On the Imbalance of the Dielectric Constant of the $PbLi_xNb_{3x}Zr_{0.51}Ti_{0.49-4x}O_{3}$ Compound

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July, 5 1996

Abstract

In the present paper, the dielectric behaviour of the $PbLi_xNb_{3x}Zr_{0.51}Ti_{0.49-4x}O_{3}$ (PLNZT) system is analyzed. It is shown that the decrease in the dielectric constant with respect to an increase of the impurity content may be due to an aggregation trend of the interacting off-centre dipoles rather than due to cooperative phenomena which renormalizes the dipole moment of the off-centre impurity.

PACS 64.70Kb - Solid-solid transitions
PACS 77.22Gm - Dielectric loss and relaxation
PACS 77.84Dy - Niobates, titanates, tantalates, PZT ceramics, etc.
Off-centre impurity doped perovskite compounds like $PbMg_{1/3}Nb_{2/3}O_3$ ($PMN$), $PbSc_{1/2}Ta_{1/2}O_3$ ($PST$), $K_{1-x}Li_xTaO_3$, with $x < 0.022$, ($KLT$) belong to the large family of relaxors. These relaxor systems currently receive a great deal of interest due to the fact that, in very small concentrations, the off-centre impurities are able to stabilize the ferroelectricity within relatively large domains of the crystals. Experimentally, for a relaxor behaviour, the dielectric constant must show a maximum as a function of the off-centre impurity content. When the off-centre impurity content is increased the dielectric constant increases initially and then, above a critical concentration, it decreases asymptotically. The critical concentration above which the dielectric constant decreases with respect to the impurity content is larger than the limiting concentration needed for "ordering" to occur. In the case of the KLT system, for example, the critical concentration is $x_c = 2.8 \times 10^{-2}$ while, relatively large macroscopic, uniformly polarized regions with a length scale of at least $10^3 - 10^4 \text{ Å}$ appears when $0.6 \times 10^{-2} < x < 1.6 \times 10^{-2}$.

Recent experimental results have revealed a similarity between the dielectric constant of $K_{1-x}Li_xTaO_3$ ($KLT$) and $PbLi_xNb_{3-x}Zr_{0.51}Ti_{0.49-x}O_3$ ($PLNZT$). This suggests the existence of a possible off-centre configuration for the impurities which have been introduced in the PZT host matrix. The behaviour of the dielectric constant of $PLNZT$ with respect to the impurity concentration ($Nb$ and $Li$) shows a maximum at $x_c = 1.3 \times 10^{-2}$. The initial increase of the dielectric constant is understood in terms of a self-consistent mean-field approach and the theoretical results agree well with the experimental data (see Fig. 1). The decreasing trend of the dielectric constant for $x > x_c$ has been tentatively attributed to cooperative phenomena which reduce the effective dipole moment of the off-centre impurity (see the curve $\varepsilon_1$ in the Fig. 1). Agreement with experimental data is rather poor.

As is known, the most intriguing property of off-centre systems is that they carry a permanent electric dipole moment. Because of this, when impurities of this kind are introduced in a host matrix, the permittivity $\varepsilon$ of the crystal increases and becomes strongly dependent on frequency. Increasing the content of the off-centre dipoles within a well-established range, the ferroelectric interaction strengths between off-centre dipoles overcomes the strength of the extra random fields. This stabilizes the ferroelectricity. Moreover, when the dipole concentration exceeds the critical one (usually,
larger than the limiting concentration needed for "ordering" to occur[1], additional complexity in the dynamical behavior may appear. On one side, dipolar correlations occur, and these not only reduce the polarizability of the system[2] (this decreases the dielectric constant) but functionally change the dipole-dipole interaction energy dependence on the spacing of dipoles[2, 4]. On the other hand, the dipolar interaction between randomly distributed off-centre impurities facilitates the aggregation of a small fraction of impurity content. See, for example, the case of the KLT system; \((\text{Li}^+)_2\) are most frequently present above the critical concentration[3, 11, 10, 11]. This leads to an extremely long relaxation time[9, 11, 12], having implications for the hysteresis loop as well as for the dielectric constant[5]. The same behavior has been qualitatively seen within the SCT system[7] where, in addition to conventional non-linear response, important paraelectric cluster contributions were revealed. As in the previous case, this may be understood as a consequence of the aggregation of the interacting off-centre \(\text{Ca}^{++}\) dipoles.

In the present paper, it is shown that the decrease in the dielectric constant of the PLNZT system with respect to the increase in impurity content[8] may be due to the aggregation trend of the interacting off-centre dipoles rather than due to cooperative phenomena which renormalize the dipole moment of the off-centre impurity.

The initial increase of the dielectric constant with respect to impurity content (see in Fig. 1 below of \(x_c\)) can be described by a self-consistent mean-field theory using a Clausius-Mossotti equation

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} + \frac{4\pi}{3} x (\chi_o \text{Li} + 3\chi_o \text{Nb}) ,
\]

where \(\varepsilon_0\) is the permittivity of the host matrix which in our case has a high polarizable character, and \(\chi_{o \text{Li},\text{Nb}}\) stands for the single-particle polarizability of noninteracting impurities. In the framework of classical theories[2], the latter is expressed by

\[
\chi_{o \text{Li},\text{Nb}} = \frac{2d_{o \text{Li},\text{Nb}}^2}{3\Delta} \lambda h \left( \frac{\Delta}{2kT} \right) \simeq \frac{d_{o \text{Li},\text{Nb}}^2}{3kT} ,
\]

where \(\Delta\) is the tunneling energy and, usually, \(\frac{\Delta}{k_B} \approx 1K\), and \(d_{\text{Li},\text{Nb}}\) are the intrinsic dipole moments determined by the off-center displacement magnitude of Li and Nb respectively. Agreement between the theoretical (eq. 1) and
experimental curves for the increasing region was obtained for $d_{Li}^2 + 3d_{Nb}^2 \simeq 0.0075 e^2 10^{-20} m^2$ [8]. When cooperative phenomena occur, the single-particle polarizability is expressed by [2]

$$
\chi_{Li,Nb}^0 = \chi_{o Li,Nb} \left( 1 - x \frac{4\pi d_{Li,Nb}^2}{3 kT \varepsilon_0} \right),
$$

(3)

where

$$
d^o = \frac{\gamma \varepsilon_0}{3} d_{Li,Nb}
$$

(4)

is the effective dipole moment of the impurity in a highly polarizable matrix [2]. Equation (3) correctly describes the single-particle polarizability within the framework of the self-consistent mean-field approximation which means $x \gg x_c$. In this case ($x \gg x_c$), the mean spacing between the impurities becomes small enough to reduce the fluctuations of the local fields (it is known that the existence of the fluctuations of the local fields invalidates the mean-field theories [2]). The dielectric constant for the decreasing part has been calculated [8] using (3) (see in Fig. 1 the curve $\varepsilon_1$). As one can see agreement with the experimental data in this region is rather poor.

Let us assume that, for different reasons (mainly, related to the off-centre dipole pairwise interaction discussed in the introduction), the impurities aggregate in small clusters. In all probabilities, the aggregation process is strongly mediated by the peculiar nature of the off-centre crystalline field which, as is known, has a certain number of separate potential minima around the normal position in the host lattice. Another argument which supports the above supposition is the case of Na-doped fullerites [13] where the solute is identified both in off-centre locations [14, 15] and in small clusters within the octahedral interstices [16]. In our case, the aggregation phenomenon may lead to the appearance of an effective dipole moment (smaller than that corresponding to a free off-centre dipole). On the other hand, it may obstruct, progressively, the reorientation possibility of the permanent off-centre dipoles until these are complete blocked. The former case occurs as long as the potential wells of the off-centre configuration is only partially occupied. The latter case occurs when the dipoles are completely blocked and should coincide with the occupation of all the potential wells of the off-centre configuration. In fact, concerning the last situation, we may say that the dipole moment no longer exist. Note that, actually, the off-centre potential is realized for a single substitutional particle interacting with the host ions. The
balance between the repulsive and the polarization forces destabilizes the central equilibrium. In the case of more particles, the potential curvature of the off-centre configuration may be drastically changed, but it will be disregarded herein.

The aggregation phenomena assume that in our case, over the critical concentration, the substitutional impurities are not uniformly spread over the corresponding vacancy sites of the host matrix. They prefer, with a higher probability, to form small intercalated clusters (dimers, trimers, etc). In this view, the added impurities, whose number is \((N - N_c)\), where \(N_c\) is the initial (critical) number of off-centre impurities, get places on the available off-centre sites which are in a total amount of \(n \times N_c\), where \(n\) is the number of the potential wells in a given off-centre configuration. The remaining number of the free off-centre dipoles is \(N_c \times (1 - P) - (N - N_c) \times P = N_c - N \times P\), where \(P\) is the probability for an added impurity to occupy one potential well of the off-centre configurations. Neglecting the fact that this probability should depend on the strength of the off-centre dipole pairwise interaction, it may be readily approximated by \(P = \frac{(nN_c - (N - N_c))!}{nN_c!(N - N_c)!}\). The dielectric constant of the system characterized by the above number of the off-centre dipoles becomes

\[
\varepsilon_2 = \varepsilon_o \left( \frac{1}{\varepsilon_o + 2} + 2(x_c - Px) \chi_o \right). 
\]

In Fig. 1 experimental data is shown for the dielectric constant of the PLNZT system versus the impurity content [8]. Also, theoretical curves are given for its decreasing region which correspond both to the cooperative phenomena approach (see \(\varepsilon_1\)) and to the aggregation phenomenon approach (see \(\varepsilon_2\)). As one can observe in the case of the curve \(\varepsilon_2\), agreement with the experimental data is improved. This means that for the PLNZT system, there exists an aggregation trend of the off-centre impurities when their content overcomes a critical point.

Within the present paper, we have shown that, under some circumstances, especially related to the aggregation phenomenon of impurities mediated by off-centre configurations, the dielectric constant corresponding to the off-centre impurity doped crystals may decrease with the increase of the off-centre impurity content. Aggregation phenomena of these kinds of impurities have been seen experimentally by various techniques [4, 7] and, as one observes, studying the change of the dielectric constant by the increase of the...
content of the off-centre impurities may also, be a useful tool in this respect. 

Acknowledgement. The author thanks Dr. J. Lawson for technical help. Also, he would like to thank Professor E. Tosatti for his kindly hospitality during the stay at ICTP - Trieste.

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Figure Captions

Figure 1 - Dielectric constant $\varepsilon$ versus impurity content $x$ for the PLNZT system (experimental data available from [8]; $\varepsilon_1$ - theoretical results within the cooperative phenomena approach, $\varepsilon_2$ - theoretical results within the aggregation phenomenon approach.