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LETTER

Effect of elemental diffusion on temperature coefficient of piezoelectric properties in KNN-based lead-free composites

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Wide range of lead-free piezoelectric ceramic compositions have been investigated in order to replace (Pb,Zr)TiO_3 (PZT) owing to the concerns of environmental pollution. Among these reported lead-free compositions, $(K_{0.5}Na_{0.5})NbO_3$ (KNN) based ceramics have emerged as one of the promising candidate owing to their excellent piezoelectric properties and high Curie temperature (T_C) [1–14]. However, KNN-based compositions show inferior stability of piezoelectric property as a function of temperature due to the presence of intermediate orthorhombic to tetragonal phase transition [10–14]. Figure 1 shows the variation of electromechanical coupling factor (k_p) and dielectric constant as a function of temperature in KNN-based ceramics. As seen in Fig. 1a, high temperature coefficient of piezoelectric properties can be explained based upon the polymorphic phase transition in KNN-based ceramics. The peaks in k_p and dielectric constant were located at the phase transition temperatures for all the KNN-based compositions. However, by noticing the changes in slope in Fig. 1, we can arrive at the possibility of compensating the trend since the phase transition temperatures shift with solid solution as shown in Fig. 1b. This lead us to the design of new microstructures such as island–matrix structure (type I) and layered structure (type II) as illustrated in Fig. 2a, b. The gradient in color in these figures indicates the effect of elemental diffusion between

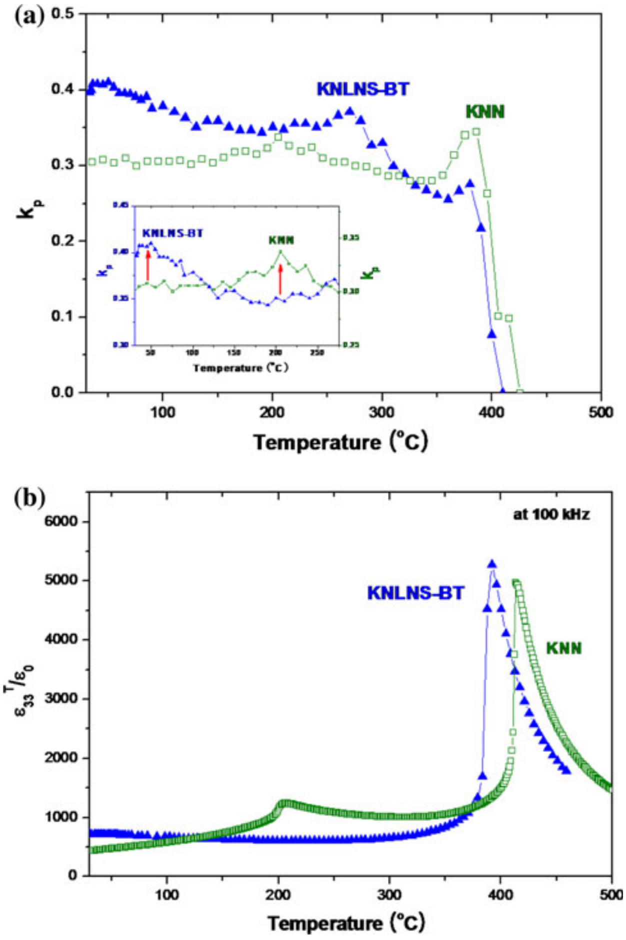

Fig. 1 Variations of **a** k_p and **b** dielectric constant as a function of temperature in KNN-based ceramics [LCR meter (HP model 4284)]

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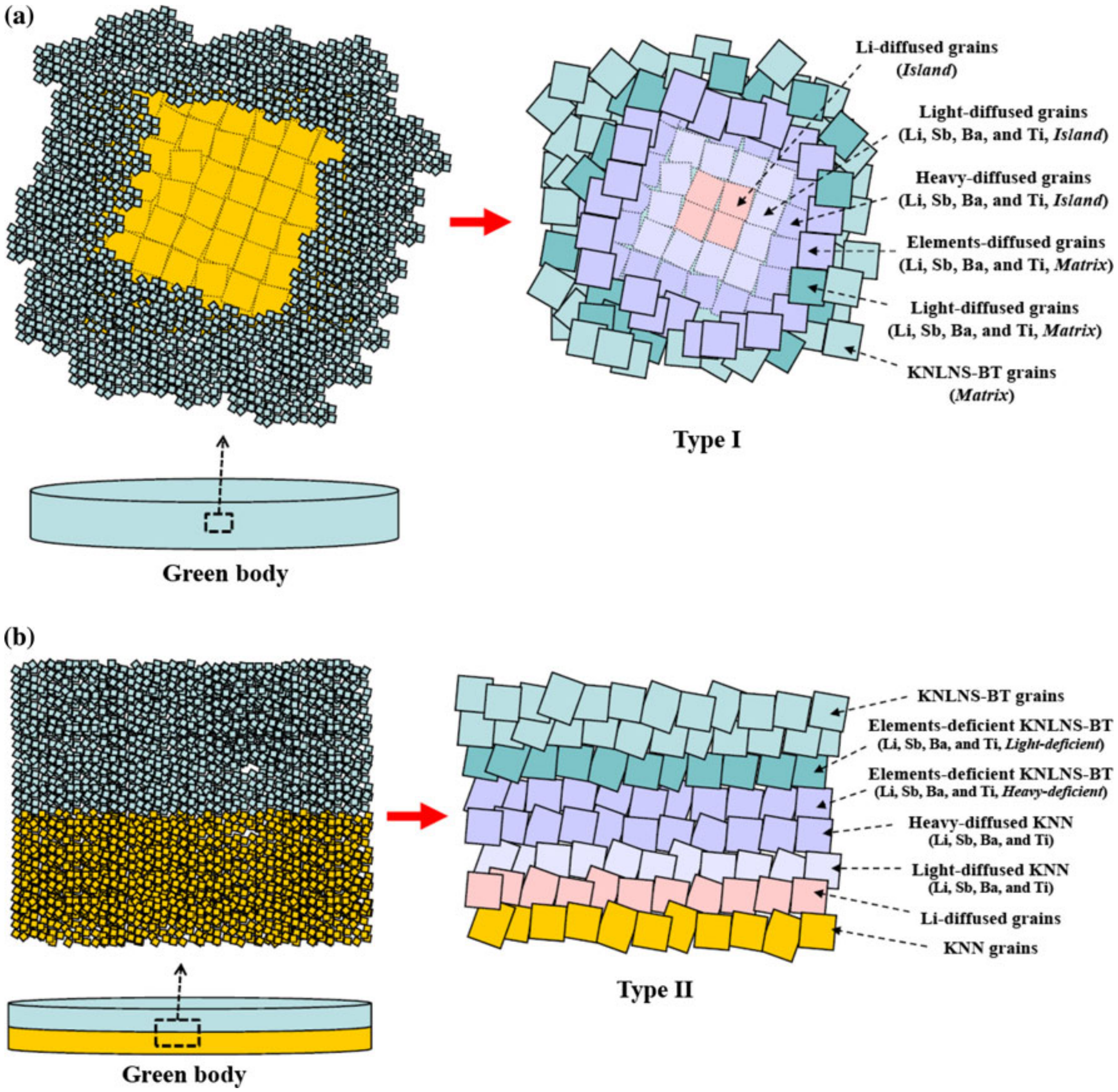

Fig. 2 Schematic diagrams of microstructure formation in **a** island–matrix (type I) and **b** layered structure (type II)

the two phases which occurs during the high temperature sintering.

It can be seen in Fig. 1a that k_p increases with temperature up to 210 °C in pure KNN which corresponds to phase transition point between orthorhombic and tetragonal phases T_{O-T}. In the case of modified KNN compositions a decreasing trend in k_p can be observed in that same range, except that for $(K_{0.48}Na_{0.48}Li_{0.04})NbO_3$ (KNLN) in which case T_{O-T} lies at ~120 °C. The decreasing trend is related to the fact that T_{O-T} for modified compositions lies near room temperature. Using this information, we decided to select the components of our composites as pure KNN and 0.99 $(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.98}Sb_{0.02})O_3$–0.01$BaTiO_3$ [KNLNS–BT]. In type I and II microstructures, these two compositions are expected to compensate the temperature dependence as shown in the inset of Fig. 1a. KNLNS–BT ceramics show one peak close to room temperature while the other is located at ~280 °C as shown in Fig. 1a, thus low temperature coefficient of this composite can be maintained up to 280 °C. This peak of KNLNS–BT might be related to the changes in domain structure as the material approaches para-electric phase from ferroelectric tetragonal phase.

KNN and KNLNS–BT powders were calcined at 950 °C for 3 h and KNN was sintered at 1100 °C for 2 h. Sintered KNN was crushed using mortar and pestle and its particle size was controlled to be in the range of 25–150 μm by sieving. Crushed KNN powders and ball-milled KNLNS–BT powders (~0.2 μm) were mixed in the weight ratio of 0.5/0.5. Both type I and type II structures were pressed into disks under pressure of 100 kgf/cm^2 and sintered at

1060 °C for 2 h. The samples were poled in silicone oil at 120 °C by applying DC field of 4 kV/mm for 60 min. All electrical measurements were done on aged samples (24 h after poling).

Figure 2a, b shows the schematic diagrams of the microstructure indicating the effect of sintering on type I and II composites. The formation of type I and II as predicted in the schematics was confirmed by scanning electron microscopy (SEM, FEI Quanta 600 FEG) on sintered samples as shown in Fig. 3a. This figure shows the microstructure variation of type I specimen as a function of sintering temperature and elemental analysis conducted by using energy dispersive X-Ray Spectrometer (EDX, Bruker QUANTAX 400, high speed Silicon Drifted Detector) as shown in Fig. 3b. The elemental diffusion must be considered in these systems, which is bound to occur due to concentration difference of elements between KNN and KNLNS–BT. The rate of diffusion is given by Fick's law as:

$$\text{Rate of diffusion} \propto \frac{\text{surface area} \times \text{concentration difference}}{\text{distance}}$$

The concentration difference of elements between KNN and KNLNS–BT is listed in Table 1. Among the various

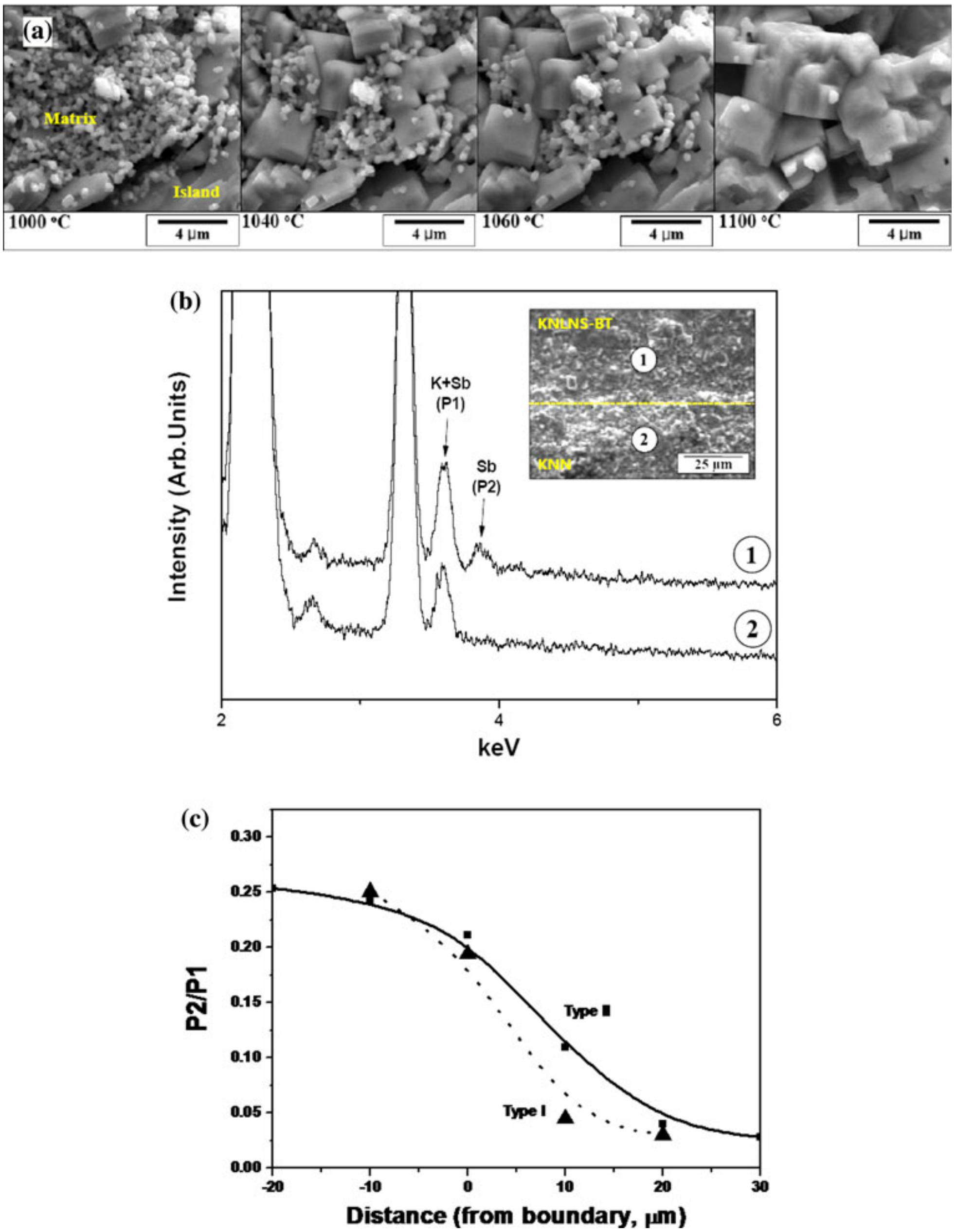

Fig. 3 **a** SEM images of type I as a function of sintering temperature, **b** EDX analysis in type II, and **c** P2/P1 variations with distance from the boundary between KNN and KNLNS–BT grains in type I and II

Table 1 Ionic fractions, radii, and doping effect (on phase transition points) of elements in KNN and KNLNS–BT ceramics: Li ion is smaller than the other ions at A site [15]

	K^+	Na^+	Li^+	Ba^{2+}	Nb^{5+}	Sb^{3+}/Sb^{5+}	Ti^{4+}
Ion fraction							
KNN	0.25	0.25	0	0	0.5	0	0
KNLNS–BT	0.2376	0.2376	0.0198	0.005	0.4851	0.0099	0.005
Difference	0.0124	0.0124	*0.0198*	0.005	0.0149	0.0099	0.005
Ion radius (Å)							
A site (CN = 12)	1.64	1.39	–	1.61			
B site (CN = 6)	(1.38)[a]	(1.02)[a]	*(0.76)*[a]	(1.35)[a]	0.64	0.76/0.60	0.605
Doping effect (in KNN ceramics)							
$T_{O\text{–}T}$			↓	↓		↓	↓
T_C			↑	↓		↓	↓

Italicized value for Li is shown to indicate that it behaves differently than other dopants in KNN

[a] Ionic radii of A site at CN = 6 (for the comparison of ions size)

elements present in these compositions, Li-ion diffusion could have higher rate because of large concentration difference and its small ionic size. Island particles (25–150 μm) have larger size than that of matrix particles (~0.2 μm) in type I composite as shown in Fig. 2a. In type II composite, all the particles have similar particle size of ~0.2 μm as shown in Fig. 2b. Thus, it can be expected that the contact surface area at the interface between KNN and KNLNS–BT particles might be smaller in type I than type II promoting the elemental diffusion. This prediction was confirmed by experiment and results are shown in Fig. 3c. Considering total volume of specimens, the interface area is much larger in type I than that in type II. The elemental diffusion can occur over the whole volume of specimen in type I but it is restricted at the boundary of between KNN and KNLNS–BT layers in type II. The analysis shown in Fig. 3c is approximate due the limitation of SEM-EDS in resolving the elemental concentration but it captures the essential trend.

In order to analyze the effect of elemental diffusion, the variation of piezoelectric properties and dielectric constant as a function of temperature was investigated as shown in Fig. 4. The variation of dielectric constant and k_p for type I is shown in Fig. 4a along with that of individual components. The changes in the dielectric behavior can be easily explained by taking into account elemental diffusion. The Curie temperature (T_C) of KNN was moved from ~410 to ~430 °C [P1 in Fig. 4a], although $T_{O\text{–}T}$ was varied to lower temperature (P3). This indicates the higher diffusion rate for Li-ion as compared to that of the other elements. Table 1 lists the doping effect on transition temperatures in KNN ceramics. Most of the dopants decrease the phase transition point when incorporated in KNN, but Li-ion increases the T_C. The point marked as P2 in this figure shows the variation of $T_{O\text{–}T}$ in KNLNS–BT ceramics. Similar to P1, P2 can be significantly changed by elemental

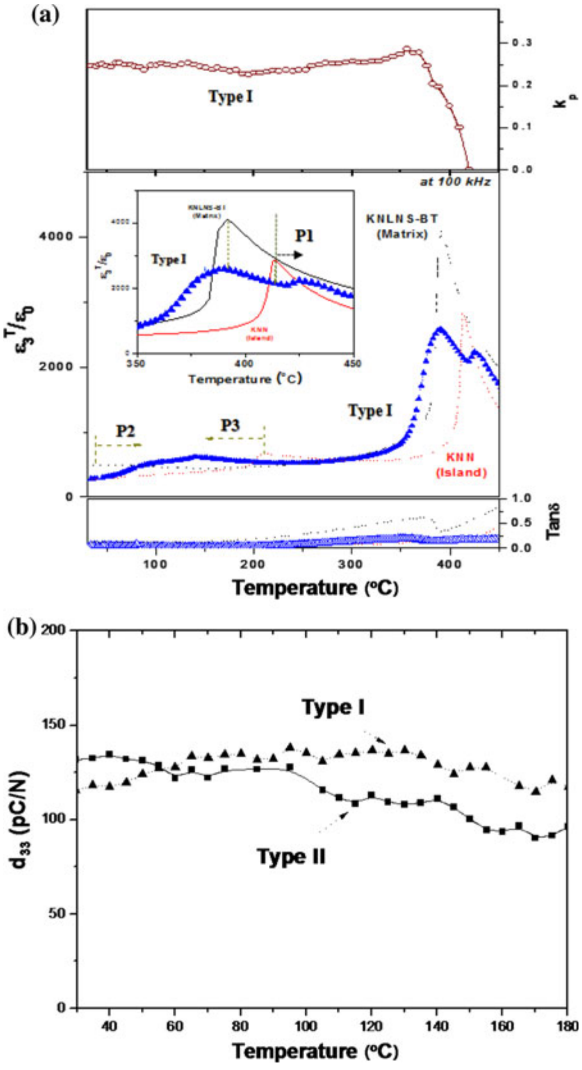

Fig. 4 Variations of **a** k_p, dielectric constant and **b** d_{33} as a function of temperature in type I and II [measurements were conducted using aixPES from aixacct systems GmbH (Aachen, Germany)]

diffusion from matrix in to island. The ions such as Li, Sb, Ba, and Ti diffuse from matrix in to island and this will lead to decrease in P2. These changes in dielectric behavior lead to flat k_p variation with temperature as shown in Fig. 4a. k_p shows almost flat trend up to ~270 °C and is stable up to ~360 °C in type I microstructure.

Figure 4b shows the variation of d_{33} as a function of temperature for both type I and II clearly demonstrating the differences in the behavior of these two microstructures related to changes in the phase transitions. The decreasing slope of piezoelectric property in KNLNS–BT is larger than the increasing one in KNN as shown in Fig. 1a. Hence, the slope of KNLNS–BT must be reduced in order to obtain the flat variation in modified structures. In case of type II, since the elemental diffusion occurs in a narrow region at the interface of two layers, the decreasing trend of d_{33} can be observed in temperature range of 30–180 °C which is similar to that of k_p in Fig. 1a. This indicates that diffusion was not enough to compensate for the changes in slope. On the contrary, type I shows almost flat variation of d_{33} in the temperature range of 30–180 °C as shown in Fig. 4b. This can be explained by the elemental diffusion which occurs over the whole volume of specimen (interface of island and matrix) leading to compensation of slope of KNLNS–BT. The diffusion also results in the broadness of the phase transitions (P2 and P1) as shown in Fig. 4.

In summary, our results demonstrate type I microstructure or "island–matrix" configuration, which can provide flat piezoelectric response up to ~180 °C. The results were explained on the basis of elemental diffusion that occurs at the interface of island and matrix leading to compensation of slopes in piezoelectric properties of individual KNN and KNLNS–BT components.

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