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Letter

Phase transition-induced high electromechanical activity in $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ lead-free ceramic system

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A B S T R A C T

A high electromechanical activity is observed in the $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0, 0.02$, and 0.03) lead-free ceramic system at and around the orthorhombic (O)–tetragonal (T) phase transition temperature (T_{O-T}). This activity is found to originate from an O–T phase transition region at ambient temperature rather than a classical morphotropic phase boundary (MPB) region intrinsic in the $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) lead-based ceramic system. Li modification enables a large decrease in T_{O-T} instead of constituting a classical MPB. In contrast to the nearly temperature-independent classical MPB behavior in the PZT system, the strong temperature-dependent phase transition behavior in the system may impose a challenge to temperature demanding applications.

Traditional piezoelectric ceramic systems, such as $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT), due to the constitution of large amounts of toxic lead (Pb), will be totally restricted from "green" products in the near future from the viewpoint of environmental protection [1,2]. Accordingly, the development of environmentally friendly lead-free ceramic systems has been an urgent demand in the recent decade. Among all the possible lead-free systems, the $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based systems have received the most positive attention because their electromechanical properties can be greatly enhanced using Li and Ta in substitution for K (Na) and Nb, respectively [3–9]. The more general system $(K,Na,Li)(Nb,Ta,Sb)O_3$, which not only can be synthesized by the conventional pressureless solid-state sintering method [6–9], but also possesses high piezoelectric d_{33} values of >300 pC/N in polycrystalline ceramics and >400 pC/N in textured ceramics [10], has been widely accepted as a practicable lead-free replacement for the lead-based systems.

It has been reported that the good electromechanical properties exhibited by the Li- and Ta-modified KNN-based $[(K,Na,Li)(Nb,Ta)O_3]$ lead-free system are related to the existence of a "morphotropic phase boundary" (MPB) between the orthorhombic (O) and tetragonal (T) phases [3–10]. In fact, the classical MPB presented in the PZT lead-based system has a narrow composition region, whereby the coexistence of two different phases (or a transitional phase with lower symmetry such as monoclinic) occurs nearly vertical along the temperature scale and the electromechanical properties at a composition in close proximity to that MPB are nearly temperature independent [11]. Here, it turns to two physically interesting and technologically important questions about whether the recently reported O–T "MPB" in the $(K,Na,Li)(Nb,Ta)O_3$ system is a classical MPB similar to that intrinsic in the PZT system, and whether the high electromechanical activity associated with such O–T "MPB" has temperature stability as good as that with the classical MPB. In this work, we aim to investigate the temperature dependence of electromechanical properties of a representative $(K,Na,Li)(Nb,Ta)O_3$ lead-free piezoelectric ceramic system: $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0, 0.02$, and 0.03) so as to find out the origin of the phase transition behavior, the nature and validity of the recently reported O–T "MPB", and the temperature stability of the electromechanical activity.

$[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0$, 0.02, and 0.03) ceramics were synthesized using a conventional solid-state reaction technique [3,10,11]. The compound with $x = 0.03$ was recently reported to appear near the O–T "MPB" with good electromechanical properties [6,10]. The starting chemicals were K_2CO_3 (99.5%), Na_2CO_3 (99.9%), Li_2CO_3 (99.9%), Nb_2O_5 (99.9%), and Ta_2O_5 (99.9%). The precursor powder was calcined at 900 °C for 2 h in a K_2O- and Na_2O-rich atmosphere, and the pressed pellets were sintered at 1160 °C for 1 h in air. The typical density of the sintered ceramics was determined to be >4300 kg/m^3 using Archimedes' method. The temperature dependence of relative permittivity for the unpoled ceramics was evaluated at 1 kHz using a LCR meter (HIOKI 3532) with a temperature chamber. By immersing the ceramics in a silicon oil bath, they were poled with an electric field of 30 kV/cm at 140 °C for 30 min before being naturally cooled to room temperature under the electric field. The unipolar electrostrain curves of the poled ceramics

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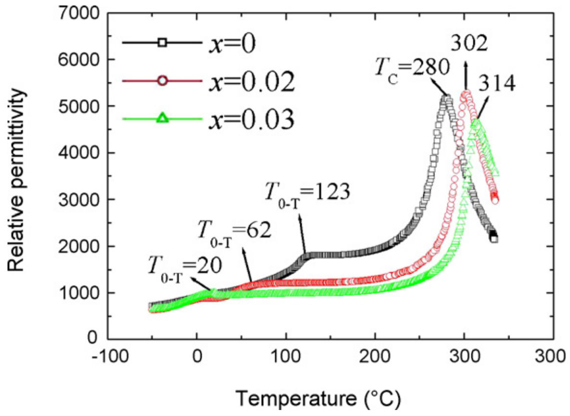

Fig. 1. Temperature dependence of relative permittivity for unpoled $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0$, 0.02, and 0.03) ceramics at 1 kHz.

were measured at 5 Hz using a precision ferroelectric test system (Radiant Workstation) and a photonic displacement sensor (MTI 2000) under different temperatures in a temperature-controlled silicon oil bath. The piezoelectric coefficient (d_{33}) and electromechanical coupling coefficient (k_p) as a function of temperature for the poled ceramics were obtained, respectively, using a d_{33} meter (IOA-CAS ZJ-3A) and an impedance analyzer (Agilent 4294A), both with a temperature chamber.

Fig. 1 shows the temperature dependence of relative permittivity for the unpoled $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0$, 0.02, and 0.03) ceramics at 1 kHz. For the ceramics without Li modification ($x = 0$): $(K_{0.5}Na_{0.5})(Nb_{0.8}Ta_{0.2})O_3$, two obvious dielectric peaks, which correspond to the phase transitions from O to T at $T_{O-T} = 200$ °C and from T to C (cubic) at $T_C = 420$ °C in KNN ceramics [3], are found to appear at much lower temperatures of 123 and 280 °C, respectively. By increasing the Li content ($x = 0.02$ and 0.03), T_{O-T} shifts downward to the lower temperature side, while T_C shifts upward to the higher temperature side. It is noted that T_{O-T} of the $[(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}](Nb_{0.8}Ta_{0.2})O_3$ ceramics ($x = 0.03$) has undergone significant downward shifts to around room temperature of 20 °C in comparison with the $(K_{0.5}Na_{0.5})(Nb_{0.8}Ta_{0.2})O_3$ ceramics ($x = 0$) of 123 °C and the $[(K_{0.5}Na_{0.5})_{0.98}Li_{0.02}](Nb_{0.8}Ta_{0.2})O_3$ ceramics ($x = 0.02$) of 62 °C.

Fig. 2(a)–(c) illustrates the unipolar electrostrain curves at 5 Hz for the poled $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0$, 0.02, and 0.03) ceramics at different temperatures of 0–160 °C, whereas Fig. 2(d) summarizes the variations of the maximum strain at 30 kV/mm with temperature for the ceramics in Fig. 2(a)–(c). For the $(K_{0.5}Na_{0.5})(Nb_{0.8}Ta_{0.2})O_3$ ($x = 0$) ceramics, the maximum electrostrain of 0.12% at 30 kV/cm is obtained at 120 °C [Fig. 2(a) and (d)]. This temperature is referred to $T_{O-T} = 123$ °C in Fig. 1, and a slight deviation from this T_{O-T} leads to a large reduction in the electrostrain values [Fig. 2(a) and (d)]. For the $[(K_{0.5}Na_{0.5})_{0.98}Li_{0.02}](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0.02$) ceramics, a reduced maximum electrostrain of 0.11% at 30 kV/cm is observed at their T_{O-T} of 60 °C [Fig. 2(b) and (d)]. Away from this T_{O-T}, the electrostrain values decrease rapidly. For the $[(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0.03$) ceramics near the recently reported O–T "MPB", a further reduced maximum electrostrain of 0.10% at 30 kV/cm is achieved at their T_{O-T} of 20 °C [Fig. 2(c) and (d)]. Similar to the ceramics with $x = 0$ and 0.02, the electrostrain values decrease greatly once the operating temperature is away from this T_{O-T}. The above observations indicate the presence of a highly temperature-dependent electromechanical behavior at and around T_{O-T}, besides a common mechanism of temperature impact, in our $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ceramics.

Fig. 3 plots the piezoelectric coefficient (d_{33}) and electromechanical coupling coefficient (k_p) as a function of temperature for the poled $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0$, 0.02, and 0.03) ceramics, together with the corresponding d_{33} and k_p values associated with the classical MPBs for the $Pb(Zr_{0.525}Ti_{0.475})O_3$ [12] and $Pb(Zr_{0.53}Ti_{0.47})O_3$ [11] ceramics, respectively. As shown in Fig. 3(a), d_{33} in $(K_{0.5}Na_{0.5})(Nb_{0.8}Ta_{0.2})O_3$ ($x = 0$) ceramics increases gradually from 152 pC/N at 0 °C to 264 pC/N at 120 °(T_{O-T}) and then decreases sharply with increasing temperature to 160 °C. For the $[(K_{0.5}Na_{0.5})_{0.98}Li_{0.02}](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0.02$) ceramics, d_{33} increases relatively rapidly from 182 pC/N at 0 °C to 247 pC/N at 60 °C (T_{O-T}) and then decreases with increasing temperature. For the $[(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}](Nb_{0.8}Ta_{0.2})O_3$ ($x = 0.03$) ceramics near the recently reported O–T "MPB", d_{33} undergoes an increasing and decreasing tend not only similar to the ceramics with

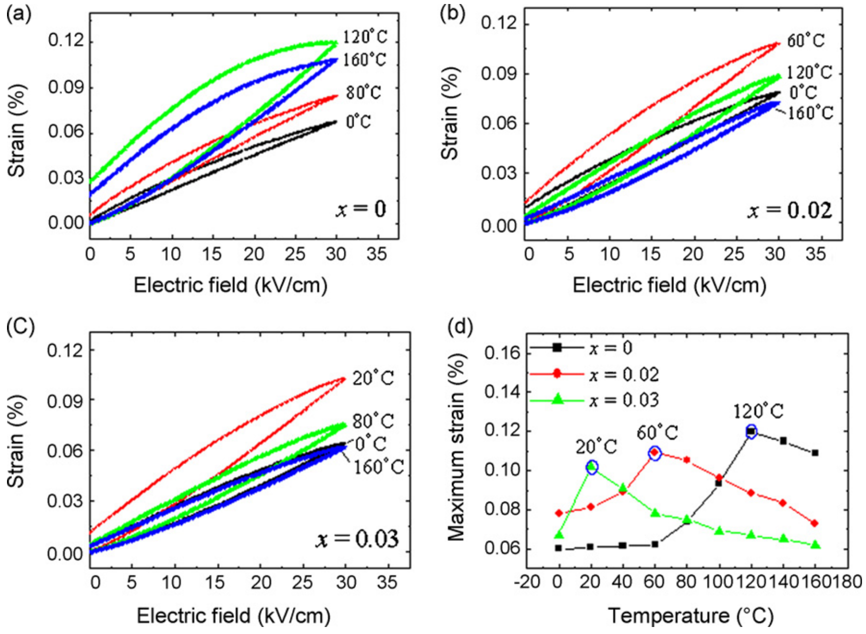

Fig. 2. Unipolar electrostrain curves at 5 Hz for poled $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ceramics with (a) $x = 0$, (b) $x = 0.02$, and (c) $x = 0.03$ at different temperatures of 0–160 °C. (d) Variations of the maximum strain at 30 kV/mm with temperature for the ceramics in (a)–(c).

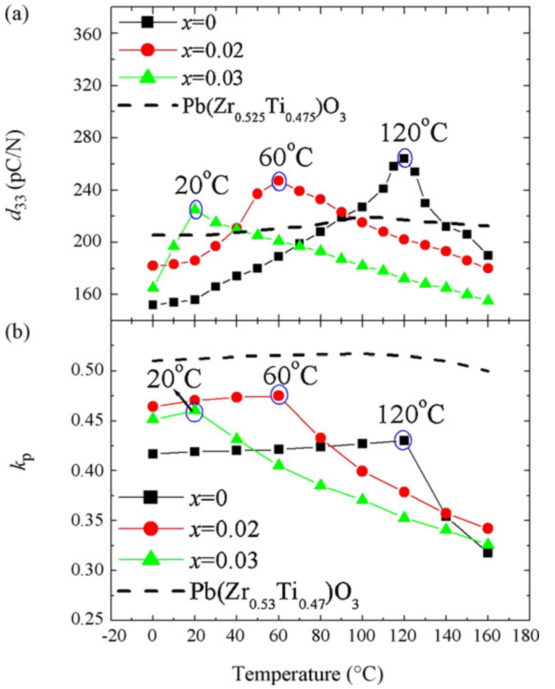

Fig. 3. (a) Piezoelectric coefficient (d_{33}) and (b) electromechanical coupling coefficient (k_p) as a function of temperature for poled $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ (x = 0, 0.02, and 0.03) ceramics, together with the corresponding d_{33} and k_p values associated with the classical MPBs for $Pb(Zr_{0.525}Ti_{0.475})O_3$ [12] and $Pb(Zr_{0.53}Ti_{0.47})O_3$ [11] ceramics, respectively.

x = 0 and 0.02 but also exhibiting the largest d_{33} of 225 pC/N at 20 °C (T_{O-T}). The temperature dependence of d_{33} exhibits similar quantitative trends to the temperature dependence of the unipolar electrostrain as shown in Fig. 2(d), suggesting that d_{33} of our $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ceramics near the recently reported O–T "MPB" depends strongly on temperature. The d_{33} result is essentially different from that of the classical MPB for the PZT system where d_{33} is almost independent of temperature as included in Fig. 3(a) for $Pb(Zr_{0.525}Ti_{0.475})O_3$ [12].

Referring to Fig. 3(b), k_p in the poled $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ceramics with x = 0 and 0.02 increases slightly with increasing temperature, reaches their maximum values of 0.43 and 0.48 at their respective T_{O-T} of 120 and 60 °C, respectively, and then decreases rapidly with increasing temperature. For the $[(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}](Nb_{0.8}Ta_{0.2})O_3$ (x = 0.03) ceramics near the recently reported O–T "MPB", a similarly large variation in k_p with temperature is also observed. Although its k_p can reach a quite high value of 0.46 at its T_{O-T} of 20 °C, k_p indeed decreases rapidly with increasing temperature above T_{O-T}. This is also very different from the invariance of k_p with temperature in the classical MPB for the PZT system as shown in Fig. 3(b) for $Pb(Zr_{0.53}Ti_{0.47})O_3$ [11].

The above investigation results clearly show that the electromechanical activity (electrostrain, d_{33}, and k_p) in our $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ (x = 0, 0.02, and 0.03) ceramics increases initially, attains the maximum at their respective T_{O-T}, and then decreases with increasing temperature. This characteristic trend can basically be preserved irrespective of the compositions, indicating that the maximization of the electromechanical activity at T_{O-T} is not related to the classical MPB but is attributed to the O–T ferroelectric phase transition instead. In fact, the ferroelectric-related phase transition is capable of providing a greater contribution to high electromechanical activity due to lattice softening in accordance with the PMN–PT and $BaTiO_3$ single crystals [13–16]. Fig. 4 gives the phase diagrams of our $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ ceramic system and the PZT ceramic system, which are constructed from the phase transition temperatures T_{O-T} and T_C of Fig. 1 and the relevant data of Ref. [12], respectively. In Fig. 4(a), an increase in Li modification leads to a shift in T_{O-T} to a lower temperature, but it is unable to constitute a classical MPB like that in the PZT system. It should be noted that the classical MPB for the PZT system represents a narrow composition region with two different phases coexisting nearly vertical along the temperature scale, as illustrated in Fig. 4(b). Therefore, the recently reported O–T "MPB" in the (K,Na,Li)(Nb,Ta)O_3 system is definitely not a classical MPB engaged in the PZT system; it should be an O–T ferroelectric phase transition region at ambient temperature. More recent studies on X-ray diffraction data and Raman scattering spectra of the (K,Na,Li)(Nb,Ta)O_3 system support our findings from microscopic perspectives [17,18]. Away from T_{O-T}, the phase transition and related domain reorientation in the ceramics result in a rapid decrease in their high electromechanical activity, giving rise to strong temperature dependence in general.

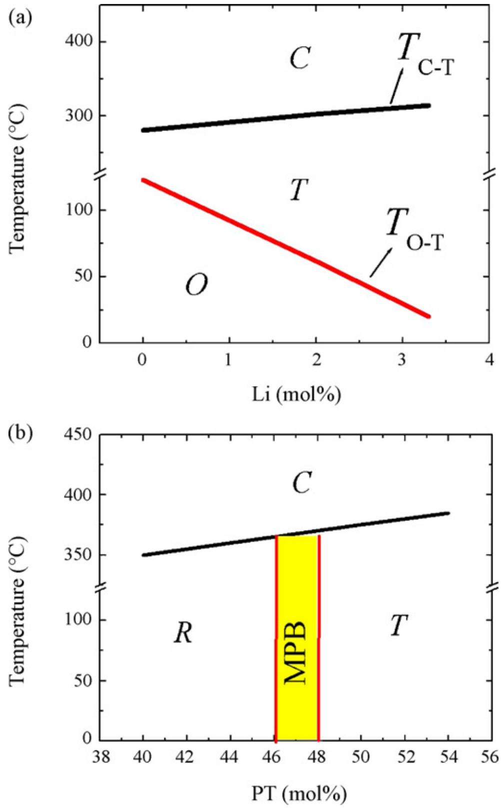

Fig. 4. Phase diagrams of (a) $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ and (b) $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) ceramic systems constructed from the phase transition temperatures T_{O-T} and T_C of Fig. 1 and the relevant data of Ref. [12], respectively. C = cubic, T = tetragonal, O = orthorhombic, and R = rhombohedral.

In conclusion, temperature dependence of electromechanical properties of $[(K_{0.5}Na_{0.5})_{1-x}Li_x](Nb_{0.8}Ta_{0.2})O_3$ (x = 0, 0.02, and 0.03) lead-free ceramics has been investigated. It has been found that the electromechanical activity of the ceramics increases rapidly to the maximum at T_{O-T} as a result of the existence of an O–T phase transition region at ambient temperature in opposition to a classical MPB region as commonly seen in the PZT system. Moreover, Li modification effectively shifts T_{O-T} to lower temperatures, but ineffectively constitutes a classical MPB. The O–T "MPB" as per the recent reports is only an O–T ferroelectric phase transition region at ambient temperature. The strong temperature dependence of electromechanical activity in the ceramics may limit their application viability.

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