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Investigation of diffuse phase transition in ferroelectric $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ ($0 \leq x \leq 1.5$) ceramics

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Abstract Substitution of Pb with Li and K in the $Pb_2KNb_5O_{15}$ phases leads to a new composition with chemical composition $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ which crystallizes with tetragonal tungsten bronze-type structure. Ferroelectric ceramics with different compositions were synthesized using solid-state reaction and complex dielectric permittivity measurements in these compounds were performed in a frequency and temperature range of 20 Hz–1 MHz and from 25 to 550 °C, respectively. Special attention was paid to the diffuse phase transition (DPT) that occurs close to the Curie temperature. The empirical equation proposed by Santos–Eiras for a phenomenological description of the temperature dependence of the dielectric permittivity (ε_r') peak is used to calculate some characteristic parameters of DPT. From the results, it must be assumed that these compounds show a diffuse phase transition with non-relaxor behavior. A basic phase diagram showing the evolution of T_m function of composition x is deduced from this study.

1 Introduction

Compounds of 'tetragonal tungsten bronze' (TTB) structure with general formula unit $A_xB_yC_zNb_5O_{15}$ form one of the greatest families of ferroelectric oxides. Their crystal structure may be described as a network of slightly distorted oxygen octahedra NbO_6 linked by the corner oxygen atoms [1]. The metallic ions A, B, and C fill the pentagonal, quadratic, and triangular cavities (with coordination numbers 15, 12, and 9) that exist between the MO_6 octahedra. Juxtaposed in the z direction, these cavities form tunnels with chains of metallic ions inside. Only large ions, like K^+, Rb^+, Cs^+, Pb^{2+}, Ba^{2+} or Na^+, can be located in A or B holes, while smaller ions like Li^+ can penetrate into C-type cavity. The great variety of TTB-type compounds is provided by the different choices of the inserted anions.

The lead-containing oxide $PbNb_2O_6$ was the first compound of TTB family in which the ferroelectric phase transition at $T_c = 575$ °C was found [2]. Since that, different TTB-type ferroelectrics were discovered [3]. The principal motivation of study of these compounds is their important electro-optical, pyroelectric, and piezoelectric properties [4–7].

In previous studies, we have shown that $PbK_2LiNb_5O_{15}$ single crystal presents a dielectric anomaly at 366 °C and an unusual behavior associated with intermediate phases. The ionic conduction related to lithium ions is evidenced in this material [8, 9]. Recently, impedance studies, i.e., electrical properties and frequency response at different temperatures of different TTB structure, have thoroughly been studied by us [10, 11].

For a given structural type, the value of T_c depends on the composition. The variations of T_c may be correlated with factors of chemical bonding such as size, coordination or electronic configuration of cations, bond covalency, and order–disorder [12].

The $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ ceramic considered in the present work belongs to PKLN family, which crystallizes in TTB phase and whose detailed structural study was already done in another work [10]. The chemical

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composition of PKLN can also be described formally from that of $Pb_2KNb_5O_{15}$ by a substitution in this compound of one of the Pb^{2+} ions by the couple (Li^+, K^+). From the observations of variation of dielectric constant with temperature, it is revealed the phase transition is a diffused phase transition (DPT) in PKLN.

In this paper, the observed diffuse phase transition in $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ [10] sample has been studied quantitatively based on recently developed phenomenological model by Santos–Eiras. The origins of diffused phase transition in $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ ceramics are also discussed. These studies permit us to present a basic phase diagram of this family compound showing the evolution of the critical temperature T_m versus x and to compare experimental results in $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ (PKGN) [13].

2 Sample preparation

The polycrystalline ceramic samples of $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ were prepared by solid-state synthesis using the following chemical reaction:

$$(2-x)\mathrm{PbO} + \frac{(1+x)}{2}\mathrm{K_2CO_3} + \frac{x}{2}\mathrm{Li_2CO_3} + \frac{5}{2}\mathrm{Nb_2O_5} \rightarrow \mathrm{Pb_{2-x}K_{1+x}Li_xNb_5O_{15}} + \frac{(1+2x)}{2}\mathrm{CO_2}$$

The starting materials were high-purity (99.9 %) powders of oxides (PbO, Nb_2O_5) and carbonates (K_2CO_3, Li_2CO_3). All these materials were weighed, mixed for 1 h. The finely crushed mixtures preheated at 400 °C for 4 h and then preheating was carried out between 1000 and 1050 °C for 10 h. These two heat treatments are intersected by crushing in order to obtain well-homogenized mixtures. Powders of these compounds were initially compacted with a pressure of 2 ton/m^2 to obtain cylindrical pastille samples having 13 mm of diameter and 1 mm of thickness. Finally, these pastilles were sintered during 4 h between 1100 and 1200 °C.

3 Results and discussion

3.1 X-ray study

The X-ray study of the $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ compounds indicates that they crystallize in the TTB structure and present single phase at room temperature depending on composition. For lowest values of x ($0 < x < 0.5$), the compositions present orthorhombic symmetry at room temperature with space group of Cm2m, while for $x > 0.55$, they crystallize in the tetragonal system space group of P4bm. We suggest also the existence of a morphotropic region around $x = 0.5$, which we will prove later. These compounds were already prepared and characterized in another our earlier work [10].

3.2 Dielectric measurements

The temperature dependence of ε'_r in $PbK_2LiNb_5O_{15}$ ($x = 1$) at various frequencies are shown in Fig. 1. From this figure, ε'_r increases gradually with increase in temperature and reaches a maximum at Curie temperature, $T_c = 350$ °C. In general, the ferroelectric phase transition for TTB structure compounds possessed not only displacive characteristic but also order–disorder characteristics [14]. Ionic size, polarizability, and electronic configuration of the ions participating in solid solution are believed to be among the factors that determine the magnitude and direction of the shift of the T_c [15].

The thermal evolution of the real part of the dielectric constant in the temperature range 40–550 °C at 10 kHz for $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ samples with $0 \le x \le 1.5$, presents different behavior according to the composition (Fig. 2). Several remarked variations are observed due to substitution of Pb^{2+} by K^+ and Li^+. Only one peak was observed in all compositions, corresponding to the phase transition of paraelectric–ferroelectric at T_c. Temperature of dielectric maximum (T_m) decreases with x indicating that K^+ and Li^+ have entered into lattice. In addition, we remark a modification of dielectric proprieties by decreasing in real permittivity when the composition x increases ($\varepsilon'_m = 4580$ for $x = 0$ and $\varepsilon'_m = 3475$ for $x = 1.5$) and also a change in the peak width of the dielectric permittivity when the composition x varies.

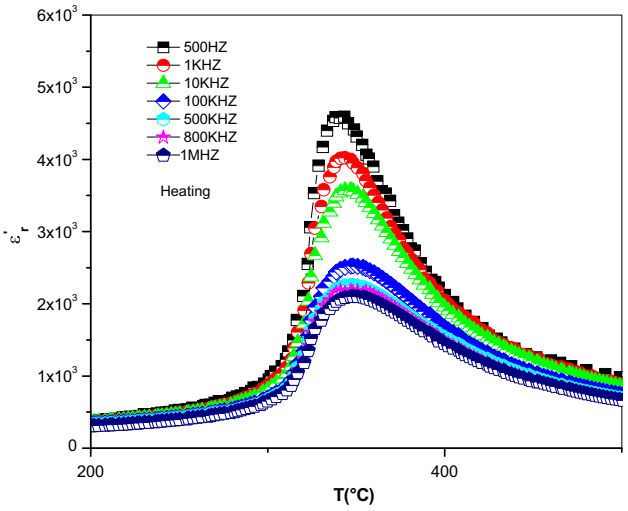

Fig. 1 Temperature dependence of the dielectric constant in the heating mode for compound of PKLN family ($x = 1$) at different frequencies

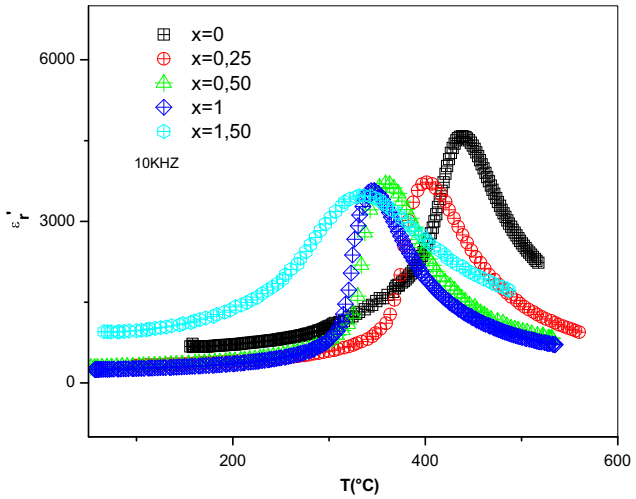

Fig. 2 Thermal evolution of ε_r' for $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ composition ceramics ($x = 0$, 0.25, 0.5, 1 and 1.5)

3.3 Diffusive nature of ferroelectric transition

As observed in Figs. 1 and 2, all samples show a relatively broad peak in the dielectric constant around the phase transition temperature which is typical for relaxor ferroelectrics or ferroelectrics with a diffuse phase transition [16, 17]. In our case, it follows from Fig. 1 that the compound has the same T_c at all frequencies, suggesting that the compound does not have any relaxor behavior. The behavior of diffusive type can be associated with the domain walls in the micro-domain of nucleating ferroelectric phase [18].

The diffusive nature of the ferroelectric phase transition can be empirically described by the parameter ΔT_{dif} [19, 20]:

$$\Delta T_{dif} = T_{0.9\varepsilon'_{max}}(f) - T_{\varepsilon'_{max}}(f)$$

where $T_{0.9\varepsilon'_{max}}(f)$ is the temperature corresponding to 90 % of ε'_{max} at the frequency f in the paraelectric region, and $T_{\varepsilon'_{max}}(f)$ is the dielectric maximum temperature at the same frequency f. For frequency $f = 10$ kHz, taken as an example and for all compositions x, we found the values of ΔT_{dif} between 20 and 40 °C, such values are quite typical for DTP.

In order to quantify the diffuseness dielectric curves degree, we used the equation proposed by Santos–Eiras [21]. According to these authors, this empirical equation represents a phenomenological temperature dependence description of dielectric permittivity which is written as:

$$\varepsilon_r' = \frac{\varepsilon_m'}{1 + \left(\frac{T - T_m}{\Delta}\right)^{\gamma}} \quad (1)$$

where ε'_m is the maximum of dielectric permittivity, T_m is the temperature of the maximum of the dielectric permittivity, γ indicates the character of the phase transition, and Δ is the peak broadening, which defines the diffuseness degree of the ferroelectric–paraelectric phase transition (F–P). For $\gamma = 1$, Eq. (1) fits a ''conventional'' first- or second-order ferroelectric phase transition, described by the Landau–Devonshire theory. For $\gamma = 2$, Eq. (1) represents the so-called complete DPT, described by Kirilov and Isupov [22]. While $1 < \gamma < 2$ the transition is "incomplete" which means that the interaction between nucleating ferroelectric clusters in paraelectric matrix begins far above T_m and plays an important role in its diffusive character [21].

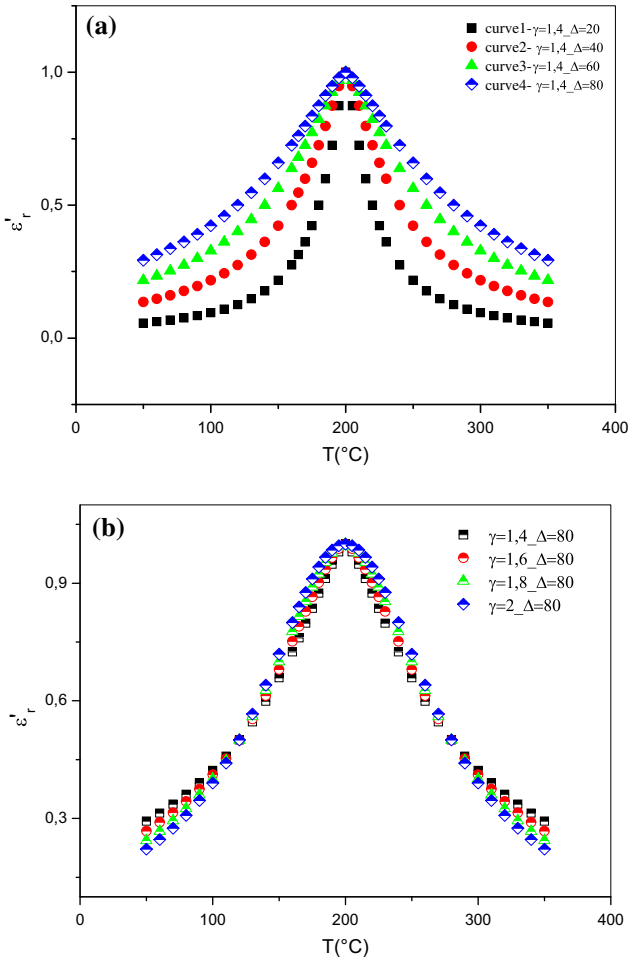

Fig. 3 Effects of the parameters Δ (**a**) and γ (**b**) in Eq. 1 on the dielectric constant ε_r' as a function of temperature

To reasonably inspect the effects related to the temperature–dielectric constant curve, Fig. 3 shows the effects of Δ for Eq. (1), on the dielectric constant as a function of temperature. We assume ε_m and T_m to be constant ($\varepsilon_m = 1$ and $T_m = 200$ °C for example), for the sake of simplicity.

Comparing Curves 1 in Fig. 3a, the dielectric constant ε_r' curve becomes less steep and the dielectric diffused characteristics are obvious when the Δ value is increased.

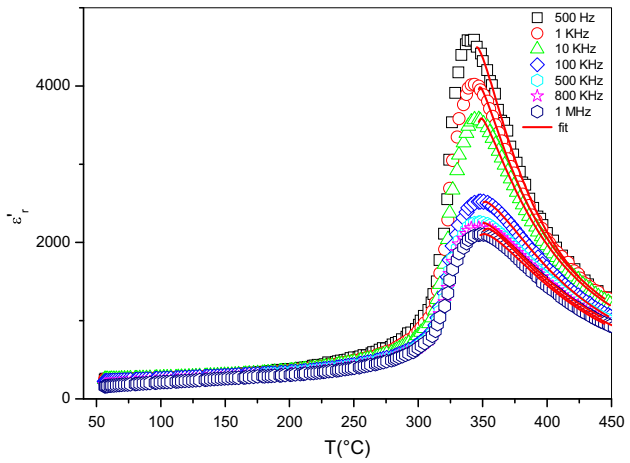

Fig. 4 Temperature dependence of ε'_r at different frequencies of PKLN ($x = 1$). Solid lines present the theoretical fit

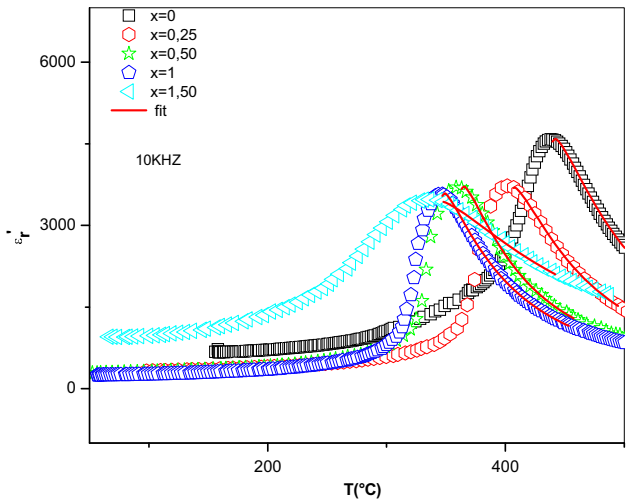

Fig. 5 Dielectric constant as a function of temperature at 10 kHz and its fitting curve by using Eq. (1) for $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ with $x = 0$, 0.25, 0.5, 1 and 1.5

Comparing curves in Fig. 3b, the change of ε'_r distribution is very small when the γ value is increased. Although the changes of γ does not generally affect ε'_r so much, a larger γ value still represents a more diffused phase transition.

In order to analyze the main characteristics of the F–P phase transition in the PKLN ceramics, the dielectric permittivity versus temperature curves were fitted with the Santos–Eiras equation (Eq. 1) at different frequencies for $PbK_2LiNb_5O_{15}$ and at different compositions x for $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ (Figs. 4, 5). The coincidence between experimental and theoretical curves validates the applied model.

The parameters ε'_m, T_m, Δ, and γ were obtained from the fitting process at $T > T_m$. The fitted parameters are listed in Tables 1 and 2. The values of ε'_m decrease with the increase

Table 1 Dielectric parameters obtained from the Santos–Eiras' relation–case of $PbK_2LiNb_5O_{15}$

Frequency	ε'_m	T_m (°C)	Δ (°C)	γ
500 Hz	4498	345	50	1.40
1 kHz	3989	348	54	1.29
10 kHz	3591	349	59	1.32
100 kHz	2519	351	76	1.48
500 kHz	2249	351	82	1.44
800 kHz	2178	354	79	1.40
1 MHz	2108	351	82	1.50

Table 2 Dielectric parameters obtained from the Santos–Eiras' relation for $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ at 10 kHz

x	ε'_m	T_m (°C)	Δ (°C)	γ
0	4588	442	69	1.38
0.25	3694	407	67	1.38
0.50	3719	365	57	1.32
1	3591	349	59	1.31
1.5	3434	347	91	1.50

in the frequency, as has been reported for relaxor ferroelectrics [23]; however, T_m remains almost constant.

For the compound $PbK_2LiNb_5O_{15}$, the parameter γ is found to be between 1.29 and 1.50, indicating an incomplete ferroelectric phase transition. For the ceramics $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$, the parameter γ is found to be between 1.31 and 1.50, which indicates an "incomplete" DPT in F–P transition. The value of the parameter γ is comparable with that observed in ferroelectric with a phase transition type diffused. The values close to $\gamma = 1.55$–1.68 reported by Santos et al. [21] for the $Pb_xBa_{1-x}Nb_2O_6$ family.

The values of Δ for PKLN showed a small increase with the increase in the frequency and the composition x. On the other hand, the diffuseness degree values Δ of the PKLN ($x = 1.5$) phase transition are higher than the others compositions x, indicating that the K^+ et Li^+ structural incorporation increases the diffuseness degree of the PKLN sample, which results in a diffuse phase transition (DPT).

A diffuse phase transition in ferroelectrics occurs as a consequence of a structural disorder that breaks the translational invariance of the lattice. The type of diffuseness observed depends both on the nature and on scale of the structural disorder. Impurities, point defects, extended defects, incomplete or inhomogeneous cation ordering, macroscopic fluctuations in chemical composition, etc., can lead to the smearing of the ferroelectric phase transition [24]. The broadening of the phase transition peaks is an important characteristic of a disordered TTB structure [25].

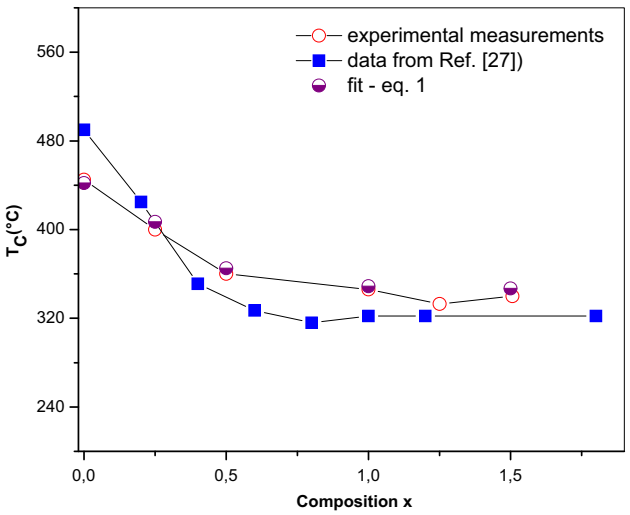

Fig. 6 Variation of the transition temperature T_c (or T_m) versus composition x for the PKLN family (our experimental measurements, data from Ref. [26] and fit using Eq. 1)

We therefore conclude that the diffuse phase transition (DPT) observed in PKLN samples can be caused for the incorporation of the K and Li cations, creating impurities and intrinsic disorder of lithium and sites and/or the distortions of TTB unit cells and consequently bigger disorder in the domains structure of this material.

After this study, it appears interesting to investigate the structure and dielectric properties of compound with general formula $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ and present a phase diagram of this family showing the evolution of the critical temperature versus x. The evolution of the characteristic transition temperature T_c (or T_m) with increasing in the composition is shown in Fig. 6 both for the family PKLN (experimental and fit using Eq. 1) and for the previously studied family $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ [26]. The temperature T_m decreases strongly as x increases for $x < 0.5$. However, T_c shows some decrease with Li and K content below $x = 0.5$. This behavior is in good agreement with experimental results in compound of the family $Pb_{2(1-x)}K_{1+x}$-$Gd_xNb_5O_{15}$ (PKGN) [13]. The authors showed similar evolution of the critical temperature versus temperature and evidenced the existence of a morphotropic region around $x = 0.35$ in PKGN.

4 Conclusion

Dielectric properties of the ferroelectric compounds of TTB structure: $Pb_{2-x}K_{1+x}Li_xNb_5O_{15}$ with $0 \leq x \leq 1.5$ (PKLN) were, for the first time, investigated in the frequency range of 20 Hz–1 MHz and a wide temperature interval. The results showed also a ferroelectric–paraelectric diffuse phase transition around the temperature of the maximum dielectric permittivity. The parameters characterizing the ferroelectric–paraelectric phase transition were determined by using the Santos–Eiras' expression. The dielectric properties of the PKLN ceramics showed an "incomplete" DPT phase transition around the temperature of the maximum dielectric permittivity (diffusivity $1 < \gamma < 2$) associated with intrinsic disorder of lithium sites and/or the distortions of TTB unit cells. These studies permit us to present the phase diagram of this family showing the evolution of the transition temperature T_m as function of the chemical composition.

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