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LETTER TO THE EDITOR

Verification of the Thomas theoretical framework for A-substituted $\text{PbB}_n\text{Nb}_m\text{O}_3$ relaxor ferroelectrics

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Abstract

A Thomas theoretical framework (Butcher J and Thomas N W *J. Phys. Chem. Solids.* 1991 **52** 595) for $\text{PbB}_n\text{Nb}_m\text{O}_3$ relaxors is verified by analysing the rate of the fall-off in the dielectric permittivity maximum, ε_m , with the concentration x for several A-substituted $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbB}^{3+}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ($\text{B}^{3+} = \text{Sc, In, Yb}$)-based solid solutions. For the solid solutions with isovalent A-substitution ($\text{Ba} \rightarrow \text{Pb}$) the experimental dependencies of the $\varepsilon_m(x)/\varepsilon_m(x=0)$ ratio on x were found to be scaled to a unique curve, $(1-x)^{\alpha(x)}$, where $\alpha(x)$ is a sharply decreasing function at small x . At intermediate values of x α values are close to eight. Only this value corresponds to the assumption of Thomas that a Nb ion is ferroelectrically active only if it is surrounded by eight Pb ions. Reasons for the deviations of α from eight at small and large x are discussed.

1. Introduction

$\text{PbB}_n\text{Nb}_m\text{O}_3$ relaxor ferroelectrics exhibit a so-called A-site dilution effect [1]: all of the A-site alloying, regardless of type (e.g. donor, acceptor, isovalent and vacancy), lower the temperature T_m of the dielectric permittivity ε maximum and increase the $\varepsilon(T)$ diffusion and ε frequency dispersion. Such a universal character of the A-site substitution effect on the properties of $\text{PbB}_n\text{Nb}_m\text{O}_3$ compounds implies that rather simple structural models can be employed for analysing the A-substituted $\text{PbB}_n\text{Nb}_m\text{O}_3$ behaviour. The most well known of such models was developed by Thomas [2] in terms of the contributions made by individual NbO_6 octahedra which are believed to be polar units and are said to be 'ferroelectrically active'. This assumption is in line with the results of the crystal field calculations in $\text{PbB}^{3+}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ($\text{B}^{3+} = \text{Yb, Sc, In}$) perovskites [3,4], carried out in the frame of the point-polarizable ion model. The calculations have shown that the field at the Nb site appears to be the largest among the local fields at the different ionic positions. This result indicates the predominant contribution of the Nb sublattice to the dielectric permittivity ε . The second important assumption of the Thomas framework is that Nb octahedra are coupled to each other via the A-site Pb ions. This assumption is also justified by the results of the above-mentioned calculations [4] showing that the fields created by Pb ions make the main contributions to the crystal field value at the Nb site. Hence, the niobium ion is ferroelectrically active only if it is surrounded by eight Pb ions. In the case when there is even one A-site ion nearby other than Pb, the Nb ion becomes

ferroelectrically inactive. Although being rather simplified, this framework correctly predicts some important trends in relaxor properties and has been widely employed by others [1, 5–7]. In order to check this model, the fall-off in the dielectric permittivity maximum ε_m , with the concentration x , for the $\text{Pb}_{1-x}\text{Ba}_x\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ solid solution ceramics were compared with the computed probability, w , of the situation when a Nb ion is surrounded by eight Pb ions [8]. Although there was a qualitative coincidence between experimental and theoretical data, the grounds for the model were not justified by separate theoretical or experimental investigations. The present work develops the Thomas model and verifies it by using the data of different experiments.

2. Results and discussion

When computing the probability w , Thomas considered a cube containing $64 \times 64 \times 64$ unit cells of the solid solution. The A ions as well as the Nb and B ions were distributed randomly throughout the corresponding atomic sites. Thereafter, the number of the ferroelectrically active octahedra was computed quantitatively for a large set of the realizations of the ionic distributions. The resulting values of w were plotted versus the concentration x and compared to the experimentally measured $\varepsilon_m(x)/\varepsilon_m(x=0)$ ratio. Qualitatively good coincidence of these data was obtained.

We found that in order to estimate the value of w one can employ a binomial distribution according to which the desirable probability is described by a simple analytical expression, $w = (1-x)^\alpha$, where $\alpha = 8$. This expression assumes the distribution of the impurities to be uniform. Indeed, the probability of finding the Nb ion surrounded by eight Pb ions is the same as the probability of finding the Pb ion in one of the positions, $1-x$, in the power eight. We compared this expression with the result of the complicated computation performed in [8] and found that the analytical expression nicely reproduces the computational results. We should draw attention to the fact that both the binomial distribution and the computational scheme employed in [8] consider the distribution of the A ion through the Pb sites for independent species, although, in fact, they do interact with each other due to the different ionic radii of the A and Pb ions. Hence, the model employed is perfectly good only in the case when the A ion has the uniform distribution function.

The analytical expression for w obtained by us offers an opportunity for a more precise verification of the Thomas framework. For this purpose we used the data on the dielectric properties of Ba- and La-substituted $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ [9–11] and Ba-substituted $\text{PbB}^{3+}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ($\text{B}^{3+} = \text{Sc, In, Yb}$) [12–14] ceramics compiled in the literature as well as our data on $\text{Pb}_{1-x}\text{Ba}_x\text{Sc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ crystals [15]. In the case of $\text{PbB}^{3+}_{0.5}\text{Nb}_{0.5}\text{O}_3$ compounds special attention was paid to eliminate the influence of compositional ordering on the results obtained. For this reason only the data for highly disordered samples have been selected. As the ε_m values of $\text{PbB}_n\text{Nb}_m\text{O}_3$ ceramics depend dramatically on the presence of even small amounts of parasitic non-perovskite phases with low ε , segregated at grain boundaries [16], ε_m values measured on single crystals were used for $x = 0$ compositions. The ceramic compositions of $\text{Pb}_{1-x}\text{Ba}_x\text{Yb}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid solutions with low x under the sintering conditions used in [14] possessed a high degree of Yb^{3+} and Nb^{5+} ordering and the ordering vanished only for compositions with $x > 0.16$. Only the data on the samples with $x = 0.2$ and 0.3 were used in our analysis because for these compositions the $T_m(x)$ dependence is approximately linear and its extrapolation to $x = 0$ gives $T_m \approx 150^\circ \text{C}$. This value agrees well with the T_m of disordered $\text{PbYb}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ceramics [17]. As the ε_m value of disordered $\text{PbYb}_{1/2}\text{Nb}_{1/2}\text{O}_3$ is yet unknown because the ceramic samples obtained in [17] contained a large amount (up to 50%) of pyrochlore phase, the ε_m value of disordered $\text{PbYb}_{1/2}\text{Nb}_{1/2}\text{O}_3$ crystals was estimated

using the ε_m values of $\text{PbYb}_{1/2}\text{Nb}_{1/2}\text{O}_3$ crystals with different values of ordering degree S [18], assuming the $\varepsilon_m(S)$ dependence for $\text{PbYb}_{1/2}\text{Nb}_{1/2}\text{O}_3$ is similar to that for $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ [19].

Figure 1 shows the concentration dependence of α deduced from the $\varepsilon_m(x)/\varepsilon_m(x=0)$ ratio at 1 kHz in the case of isovalent Ba-substitution for several solid solution ceramics. In contrast to the Thomas model, for which α equals eight and should not depend on x , the α value varies crucially with x . We fitted the critical dependence, $\alpha = x^{-n}$, to the experimental data and found the exponent $n = 0.47$. We think that the decrease of α with x corresponds to the decrease of the (polar) volume where the substitutions in the A sites are absent (near the Nb ions). This implies that the critical dependence found is no longer true at very small x where α exceeds the polar region of the pure samples (without the A-substitutions). On the other hand, probably, in the $0.2 < x < 0.4$ region the polar volume reduces to eight unit cells and the α values for all the solid solutions studied are close to eight and the $\alpha(x)$ dependence seems to be less steep than at lower and higher x values. Unfortunately, the lack of available experimental data on the A-substituted $\text{PbB}_n\text{Nb}_m\text{O}_3$ ceramics prevents us from making a definite conclusion. In order to check this observation we used our data on the $\text{Pb}_{1-x}\text{Ba}_x\text{Sc}_{0.5}\text{Nb}_{0.5}\text{O}_3$ solid solution crystals with $0 \leq x \leq 0.6$ grown by the flux method [15]. The results obtained are plotted in figure 2 and confirm that in the $0.2 < x < 0.3\text{--}0.4$ region α is close to eight and is nearly independent of x , in accordance with the Thomas framework. The decrease in α values at $x > 0.35$ is likely to be attributed to the fact that $x = 0.33$ corresponds to the percolation threshold for A-site dopants. Above this concentration they form infinite clusters, i.e. cannot be treated as independent species, implying that both the analytical expression for w obtained above and the computational scheme employed in [18] becomes invalid.

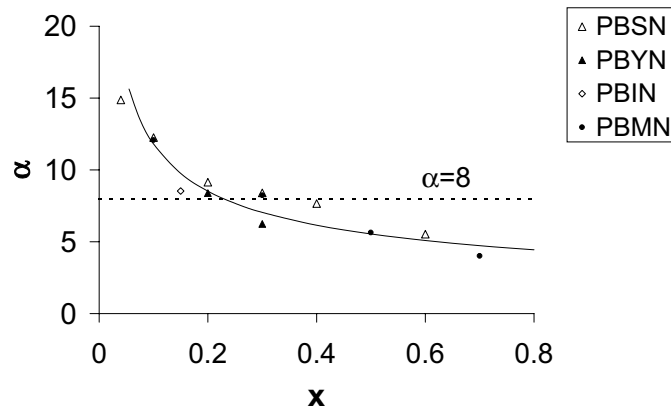


Figure 1. Concentration dependencies of exponent α deduced from the $\varepsilon_m(x)/\varepsilon_m(x=0)$ values at 1 kHz for some Ba-substituted $\text{PbB}_n\text{Nb}_m\text{O}_3$ ceramics. PBMN: $\text{Pb}_{1-x}\text{Ba}_x\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ [6]. PBSN: $\text{Pb}_{1-x}\text{Ba}_x\text{Sc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ [12]. PBIN: $\text{Pb}_{1-x}\text{Ba}_x\text{In}_{1/2}\text{Nb}_{1/2}\text{O}_3$ [13]. PBYN: $\text{Pb}_{1-x}\text{Ba}_x\text{Yb}_{1/2}\text{Nb}_{1/2}\text{O}_3$ [14]. The solid line shows the fit by $\alpha = 4x^{-0.47}$ curve.

In the case of La-substituted $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ (PMN-PT) solid solutions the situation is more complicated, as can be seen from figure 3. This is due to the fact that compensation of La^{3+} excess charge is usually achieved by changing the Mg/Nb ratio, i.e. the host matrix composition is changed with x . Nevertheless, some qualitative conclusions may be derived for these objects as well. For $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and PMN-PT with Ti content lower than critical value $x = 0.33$, corresponding to a rhombohedral-tetragonal morphotropic phase boundary [20], the character of α versus x dependence for La-doping is qualitatively

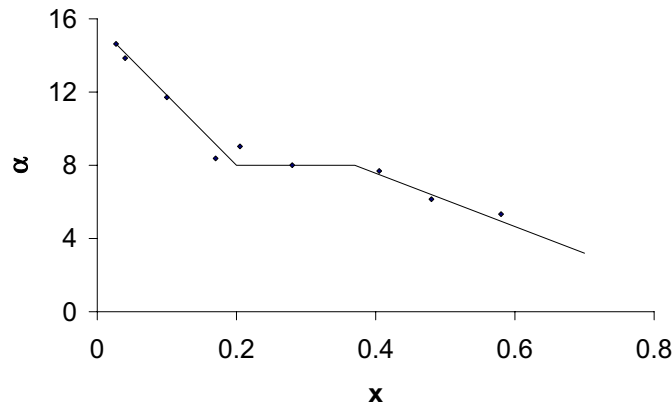


Figure 2. Concentration dependence of exponent α deduced from the $\varepsilon_m(x)/\varepsilon_m(x=0)$ values at 1 kHz for $\text{Pb}_{1-x}\text{Ba}_x\text{Sc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ crystals [15]. The solid line is a guide to the eye.

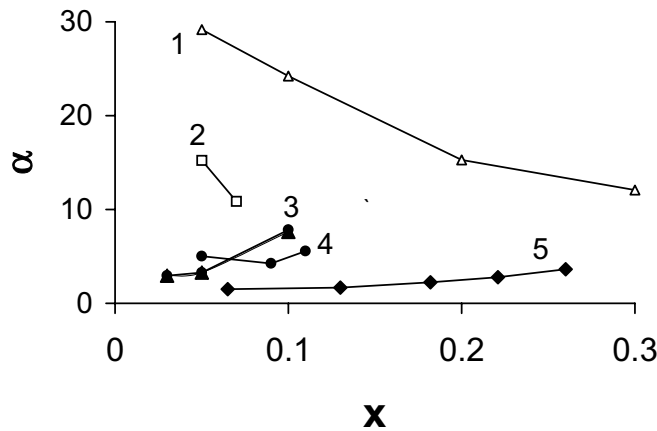


Figure 3. Concentration dependencies of exponent α deduced from the $\varepsilon_m(x)/\varepsilon_m(x=0)$ values at 1 kHz for some $(1-x-y)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_{3-x}\text{LaMg}_{2/3}\text{Nb}_{1/3}\text{O}_3-y\text{PbTiO}_3$ solid solutions (1–4) and PLZT30/70 [21] (5). 1. $y=0$ [9]. 2. $y=0.275$ [10]. 3. $y=0.35$ [11]. 4. $y=0.4$ [10]. In the case of PLZT30/70 the nominal La content was multiplied by a factor 1.5 to take account of lead vacancy concentration. Solid lines are guides to the eye.

the same as that for Ba-doping. In contrast to this, both the α values and the character of α versus x dependence for PMN-PT compositions with $x = 0.35$ and $x = 0.4$, i.e. exceeding 0.33, are sharply different. It seems that the difference between PMN-PT compositions with low and high Ti content originates from the change of ferroelectrically active sublattice (from Nb to Pb) in the vicinity of the rhombohedral-tetragonal morphotropic phase boundary. This supposition is confirmed by the fact that α values and the character of α versus x dependence similar to that observed for PMN-PT compositions with $x > 0.33$, have been obtained for PLZT ceramics using the data from [21]. It is well known [22] that in PLZT, PZT and other PbTiO_3 -based solid solutions the Pb-sublattice is ferroelectrically active. Thus the Thomas framework based on the assumption of ferroelectrically active Nb sublattice is inapplicable in the case of PMN-PT compositions with a high Ti content.

3. Summary

The experimental and theoretical studies show that the Thomas framework for the $(\text{Pb}_{1-x}\text{A}_x)\text{B}_n\text{Nb}_m\text{O}_3$ solid solutions [2,8] is true at the intermediate concentration of the isovalent impurities (from $x \approx 0.2$ to $x \approx 0.3-0.4$). At x values exceeding the percolation threshold the assumption that the A ion has a uniform distribution function does not hold. At low x range the Thomas framework should be corrected as well. The polar region volume should decrease with the concentration of the impurities. Only this result has been obtained from the fit of the experimental data in the present study. The result obtained is also in good accordance with the experimental data showing a large decrease of the polar region volume and radius with the concentration of the second component in several BaTiO_3 -based solid solutions [23,24].

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