

Structural and dielectric properties of $\text{Pb}_{0.91}(\text{La},\text{K})_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ ceramics

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Potassium-modified polycrystalline samples of PLZT, $\text{Pb}_{0.91}(\text{La}_{1-z/3}\text{K}_z)_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ [$z = 0.0, 0.1, 0.3, 0.5, 0.7$], were prepared using sol-gel technique. X-ray diffraction (XRD) of these compounds show that they can be formed in single phase at 800°C . Pellets prepared from the above powders were sintered at 1100°C . Detailed studies of the dielectric constant (ϵ) and loss tangent ($\tan \delta$) of the compounds at different frequencies (400 Hz to 10 kHz) at room temperature (RT) and temperature (RT to 350°C) suggest that the compounds undergo ferroelectric phase transition of diffuse-type on increasing K-concentration. Analysis of diffuseness of these compounds gives a value close to 2, which indicates the presence of higher degree of disorder in PLZT substituted by K. The dielectric constant (ϵ) is found to increase initially and then to decrease with increasing K concentration. © 1999 Kluwer Academic Publishers

1. Introduction

The complex compound, $\text{Pb}(\text{ZrTi})\text{O}_3$ [referred as to PZT], a member of the perovskite structure family with a general formula ABO_3 , (A = mono or divalent, B = tri to hexavalent ions) is a solid solution of ferroelectric PbTiO_3 ($T_C = 490^\circ\text{C}$) and antiferroelectric PbZrO_3 ($T_C = 230^\circ\text{C}$) in different Zr/Ti ratios [1]. The physical properties of complex ferroelectric ceramics have been found to be very sensitive to the compositional variation. Gerson [2] showed that the electro-mechanical properties of PZT ceramics could be enhanced by substituting small quantities of tri or pentavalent ions (e.g., lanthanum, neodymium, tantalum or niobium) at Pb-sites. Among various dopants at A-sites of PZT unit cell, La^{3+} ions have been found to be most suitable for increasing the density and other properties of the samples [3–6]. The $(\text{PbLa})(\text{ZrTi})\text{O}_3$ (PLZT) ceramic with 9% La concentration, being in the near vicinity of morphotropic phase boundary (MPB), has been reported to be good quadratic modular material [7]. It is, therefore, quite interesting to explore the possibilities of fine tuning of the characteristics of PLZT(9/65/35) with the help of an additional dopant at the La-site. Though much work has been done on PLZT, the effect of alkali ions doping at La-site has not been reported in PLZT compounds with different Zr/Ti ratios. Therefore, we have extensively studied the structural, electrical, piezoelectrical and pyroelectrical properties of alkali ion modified PLZT with different Zr/Ti ratios prepared by nitrate, coprecipitation and/or sol-gel technique [8, 9]. In the present work, we have synthesised K-modified PLZT ceramics with a general formula $\text{Pb}_{0.91}(\text{La}_{1-z/3}\text{K}_z)_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$

($z = 0.0, 0.1, 0.3, 0.5, 0.7$) using the sol-gel technique. The effect of potassium doping on the structural and electrical properties of the samples have been studied for the better understanding of the nature of phase transition in them.

2. Experimental

Polycrystalline samples of $\text{Pb}_{0.91}(\text{La}_{1-z/3}\text{K}_z)_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ (PLKZT) with $z = 0.0, 0.1, 0.3, 0.5$ and 0.7 were prepared by the sol-gel technique: lead acetate (99.9%, E. Merck (India) Ltd.), lanthanum acetate (99.9%, Johnson Chemical Co., India) and potassium acetate (99%, Sisco research Lab. (India) Pvt. Ltd.) were taken together in desired stoichiometry and dissolved in a minimum quantity of double distilled water. An aqueous solution of zirconyl nitrate (99%, Loba Chemie, India) was first converted into its hydroxide by adding ammonia solution (S.d.fine-chem Pvt. Ltd., India). The hydroxide was then filtered. The precipitate was thoroughly washed with doubly distilled water and kept in hot water bath after adding acetic acid (99.9%, E. Merck (India) Ltd.) and a clear solution of zirconyl acetate was obtained. It was then transferred to a beaker containing the solutions of acetates of lead, lanthanum and potassium. Required volume of titanium isopropoxide (99% pure, E. Merck Schuchardt, Germany), dissolved in an equal volume of *n*-butanol (99%, E. Merck (India) Ltd.), was taken, in which the above mixture of acetates was added slowly with constant stirring. Finally, 1.5 mol of citric acid (99.5%, E. Merck (India) Ltd.) and 1 mol of glycerol (GR grade, E. Merck (India) Ltd.) were added

TABLE I Comparison of observed (o) and calculated (c) values of d (in Å) with I/I_0 (%) in parenthesis of $\text{Pb}_{0.91}(\text{La}_{1-z/3}\text{K}_z)_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ at room temperature

hkl	$z = 0.0$	$z = 0.1$	$z = 0.3$	$z = 0.5$	$z = 0.7$
100 (o)	4.0804 (11)	4.1103 (18)	4.1140 (19)	4.1197 (17)	4.1103 (18)
(c)	4.0804	4.1102	4.1140	4.1194	4.1103
110 (o)	2.9002 (100)	2.9085 (100)	2.9094 (100)	2.9140 (100)	2.9085 (100)
(c)	2.9002	2.9084	2.9094	2.9137	2.9085
111 (o)	2.3738 (16)	2.3763 (14)	2.3757 (12)	2.3799 (12)	2.3763 (10)
(c)	2.3803	2.3763	2.3758	2.3797	2.3764
200 (o)	2.0398 (29)	2.0556 (26)	2.0570 (21)	2.0596 (22)	2.0556 (23)
(c)	2.0402	2.0551	2.0570	2.0597	2.0551
210 (o)	1.8323 (7)	1.8397 (4)	1.8399 (6)	1.8427 (5)	1.8392 (5)
(c)	1.8323	1.8397	1.8400	1.8427	1.8392
211 (o)	1.6808 (37)	1.6774 (35)	1.6799 (32)	1.6825 (34)	1.6774 (35)
(c)	1.6802	1.6776	1.6799	1.6825	1.6776
220 (o)	1.4503 (14)	1.4541 (9)	1.4547 (7)	1.4568 (8)	1.4541 (7)
(c)	1.4501	1.4542	1.4547	1.4568	1.4542

as a chelating agent for each mole of PLKZT. The resultant mixture was dried at 60 °C in an air oven to form a resin. The powders were then calcined at different temperatures (viz., 400, 600 and 800 °C) for 10 h. The X-ray diffractograms of all the samples (calcined at different temperatures) were recorded at room temperature with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) using X-ray powder diffractometer (Rigaku Miniflex, Japan) in a wide range of Bragg angles ($20^\circ \leq 2\theta \leq 70^\circ$) with $2^\circ/\text{min}$ scanning rate. The differential thermal analysis (DTA) and XRD studies suggest that the single phase compounds of PLKZT can be formed above 600 °C. The pellets of diameter 10 mm and thickness 1–2 mm were prepared at a pressure of 50 MPa using a hydraulic press and PVA binder which was burnt out during sintering at 1100 °C for 2 h. To prevent the PbO loss during high temperature sintering, an equilibrium PbO vapour pressure was established using PbZrO_3 powder. The sintered pellets were polished to make both their faces flat and parallel and electroded by high-purity ultra-fine silver paste for all the electrical measurements. Before carrying out the measurements, the samples were kept at 150 °C for 2 h and then cooled slowly, in order to cure and dry the paint. The capacitance and dissipation factor of the samples were measured at different frequencies (400 Hz to 10 kHz) at room temperature (RT) and temperature (RT to 350 °C) at frequency 10 kHz using GR 1620AP capacitance measuring assembly using 3-terminal sample holder fabricated by us to compensate for any stray capacitance. The reliability of the data obtained was checked by repeating some measurements a number of times and all the values were found to be within the experimental uncertainties ($\sim 2\text{--}3\%$).

3. Results and discussion

The X-ray diffraction peaks of calcined powders of $\text{Pb}_{0.91}(\text{La}_{1-z/3}\text{K}_z)_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ [PLKZT], calcined at 800 °C, were found to be sharp and unsplit, which indicated good homogeneity and crystallisation of the samples. All the peaks were indexed and lattice parameters of PLKZT were calculated using a com-

TABLE II Lattice parameters of $\text{Pb}_{0.91}(\text{La}_{1-z/3}\text{K}_z)_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ ceramics

Compositions, z	Rhombohedral phase		
	a (Å)	α	V (Å ³)
0.0	4.0809	89.408	67.95
0.1	4.1102	89.920	69.44
0.3	4.1140	89.987	69.63
0.5	4.1194	89.968	69.90
0.7	4.1103	89.919	69.44

puter program package with least-squares refinement method [10]. A good agreement between calculated and observed d values of all diffraction lines (Table I) of PLKZT showed that the crystal structure was rhombohedral at room temperature and was independent of the K concentration in the range of $0.0 \leq z \leq 0.7$. The refined lattice parameters and the unit cell volume of the samples with different z are given in Table II. The average particle size (P) of all the pellet samples were calculated from reflections using Scherrer's equation $P = k\lambda/(\beta_{1/2} \cos \theta)$, (where $k = 0.89$, $\beta_{1/2}$ = half peak width) and are listed in Table III. The calculated particle sizes are found to decrease with the increasing K concentration, highest being that of PLZT.

Figs 1 and 2 show the variation of dielectric constant (ϵ) and the loss tangent ($\tan \delta$) at room temperature (25 °C) with frequency. It is observed that in lower region of frequencies, both ϵ and $\tan \delta$, decrease with increasing frequency for all the values of z , exhibiting the typical characteristic of a normal dielectric. But at higher frequencies, these parameters become almost frequency independent.

Fig. 3 shows the variation of dielectric constant (ϵ) with temperature measured at 10 kHz. As in a normal ferroelectric ϵ increases gradually to its maximum value (ϵ_{max}) with increase of temperature upto the transition temperature and then it decreases for all the values of z ($0.0 \leq z \leq 0.7$), indicating the ferroelectric phase transition in PLKZT. Qualitatively, the broadened peaks of PLKZT indicate that the phase transition is of diffuse-type. Besides, it is also observed that the transition temperature of the PLKZT ceramics increases with the

TABLE III Comparison of some physical parameters of $\text{Pb}_{0.91}(\text{La}_{1-z/3}\text{K}_z)_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ ceramics at 10 kHz

Physical parameters	$z = 0.0$	$z = 0.1$	$z = 0.3$	$z = 0.5$	$z = 0.7$
ϵ_{max}	7029	7427	6692	5563	4440
$(\tan \delta)_{\text{max}}$	0.096	0.099	0.085	0.120	0.087
T_C °C	89	126.5	174.3	166.0	200
Diffusivity, γ	1.86	1.87	2.01	1.97	1.81
Gaussian diffuseness, δ_g	60	68.8	128.3	79.8	61
Measured density in gm/cm^3	8.39	8.55	8.50	8.16	7.85
Average particle size, P (Å)	200	199	187	161	155

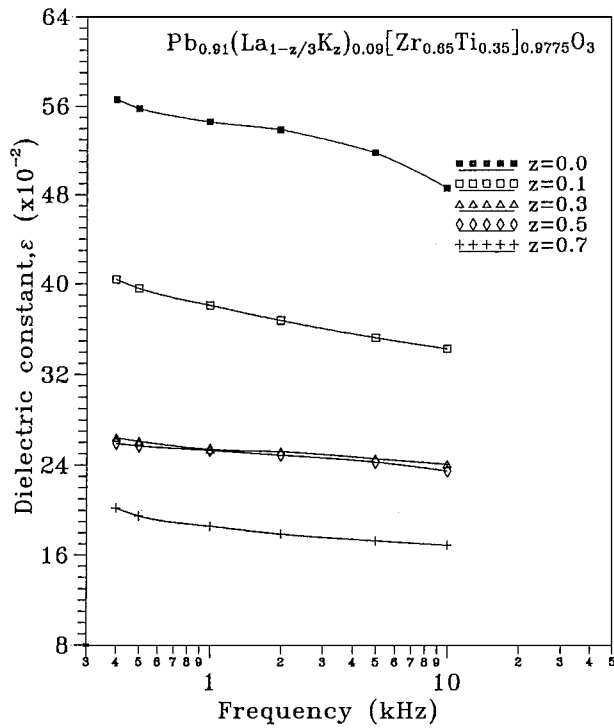


Figure 1 Variation of dielectric constant of PLKZT as a function of frequency at room temperature.

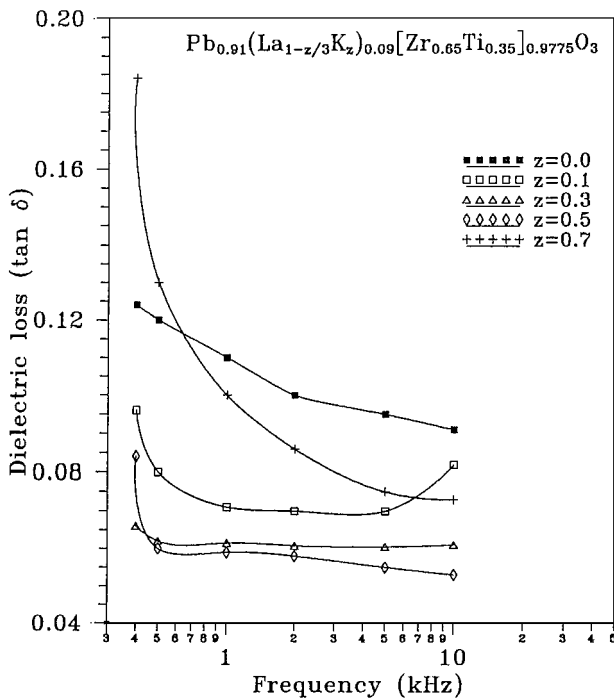


Figure 2 Variation of dielectric loss of PLKZT as a function of frequency at room temperature.

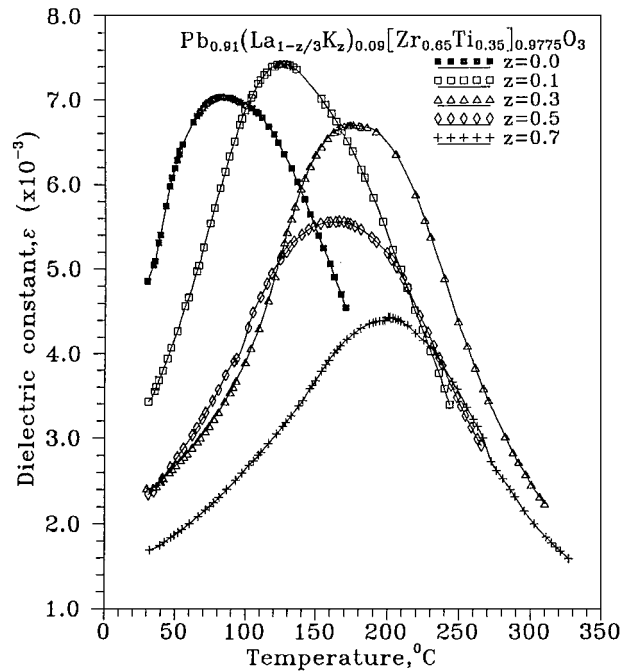


Figure 3 Variation of dielectric constant of PLKZT as a function of temperature at frequency 10 kHz.

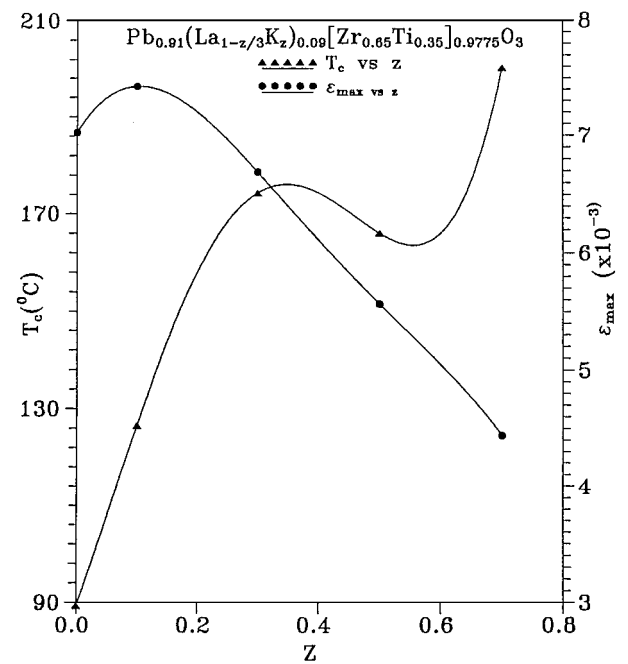


Figure 4 Variations of T_C and ϵ_{max} with potassium concentration.

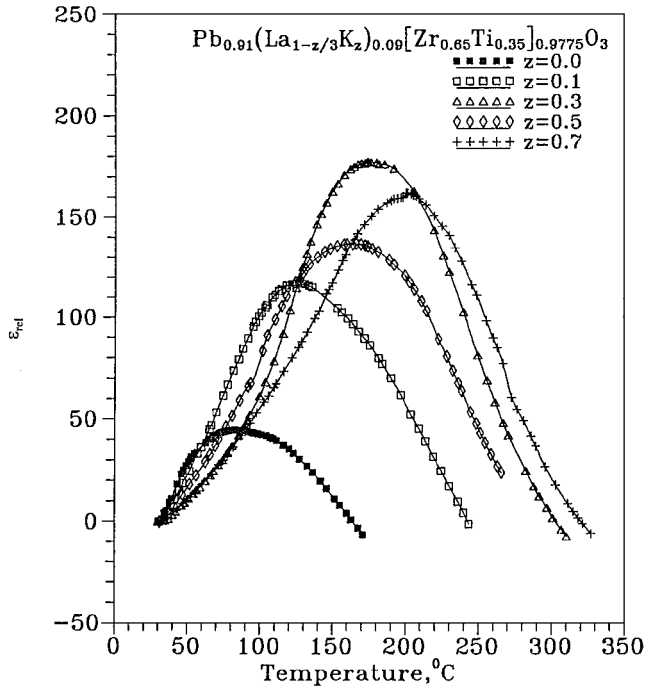


Figure 5 Variation of relative coefficient of dielectric permittivity versus temperature at frequency 10 kHz.

increase in the value of z , except for $z = 0.5$. However, the peak dielectric constant (ϵ_{\max}) increases initially upto $z = 0.1$ and then decreases with the further increase of z . A similar behaviour was observed by us in the case of Na-modified PLZT [11]. The change of T_c and ϵ with the K concentration is shown in Fig. 4.

An estimation of the relative change of the dielectric constant with reference to a certain temperature [i.e., relative dielectric constant, $\epsilon_{\text{rel}} = 100 (\epsilon_t - \epsilon_{\text{rt}}) / \epsilon_{\text{rt}}$] is an important device parameter. Fig. 5 shows the variation of ϵ_{rel} with temperature. It is found that the peak value of ϵ_{rel} of PLKZT is minimum for $z = 0$ and maximum for $z = 0.3$.

The quantitative assessment of the diffusivity of the broadened peak of the samples in the paraelectric phase was evaluated using the expression $(1/\epsilon - 1/\epsilon_{\max}) \propto (T - T_c)^\gamma$, [12] where ϵ_{\max} is the maximum value of ϵ at T_c and γ is the measure of diffuseness. The plots of $\ln(1/\epsilon - 1/\epsilon_{\max})$ versus $\ln(T - T_c)$ for PLKZT are shown in Fig. 6a–e. It is observed that the variation is almost linear. The mean values of the diffusivity γ for different z , were extracted from these plots by fitting in straight line equation, and was found to be close to 2 that indicated the phase transition was of second-order. This confirms the higher degree of disordering in the doubly doped PZT, i.e., (i) gradual decrease of spontaneous polarisation and (ii) absence of Curie-Weiss behaviour in a certain interval of temperature above the transition temperature [13, 14]. The variation of γ with the K concentration is shown in Fig. 6f. In addition, the Gaussian diffuseness, δ_g in PLKZT was calculated using the relation $\ln(\epsilon_{\max}/\epsilon) = (T - T_c)^2 / 2\delta_g^2$, over a limit of $1 \leq \epsilon_{\max}/\epsilon \leq 1.5$ [15]. The variation of $\ln(\epsilon_{\max}/\epsilon)$ versus $(T - T_c)^2$, is shown in Fig. 7. Because of the non-linearity in the variation, the values of δ_g have been evaluated at $T = T_c$ (Table III).

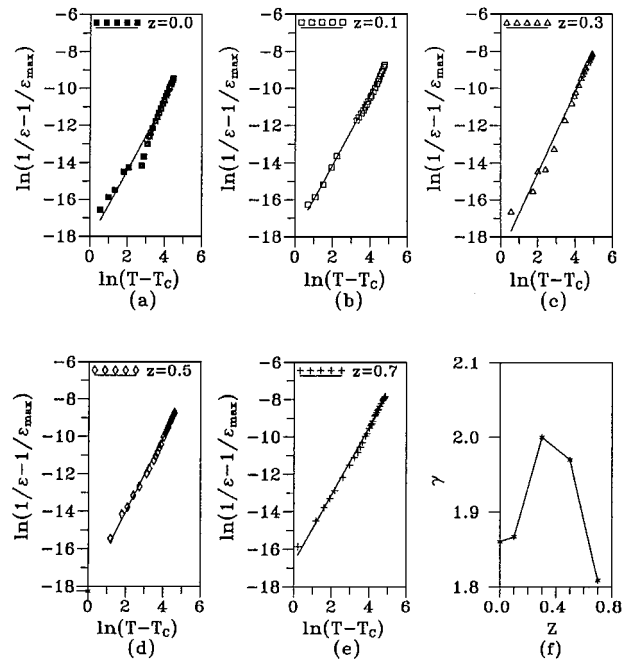


Figure 6 (a-e): Plots of $\ln(1/\epsilon - 1/\epsilon_{\max})$ versus $\ln(T - T_c)$ for PLKZT at frequency 10 kHz. (f): variation of diffusivity γ [extracted from (a-e)] with sodium concentration.

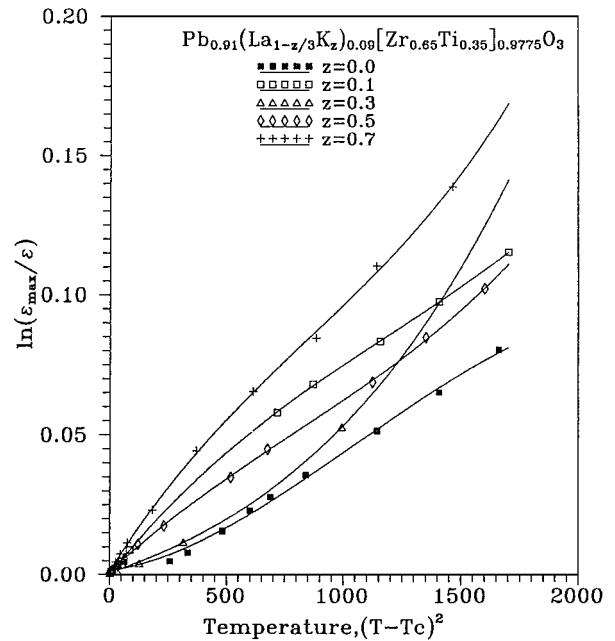


Figure 7 Gaussian diffuseness plot for PLKZT at frequency 10 kHz.

4. Conclusion

The PLKZT ceramics prepared by sol-gel technique (calcined at 800 °C and sintered at 1100 °C) exhibit better homogeneity, formation of single phase compound and useful dielectric and other electrical properties. The particle sizes calculated on the basis of Scherrer's equation are found to decrease with increase of K concentration. The dielectric constant and the loss tangent are found to decrease with increasing frequency. At room temperature, the dielectric constant is observed to decrease with the increase of K-ions. Generally, the dielectric constant is found to decrease and the transition temperature is found to increase with the increase of K-ions at La-site.

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References

1. WUL and L. M. GOLDMAN, *C. R. Acad. Sci. URSS* **46** (1945) 123.
2. R. GERSON, *J. Appl. Phys.* **31** (1960) 188.
3. G. H. HAERTLING, *Ferroelectrics* **75** (1987) 25.
4. *Idem.*, "Ceramic Materials for Electronics" (Buchanan, New York, 1991) p. 164.
5. K. H. HARDTL and D. HENNINGS, *J. Amer. Ceram. Soc.* **55** (1972) 230.
6. L. RAMJI, S. C. SHARMA and D. RAJIV, *Ferroelectrics* **100** (1989) 43.
7. G. H. HAERTLING and C. E. LAND, *ibid.* **3** (1972) 269.
8. J. MAL and R. N. P. CHOUDHARY, *Phase Transitions* **62** (1997) 119.
9. K. L. YADAV and R. N. P. CHOUDHARY, *Ferroelectrics* **141** (1993) 227.
10. E. Wu (eds.), POWD, An Interactive Powder Diffraction Data Interpretation and Indexing Program, ver. 2.1 (School of Physical Science, Flinders University of South Australia, Bedford Park, SA 5042, Australia).
11. H. R. RUKMINI, R. N. P. CHOUDHARY and V. V. RAO, *Mats. Chem. and Phys* **55** (1998) 108.
12. S. M. PILGRIM, A. E. SUTHERLAND and S. R. WINZER, *J. Amer. Ceram. Soc.* **73** (1990) 3122.
13. G. H. HAERTLING and C. E. LAND, *ibid.* **54** (1971) 1.
14. S. SHARMA, R. N. P. CHOUDHARY and R. SATI, *Phys. Stat. Sol. (a)* **133** (1992) 491.
15. S. MIGA and K. WOJCIK, *Ferroelectrics* **100** (1989) 167.

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