration, and the ceramic particles are surrounded by the polymer matrix. In other words, the ceramic particles are unconnected, that is, ‘0-3’ connectivity.

Fig. 2 represents the XRD diffraction patterns for poled specimen of PVDF + xKNNLST (volume fraction, $x = 0$, 0.5, 0.6, 0.7, 0.8 and 1). All specimens demonstrate the absence of any unwanted secondary phase. The pure PVDF and KNNLST specimens showed a typical crystalline polymer and tetragonal perovskite structure, respectively. The peaks of composite specimens become closer to those of pure KNNLST as the ceramic content increases. It is well known that dielectric constant of ferroelectric ceramics is significantly larger than that of the polymer [20]. From this result, it is considered that the sample with much more ceramic content have better piezoelectric and dielectric properties. The overall intensity of (2 0 0)/(0 0 2) peaks of KNNLST ceramics at around 45° increases with the ceramic content. In addition, the intensity ratio of (0 0 2) to (2 0 0) peak, which is proportional to the degree of domain

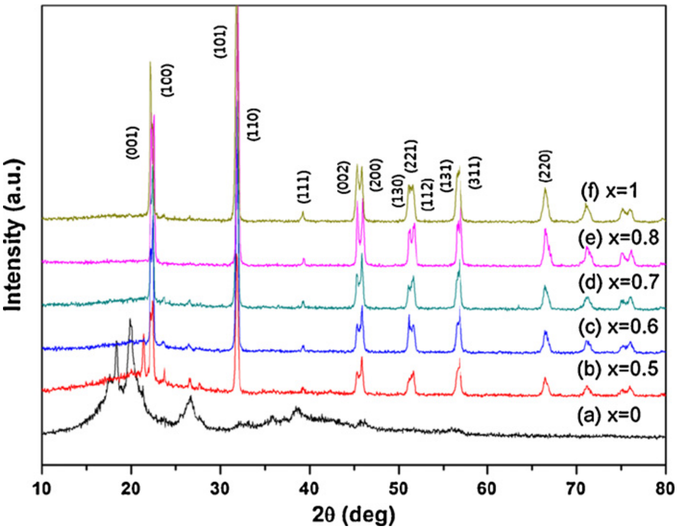

Fig. 2. X-ray diffraction patterns of pure KNNLST ceramics ($x = 1$), PVDF ($x = 0$), and KNNLST–PVDF composites. The volume fraction of ceramics (x) is given on the figure.

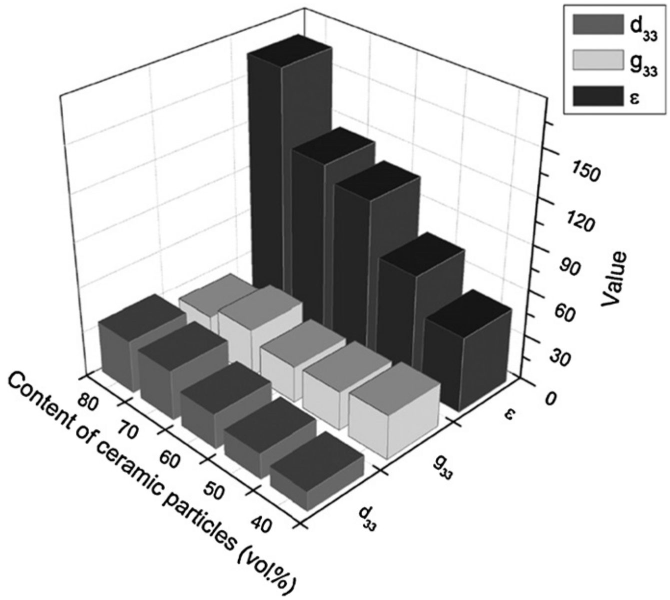

Fig. 3. The piezoelectric and dielectric properties of KNNLST–PVDF composite as a function of the volume fraction of KNNLST particles.

reorientation through poling, increases with the ceramic content possibly due to the increased connectivity of ceramic particles.

3.2. Piezoelectric and dielectric properties

The piezoelectric and dielectric properties as a function of the KNNLST volume fraction are shown in Fig. 3. Many studies report that the dielectric and piezoelectric constant increases with ceramic content in the composite [21–24]. The values of d_{33} and ε increase with the content of KNNLST ceramic in the composite. When the ceramic volume fraction is 80%, both d_{33} and ε reach maximum values of 35 pC/N and 165, respectively. However, when the volume fraction of the KNNLST is over 70%, the mechanical strength of a specimen becomes too weak to be used as flexible devices. All the d_{33} values obtained are comparable to the previous reports for PZT composites of Yamada et al. [17], Satish et al. [15] and Seema [28] who used hot-press and tape casting methods. As the ceramic content increases, the dielectric loss of composites was increased similarly to other previous reports [25,26] on piezoceramic/polymer composites. However, the large scattering in data was found for all specimens except pure KNNLST ceramics. The tan δ values are comparable to those of studies by Fries and Moulson [27] and Nhuapeng and Tunkasiri [18].

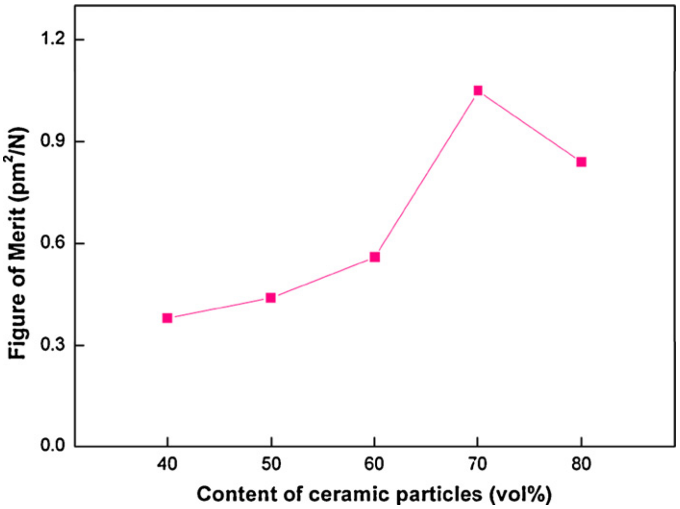

Fig. 4. Figure of merit for energy harvesting application as a function of the volume fraction of KNNLST particles.

Table 1
Physical, piezoelectric and dielectric properties of the KNNLST and KNNLST/PVDF composite.

Ceramic content (vol.%)	Density (g/cm^2)	ε_r	d_{33} (pC/N)	tan δ
40	2.54	50	13	0.02
50	2.78	74	17	0.03
60	3.25	107	23	0.03
70	3.75	117	33	0.07
80	3.47	165	35	0.05
100	4.45	1314	228	0.05

The performance of a piezoelectric material for energy harvesting is expressed as the figure of merit (FOM) like the following equation:

$$\mathrm{FOM}\ (\mathrm{pm^2/N}) = d_{33} \times g_{33} = \frac{(d_{33})^2}{\varepsilon} \qquad (1)$$

Fig. 4 shows the FOM for energy harvesting application as a function of the content of ceramics. The FOM reaches maximum when the volume fraction of ceramics is 70%. This phenomenon can be explained by counteracting effects of density on the d_{33} and ε. As can be seen in Table 1, with increasing the content of ceramics in the composite over 70%, the physical property dependent d_{33} is relatively less increased while the physical property independent ε is enhanced regardless of the density that shows a decrease at higher volume fraction of KNNLST probably due to poorer dispersion or larger trapping of air during blending.

4. Conclusions

Lead-free $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$–PVDF piezoelectric composites were prepared by a cold press technique and their microstructure, dielectric, and piezoelectric properties were characterized. Despite of simple fabrication processes, well-dispersed composites were obtained in this work. The piezoelectric and dielectric constants were found to increase with the concentration of sodium potassium niobate in the composite. However, the mechanical strength drastically degraded when the content of ceramic particles was elevated over 70% because of the lack of polymer matrix. It was found that the highest figure of merit for energy harvesting was obtained when the content of ceramics reached 70 vol.%.

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