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ANALYSIS OF THE DIELECTRIC CONSTANT DATA OF RELAXORS WITHIN A LANDAU-TYPE THEORY

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The low-field dielectric constant data obtained for the relaxor-ferroelectric solid solution (1-x)$PbFe_{2/3}W_{1/3}O_3$-x$PbTiO_3$ with x=0, 0.2, 0.3 and 0.4, were investigated using a modified Landau theory proposed for the ferroelectric relaxors. The temperature dependence of the permittivity data in relaxors deviates from the Curie-Weiss in the paraelectric phase, due to the correlations of the local polarizations that give rise to a non-zero local order parameter. The evolution with temperature of the proportion of frozen polarization and the local order parameter were estimated from the experimental permittivity data. The temperature dependence of the local order parameter shows the evolution of the system from a short range ordered relaxor to a long range ordered ferroelectric, with increasing the $PbTiO_3$ addition.

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1. Introduction

Ferroelectric relaxors are high performance materials for various applications, based on their exceptional dielectric, electromechanical and pyroelectric properties [1,2]. They are characterized by diffuse phase transition (DPT), non-Debye dielectric dispersion, deviations from the Curie-Weiss law in the paraelectric phase and zero spontaneous macroscopic polarization. Among them, a large number of Pb-based perovskites $Pb(B_1B_2)O_3$ were studied: $Pb(Mg_{1/3}Nb_{2/3})O_3$ [2,3], $Pb(Sc_{1/2}Ta_{1/2})O_3$ [4] and $Pb(Fe_{2/3}W_{1/3})O_3$ [5,6]. The main properties of these systems were explained in terms of polar microregions with non-zero local polarization and short range order (SRO) [1,7,8]. Lead-iron tungstate $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) is a disordered relaxor with Fe^{3+} and W^{6+} ions randomly occupying the B-centres of the unit cell ABO_3. The transition relaxor-paraelectric is not accompanied by structural changes, the material remaining pseudo-cubic down to 10K [9]. The ferroelectric long-range order (LRO) can be induced by the presence of $PbTiO_3$ (PT). A Morphotropic Phase Boundary (MPB), where the pseudo-cubic and tetragonal phases coexist, was found in (1-x)PFW-xPT at T=300K, in the range of compositions $x \in (0.20, 0.37)$ [9-11].

The quantitative description of the transition from relaxor with SRO to ferroelectric LRO by increasing the amount of ferroelectric material in the solid solution is an important feature for understanding the dielectric behaviour of these systems. In the present work, the dielectric data obtained for (1-x)PFW-xPT with various compositions are analysed in the frame of modified Landau cluster theory, by considering the local frozen polarization of the relaxor system.

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2. Experiment

The ceramics (1-x)PFW-xPT with the compositions x=0, 0.2, 0.3 and 0.4 were prepared using a conventional mixed-oxide route [6]. The phase symmetry of the system was checked by XRD using the Rietveld method [6,9,10]. At a fixed temperature, a transition from pseudocubic to tetragonal phase takes place with increasing x, with a large range of compositions for MPB. Consequently, the dielectric response has to reflect the transition from SRO relaxor to LRO ferroelectric, with possible anomalies around MPB, as reported in other relaxor-ferroelectric solid solutions [1,2]. The permittivity and losses were measured at various frequencies f∈ (1kHz, 1MHz) and temperatures (10, 600)K with an impedance/gain phase Analyser (Solartron Model 1260, Farnborough, U.K) with a low-temperature chamber Model Displex APD (Cryogenics, Allentown, PA).

With increasing the addition of ferroelectric PT (x), the character of the phase transition is changing from diffuse, typical for relaxors, as showed as example in Fig. 1 for x=0.2, to a sharp one, characteristic of ferroelectrics. This transition is visible in Fig. 2 where the permittivity of (1-x)PFW-xPT solid solutions at few compositions is plotted as a function of temperature, at a fixed frequency f=100kHz. The temperature corresponding to the maximum value of the dielectric constant is increasing from T_m=180K for PFW (x=0) to T_m=382K for 0.6PFW-0.4PT compound.

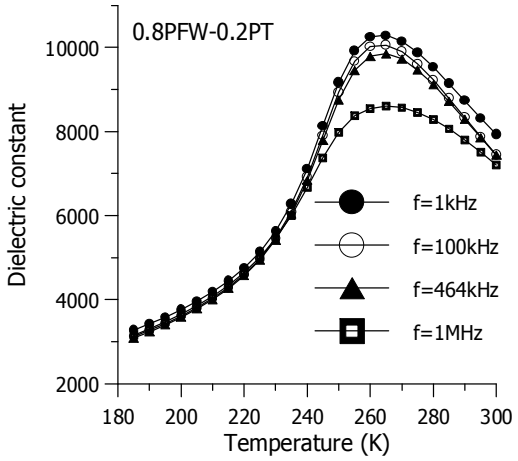

Fig. 1 Permittivity *vs.* temperature at various frequencies for 0.8PFW-0.2PT ceramic.

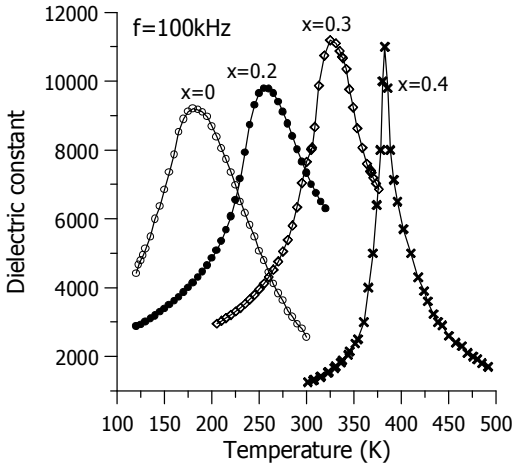

Fig. 2 Permittivity *vs.* temperature of (1-x)PFW-xPT with x=0, 0.2, 0.3 and 0.4 at f=100kHz.

3. Theory and discussion

A Landau-Devonshire (LD) cluster theory that allowed the evaluation of the degree of local order and the proportion of local frozen polarization from the experimental dielectric non-linearity in relaxors was proposed for the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ system [12]. In order to obtain information about the evolution of the local order parameter with temperature and composition, a similar approach was used here for the relaxor-ferroelectric solid solution (1-x)PFW-xPT. The relaxor system is characterised by a field-induced macroscopic polarization P and each nanopolar region (i) by the lattice-site number n_i and its local polarization P_i. The LD free-energy of such system is [12]:

$$F = \frac{1}{2}N\alpha(T)P^2 + \frac{1}{2}\sum_{(i)} n_i\alpha_i(T)P_i^2 + \frac{1}{4}N\beta P^4 + \frac{1}{4}\beta'\sum_{(i)} n_i P_i^4 + \frac{1}{2}\gamma P^2\sum_{(i)} n_i P_i^2 + .. \qquad (1)$$

where N is the total number of lattice sites, $\alpha(T)$ and $\alpha_i(T)$ are LD parameters related to the Curie-Weiss global and local temperatures:

$$\alpha(T)=\frac{T-T_0}{\varepsilon_0 C},\qquad \alpha_i(T)=\frac{T-T_{0i}}{\varepsilon_0 C_i}, \tag{2}$$

C, C_i are the corresponding Curie constants and β, β' and γ the LD coefficients. In this approach, only the interaction between the macroscopic polarization and the local ones was considered, trough the last term in eq. (1), and not the correlation between the individual local polarizations. Using the equilibrium conditions for the local polarizations P_i: $\partial F/\partial P_i=0$, it results:

$$P_i^2=P_{i0}^2-\frac{\gamma P^2}{\beta'}=-\frac{\alpha_i(T)}{\beta'}-\frac{\gamma P^2}{\beta'}, \tag{3}$$

where P_{i0} is the frozen polarization in the equilibrium non-polar state, when global polarization is $P=0$. By substituting eq. (3) in (1), the average free energy becomes:

$$\overline{F}=\frac{1}{2}Na(T)P^2+\frac{1}{4}Nb(T)P^4+cst., \tag{4}$$

where a(T) and b(T) are the re-normalized LD coefficients defined as:

$$\begin{cases} a(T)=\alpha(T)+\gamma q(T) \\ b(T)=\beta-\gamma^2 n(T)/\beta' \end{cases}, \qquad \text{and:} \begin{cases} n(T)=\sum\limits_{(i)} n_i/N \\ q(T)=\sum\limits_{(i)} n_i P_{i0}^2/N \end{cases}. \tag{5}$$

The quantities n(T) and q(T) are directly related to the nanopolar clusters in the relaxor material: n(T) is the density of the lattice sites with frozen polarization and q(T) is a local order parameter associated with the average square value of the local polarization. The low-field dielectric constant is obtained as:

$$\varepsilon^{-1}(T)=\left.\frac{\varepsilon_0 E}{P}\right|_{E=0}=\varepsilon_0 a(T)=\frac{T-T_0}{C}+\varepsilon_0\gamma q(T). \tag{6}$$

This relation shows that the deviations of the permittivity from the Curie-Weiss law are due to the existence of a local non-zero order parameter q(T) far above the temperature T_0. Consequently, eq. (6) provides a method for estimation of the local order parameter q(T). The low-field dielectric data obtained at f=100kHz, for each composition were fitted with the Curie-Weiss law at temperatures far from the Curie region and the constants T_0 and C were found. Using these constants, the function of temperature f(T) proportional with the local order parameter was numerically computed:

$$f(T)=\varepsilon^{-1}(T)-\frac{T-T_0}{C}. \tag{7}$$

An example of such calculation is presented in Fig. 3, where the temperature dependence of the reciprocal permittivity and the function f(T), calculated for the composition x=0.2 are shown. Due to the impossibility of estimation of the LD coefficient γ, the actual values of the function $f(T)=\varepsilon_0\gamma q(T)$ estimated from eq. (7) were extrapolated at 0K. The local order parameter q(T) was considered equal to the ratio between f(T) at each temperature, to its corresponding value at 0K.

Fig. 4 shows the local order parameter *vs.* temperature, for various compositions. In the relaxor state, the local polarizations do not experience suddenly their phase transition and a continuously increasing of the local order parameter with decreasing temperature is observed. On this representation one can notice the evolution of the system from SRO to a higher ordered state of the system. For low x, the local order parameter still has non-zero values far above the Curie-Weiss temperature T_0. In the case of PFW (T_0=173K), q(T) is non-zero up to 280K. In the ferroelectric state, for x=0.4, the local order parameter becomes zero at 420K, closer to the Curie-Weiss temperature of

384 K. This behaviour is consistent with recent results in the Raman activity of the PFW-PT, in which clear indications of the nanopolar ordering far away from the Curie region for low x compositions were found [9,10]. The increasing of the slopes dq(T)/dT with increasing x in Fig. 4 is also in agreement with the tendency of the phase transition to change from a DPT (relaxors) to a sharp one, obtained in the ferroelectric state.

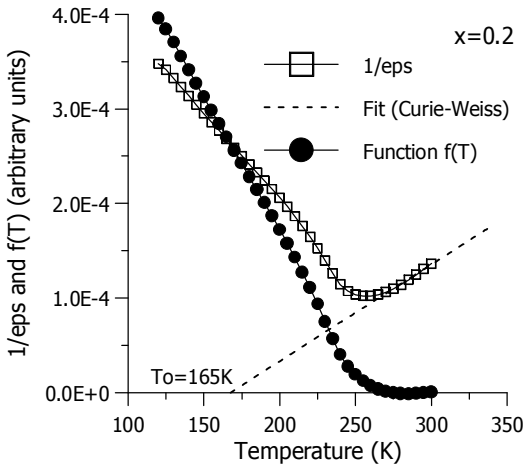

Fig. 3 Reciprocal permittivity *vs.* temperature and f(T) computed for 0.8PFW-0.2PT sample.

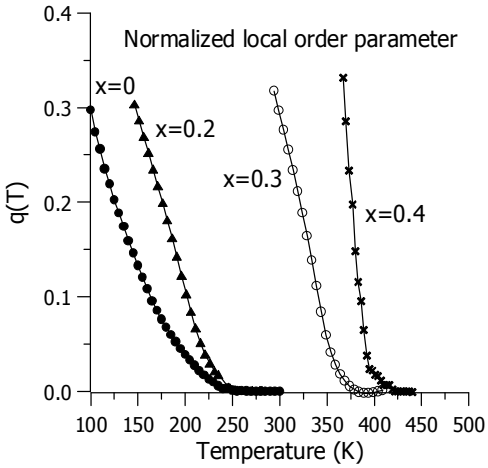

Fig. 4 The local order parameter q(T) as a function of temperature for various x.

4. Conclusions

Using the modified LD model that considers the contributions of the macroscopic and the local polarization, a re-normalisation of the Landau coefficients was obtained. Consequently, deviations of the permittivity from the Curie-Weiss law appear due to the non-zero local order parameter (the average local square polarization). The analysis of the experimental dielectric data obtained for (1-x)$PbFe_{2/3}W_{1/3}O_3$-x$PbTiO_3$ ceramic materials gives a realistic description of the DPT. The dielectric response obtained for various x confirms the results found in the structural and Raman study [9,10], *i.e.* the evolution of the solid solution from a SRO relaxor to a LRO ferroelectric system.

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