Lead-free piezoelectric ceramics vs. PZT?

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Abstract Investigations in the development of lead-free piezoelectric ceramics have recently claimed properties comparable to that of PZT-based materials. In this work, the dielectric and piezoelectric properties of the various systems were contrasted in relation to their respective Curie temperatures. Analogous to PZT, enhanced properties are noted for morphotropic phase boundary (MPB) compositions in the Na,BiTiO$_3$–BaTiO$_3$ and the ternary system with K,BiTiO$_3$, but offer properties significantly lower than that of PZTs. The consequence of a ferroelectric to antiferroelectric transition well below T_C further limits their usefulness. Though comparable with respect to T_C, enhanced properties reported in the K,NaNbO$_3$ family are the result of increased polarizability associated with the $T_{\text{orthor-tetragonal}}$ polymorphic phase transition being compositionally shifted downward and not from a MPB as widely reported. As expected, the properties are strongly temperature dependent unlike that observed for MPB systems.

Keywords Piezoelectric · Lead-free ceramic · PZT

1 Introduction

In the past, innovations in actuators and ultrasonic transducers have been the driving force for new developments in piezoelectric ceramics. Currently, the driving force is the result of environmental regulations [1]; hence, an enormous insurgence in the compositional development of lead-free piezoelectric materials.

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Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) and related compositions have been the mainstay for high performance actuators and transducers, owing to their superior dielectric, piezoelectric, and electromechanical coupling coefficients. Compositionally, PZT ceramics lie near a morphotropic phase boundary (MPB) separating tetragonal and rhombohedral phases, at ∼ x=0.48 PT, shown in Fig. 1. MPB compositions have anomalously high dielectric and piezoelectric properties as a result of enhanced polarizability arising from the coupling between two equivalent energy states, i.e., the tetragonal and rhombohedral phases, allowing optimum domain reorientation during the poling process. Further modifications using acceptor and donor dopants give us the wide range of piezoelectric compositions we have today. Excellent reviews on piezoelectric ceramics, including both modified and undoped PZT ceramics, are given by Jaffe et al. [2, 3], and Herbert et al. [4, 5].

Recently, lead-free based piezoelectrics have been reported to offer comparable properties to that of PZT ceramics, making them viable candidates for various applications [6–27]. In this paper, we present an overview of the current developments in lead-free piezoelectric ceramics and contrast them to lead-based perovskite materials. Specifically, we discuss the "origin" of the enhanced properties reported in relation to their underlying crystallographic structure relationships, i.e. polymorphic and morphotropic phase boundaries.

2 Background on piezoelectric ceramics

Among the important material parameters for piezoelectric ceramics, electromechanical coupling (k_{ij}), dielectric constant (K), or relative permittivity $\varepsilon/\varepsilon_0$, and associated piezoelectric coefficients (d_{ij}) are key parameters. In
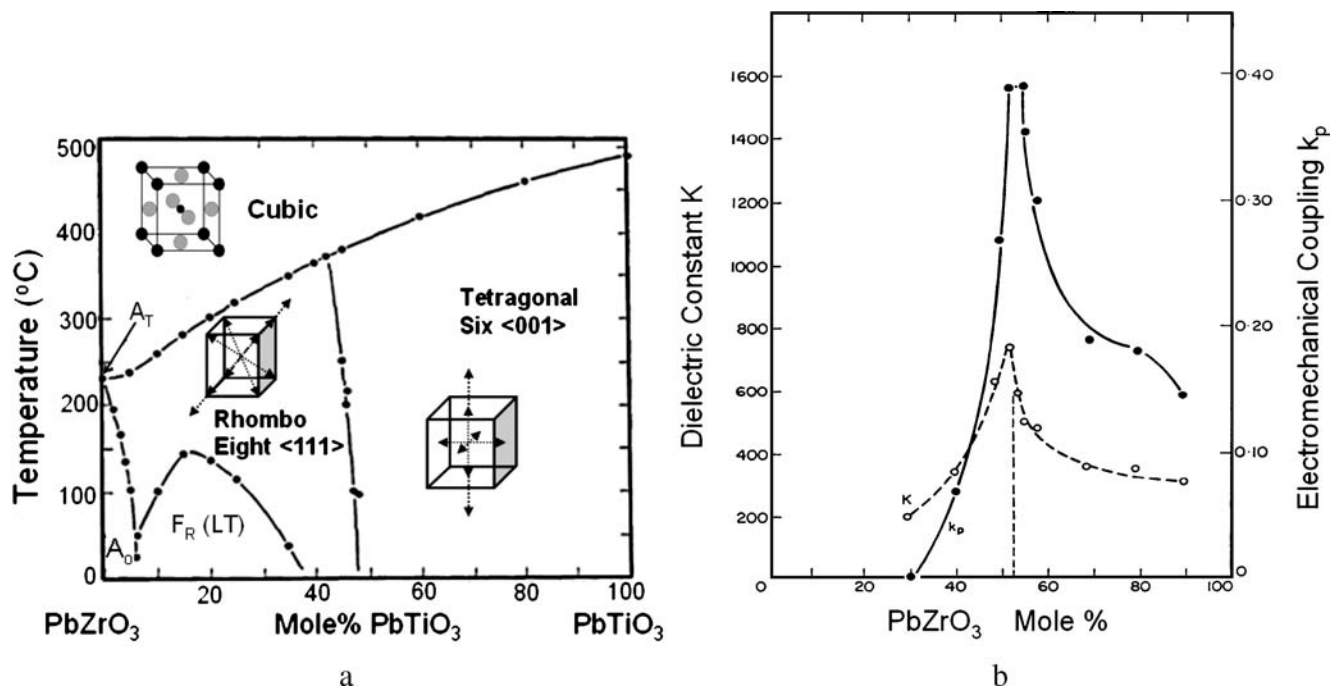
Fig. 1 Morphotropic phase boundary and enhanced dielectric and piezoelectric properties in the Pb(Zr,Ti)O$_3$ system. (after [2, 3]) MPB is defined as an abrupt structural change within a solid solution with composition. *Note*: The MPB is nearly temperature independent

general, the piezoelectric properties of a ferroelectric ceramic can be expressed using the simplistic term,

$$d_{ij} \sim 2Q_{ij}K\varepsilon_o P_i \qquad (1)$$

where d_{ij} is the piezoelectric coefficient, P_i the remnant polarization on poling, K the dielectric constant, ε_o the permittivity of free space, and Q_{ij} the electrostriction coefficient. Since both Q_{ij} and P_i exhibit little dependence

Table 1 Dielectric and piezoelectric properties of lead free perovskite piezos "past and present."

Material	$\varepsilon/\varepsilon_0$	Loss	d_{33} (pC/N)	k_p	k_{33}	T_c (°C)	T_{O-T}/T_d (°C)	Ref.
BaTiO$_3$	1,700	0.01	190	0.36	0.5	115	0	[26, 27]
BaTiO$_3$–CaTiO$_3$–Co	1,420	0.005	150	0.31	0.46	105	−45	[26, 28]
(K$_{0.5}$Na$_{0.5}$)NbO$_3$ (HP)	500	0.2	127	0.46	0.6?	420		[30, 31]
(K$_{0.5}$Na$_{0.5}$)NbO$_3$	290	0.4	80	0.35	0.51	420	195	[32]
KNN-Li (7%)	950	0.084	240	0.45	0.64	460	~20	[7]
KNN-Li3%; Ta20%	920	0.024	190	0.46	0.615	310	50	[7]
KNN-LF4*	1,570	/	410	0.61	/	253	25	[6]
KNN-SrTiO$_3$ (5%)	950	/	200	0.37	/	277	27	[8]
KNN-LiTaO$_3$ (5%)	570	0.04	200	0.36	/	430	55	[9]
KNN-LiNbO$_3$ (6%)	500	0.04	235	0.42	0.61	460	70	[10]
KNN-LiSbO$_3$ (5%)	1,288	0.019	283	0.50	/	392	45	[11]
NBT-KBT-LBT	1,550	0.034	216	0.401	/	350	160	[17]
NBT-KBT-BT	820	0.03	145	0.162	0.519	302	224	[34]
NBT-KBT-BT (MPB)	730	0.02	173	0.33	0.59	290	162	[34]
NBT-KBT-BT	770	0.034	183	0.367	0.619	290	100	[22]
SBT-KBT90	870	0.04	110	0.15	0.507	296	/	[unpublished]
SBT-KBT85	1,000	0.05	120	0.16	0.491	250	/	[unpublished]
BBT-KBT90	837	0.05	140	0.23	0.538	297	144	[unpublished]
BBT-KBT80	630	0.04	95	0.15	0.361	290	238	[unpublished]
Sr$_2$NaNb$_5$O$_{15}$*	1,100	/	120	/	/	280	/	[29]

* Textured; T_{O-T}: Orthorhombic to tetragonal phase transition; HP: Hot Pressed;
NBT: (Na$_{0.5}$ Bi$_{0.5}$)TiO$_3$; KBT: (K$_{0.5}$ Bi$_{0.5}$)TiO$_3$; LBT: (Li$_{0.5}$Bi$_{0.5}$)TiO$_3$;
BT: BaTiO$_3$; SBT: (Sr$_{0.7}$Bi$_{0.2}$)TiO$_3$; BBT: (Ba$_{0.7}$Bi$_{0.2}$)TiO$_3$
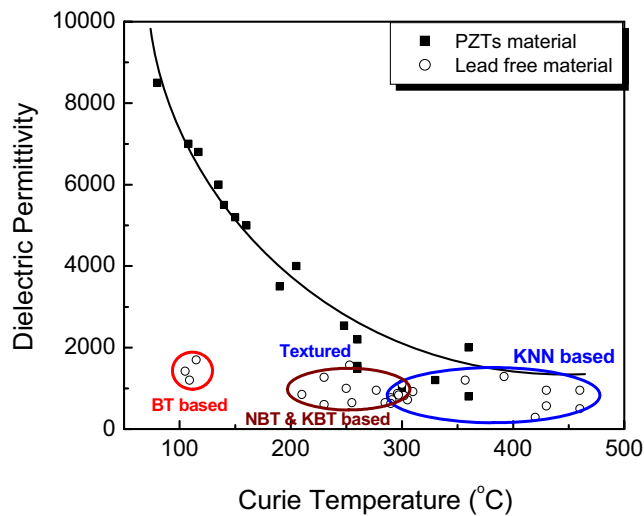
Fig. 2 Room temperature value of ε_r as a function of T_C for various piezoceramics
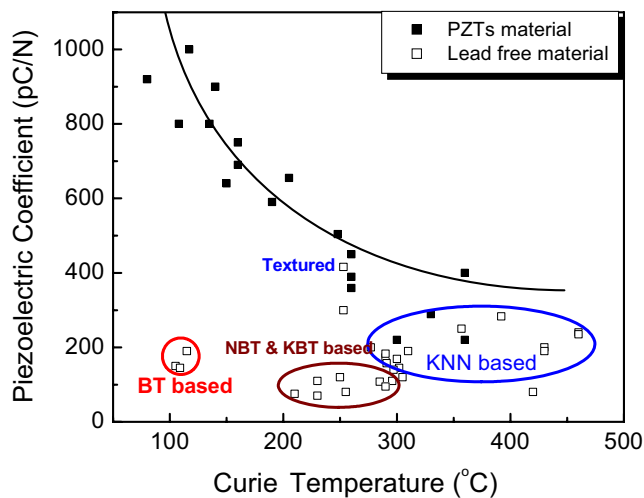
Fig. 3 Room temperature value of d_{33} as a function of T_C for various piezoceramics

on composition or temperature below T_C in ferroelectric ceramics such as PZT, the piezoelectric coefficient d_{ij} and

dielectric constant K are interrelated (i.e., a ceramic with high piezoelectric coefficient also exhibits a large dielectric constant). To achieve a high dielectric constant or piezoelectric coefficient, MPB-based ceramics are further engineered by compositionally adjusting the Curie temperature (T_C) downward relative to room temperature. A reduction in T_C, however, results in more temperature dependent properties and less polarization stability (i.e., aging and loss of piezoelectric activity). As a general rule of thumb, piezoelectric materials can be safely used to approximately one half T_C without significant reduction in piezoelectric activity. Therefore, not only must the dielectric and piezoelectric properties of a transducer material be considered, but also the T_C and any polymorphic phase transition that may occur.

3 Lead-free piezoelectrics

Recent reports on lead-free piezoelectrics can be categorized into two main perovskite families: (1) $K_{0.5}Na_{0.5}NbO_3$ (KNN), and (2) $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) [6–25]. Room temperature values of the dielectric, piezoelectric, and electromechanical properties have been compiled and tabulated in Table 1. In addition to the KNN and NBT families, properties for BaTiO₃-based piezoelectrics are also included [26–28]. Relaxor-based piezoelectrics of (Ba)Sr₀.₇Bi₀.₂TiO₃–K₀.₅Bi₀.₅TiO₃ [Zhang, Xia and Shrout, unpublished] and tungsten bronzes [29], though included, will not be discussed owing to their relatively low properties.

For comparison with PZT materials, the room temperature values of K, d_{ij}, and coupling are plotted as a function of T_C and shown in Figs. 2, 3, and 4, respectively. As stated above, the dielectric and piezoelectric properties are intrinsically enhanced relative to a decrease in Curie temperature T_C for PZT-based materials, with only a modest (if any) enhancement noted for the three families of lead-free perovskites. In terms of the electromechanical coupling coefficients (k_p and k_{33}), no corresponding relationship with T_C for PZT or lead-free systems is observed.

Fig. 4 Room temperature electromechanical coupling k_p (*left*) and k_{33} (*right*) for various piezoelectric ceramics. (The data in Figs. 2, 3 and 4 are obtained from [2, 3, 6–32])
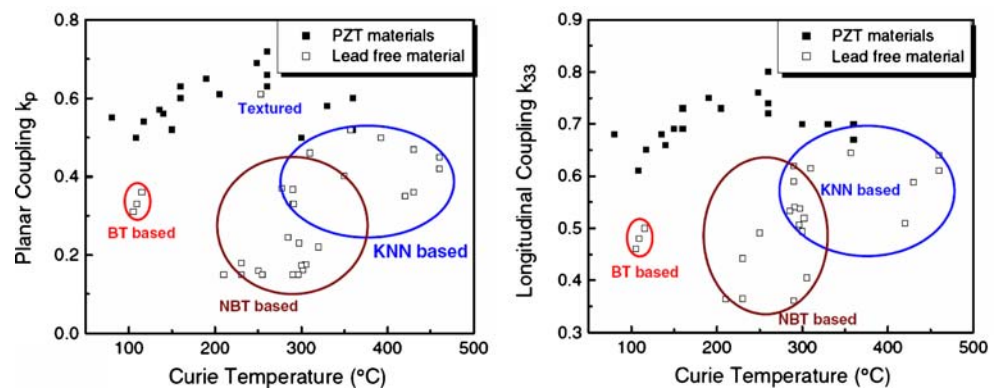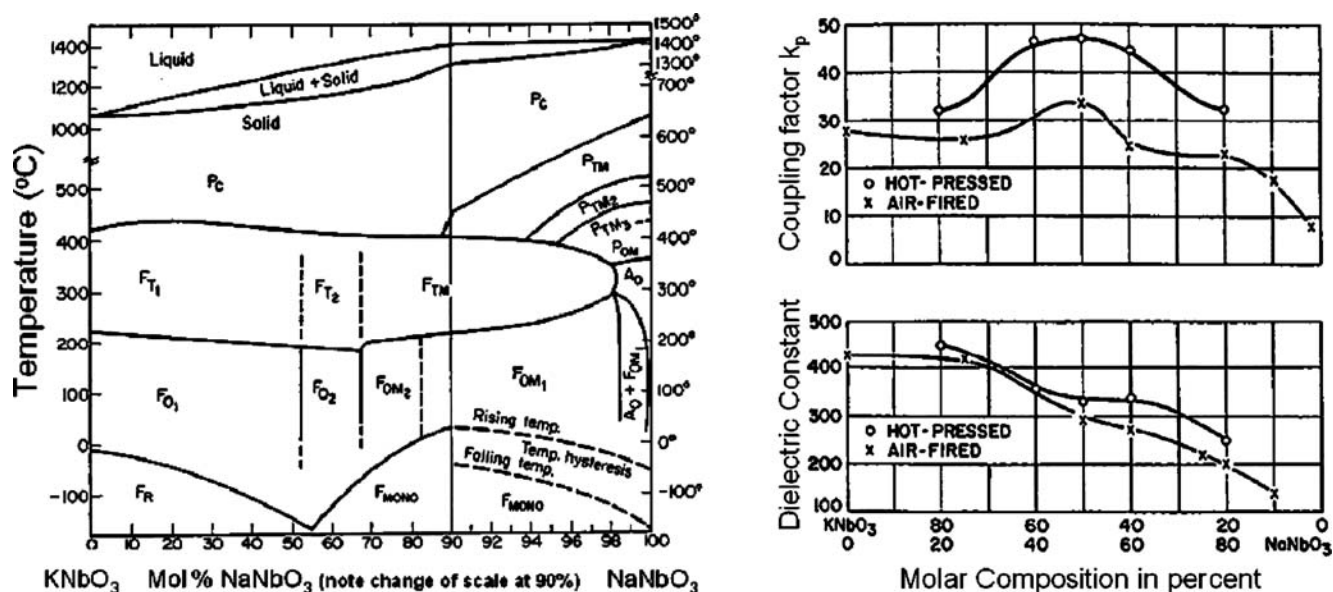
Fig. 5 Phase diagram for the KNbO$_3$–NaNbO$_3$ system (after [2, 3]) and dielectric and piezoelectric properties as a function of composition (after [30])

Though BaTiO$_3$ was the first polycrystalline piezoelectric ceramic, its inherently low T_C and numerous polymorphic phase transitions limit its overall usefulness.

From the overview of the properties presented above, several questions arise. For the case of the KNN family, are the properties reported currently superior to that of the past? What is the origin of the enhanced properties that have been widely reported? For the KNN and NBT families, are the T_Cs reported valid in relation to temperature usage range?

4 (K$_{0.5}$Na$_{0.5}$)NbO$_3$ system: past and present

The phase diagram for the solid solution $(1-x)$KNbO$_3$–(x) NaNbO$_3$ system is given in Fig. 5. Reported in 1955, a morphotropic phase boundary was reported at $x \sim 0.5$ separating two orthorhombic ferroelectric phases. A broad maximum in the planar coupling coefficient was observed with no enhancement in the dielectric properties for either air-fired or hot pressed material. Table 2 presents dielectric and piezoelectric data for KNN-MPB compositions reported prior to 1962 and for material recently processed using "optimal" processing and various fluxes. As noted, no significant differences are observed.

## 5 Enhanced properties: morphotropic phase boundary vs. polymorphic phase transition

Analogous to PZT, a morphotropic phase boundary separating ferroelectric tetragonal, and rhombohedral phases exists in the Na$_{0.5}$Bi$_{0.5}$TiO$_3$–BaTiO$_3$ and related ternary system with K$_{0.5}$Bi$_{0.5}$TiO$_3$ [23] (the former form was shown in Fig. 6a). Both the dielectric and piezoelectric properties are significantly enhanced, as evident in Fig. 6b. Unlike that of the PZT system, the MPB is strongly curved, and prior to the prototypic cubic transformation, a phase transformation to an anti-ferroelectric phase occurs, as shown in Fig. 7. The consequence of this transformation is a loss of polarization and thus piezoelectric activity. Figure 8 shows pyroelectric data reflecting that the temperature of depolarization (T_d) is significantly lower than T_C. The T_d values are listed in Table 1.

For the KNN family, reports of the enhanced dielectric and piezoelectric properties were attributed to a morphotropic boundary separating orthorhombic and tetragonal phases [7–10]. The reported orthorhombic-tetragonal MPB is actually a polymorphic phase transition analogous to that found in BaTiO$_3$, Na,CdNbO$_3$ and KNbO$_3$ (see Fig. 9), where the increased polarizability associated with a temperature transition leads to increased dielectric and

Table 2 Dielectric and piezoelectric properties of KNN ceramics: "past" and "present."

Properties	Air-fired 1959 [32]	Hot pressed 1962 [30]	Standard 2005 [14]	CuO flux 2005 [14]	KCT flux 2005 [12, 13]
K	290	490	429	231	–
d_{33} (pC/N)	80	127	98	86	90 (High field-190)
k_p(%)	36	~46	33.4	37.8	41

Fig. 6 Phase diagram for NBT–BaTiO$_3$ (**a**) and temperature behavior (**b**) (after [23])

a

b
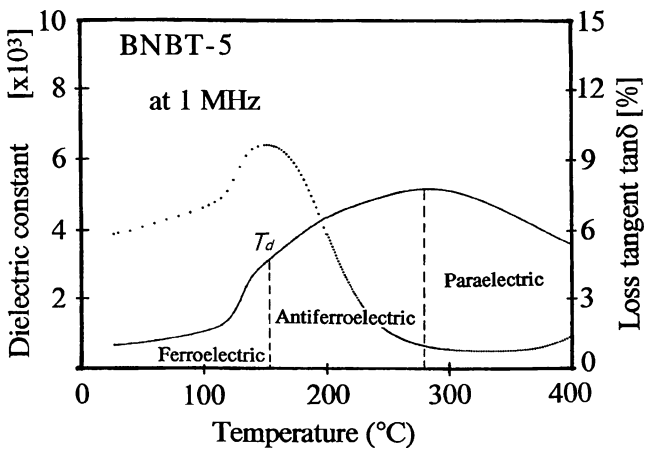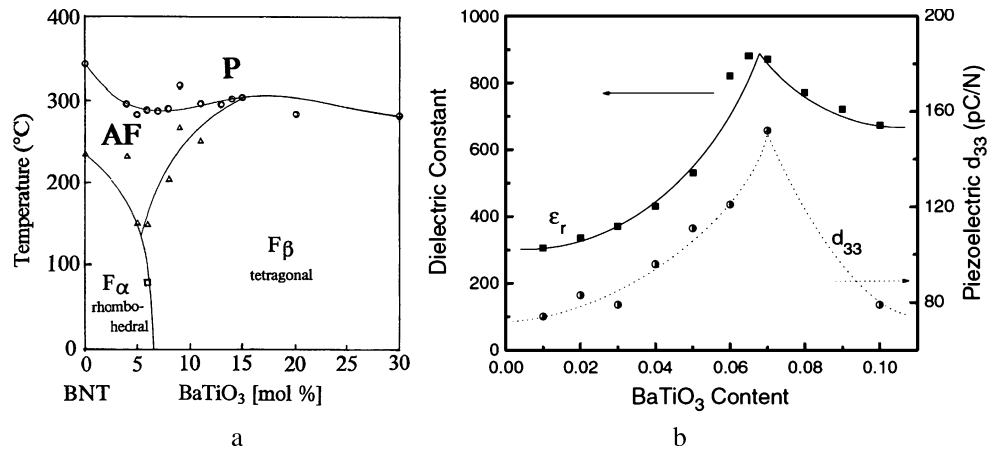
Fig. 7 Phase transformation in the NBT-BT system (after [23])
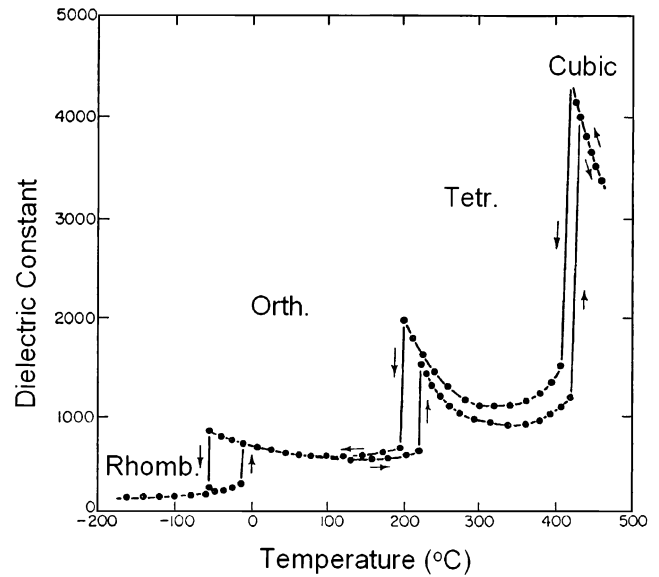
Fig. 9 Dielectric constant versus temperature for KNbO$_3$, showing the various polymorphic phase transitions (after [2, 3, 33])
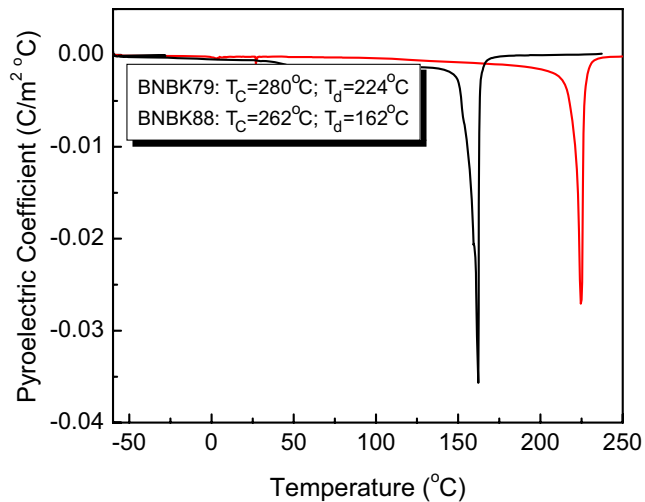
Fig. 8 Depolarization (T_d) temperature of two compositions in the NBT-BT-KBT system, as determined by pyroelectric measurements

Fig. 10 Transition temperature for modified KNN systems. (data got from [8–10])

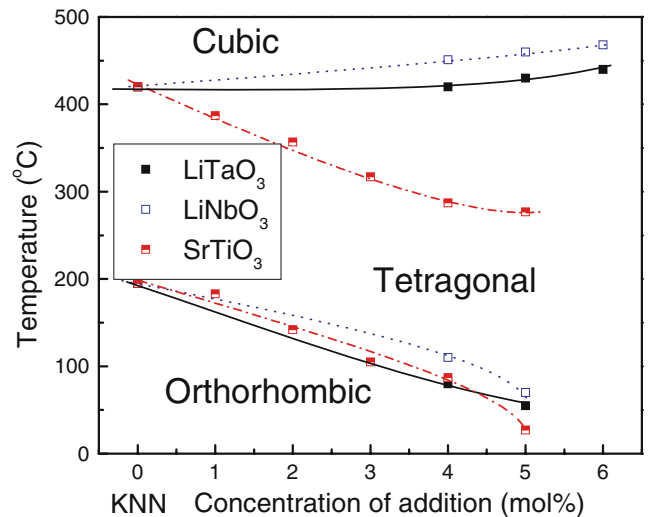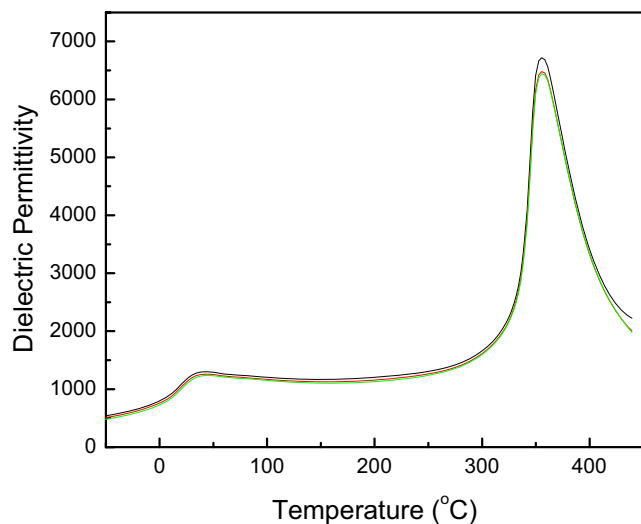**Fig. 11** Dielectric permittivity as a function of temperature for KNN-LS 5% materials

piezoelectric properties. This enhancement in piezoelectricity of current KNN ceramics has been achieved by compositionally shifting the T_{O-T} downward with additives such as LiTaO$_3$, LiNbO$_3$, LiSbO$_3$ and SrTiO$_3$ [8–11], as reflected in Figs. 10 and 11. This strong dependence with temperature is clearly shown in Fig. 12, with a maximum in coupling k_p and d_{31} for the modified KNN systems.

6 Summary

The dielectric and piezoelectric properties of lead free perovsikes were categorized in two main systems (1) KNN family and (2) NBT-based family, were summarized and compared to lead based perovskite PZT system as a
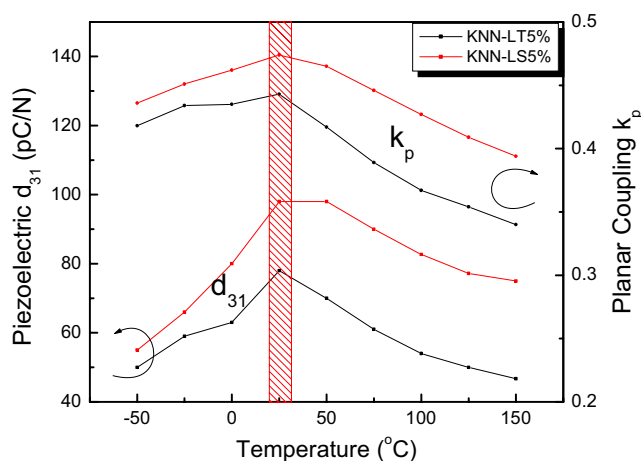
function of T_C. Analogous to PZT, enhanced properties are observed for the NBT-BT system near their MPB composition, while for KNN-based materials, the improvement of the piezoelectric behavior is related to the polymorphic phase transition temperature, compositionally shifted down to near room temperature. As expected, the properties are strongly temperature dependent [35].

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Fig. 12 Piezoelectric coefficient d_{31} and planar coupling k_p as a function of temperature for modified KNN systems

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