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Empirical scaling of the dielectric permittivity peak in relaxor ferroelectrics

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Dielectric permittivity ε as a function of temperature is measured in $PbMg_{1/3}Nb_{2/3}O_3$ and a number of other relaxor ferroelectrics with the perovskite structure. It is found that the data taken from the high-temperature slopes of the diffused permittivity peaks of all the materials studied can be collapsed onto a single scaling line derived from the formula $\varepsilon_A/\varepsilon = 1 + 0.5(T-T_A)^2/\delta^2$, where ε_A, T_A, and δ are the parameters depending on the composition. This formula describes the static conventional relaxor susceptibility, which provides the dominant contribution to the permittivity peak at temperatures above the temperature of the maximum. In the close vicinity of the peak temperature and below, the scaling is disturbed due to the conventional relaxor dispersion.

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The broad peak in the temperature dependence of dielectric permittivity ε is one of the main features of relaxor ferroelectrics. In classical relaxors, strong frequency dispersion is observed at the low-temperature slope of this peak, while the high-temperature slope is almost independent of frequency, so that the position of the permittivity maximum, T_m, shifts to higher temperatures with increasing frequency, satisfying the characteristic Vogel-Fulcher behavior.[1] Because of the smearing of the anomaly of the permittivity (and some other properties), relaxors look like, and are usually classified as, ferroelectrics with diffused phase transition. At temperatures well below T_m a nonergodic relaxor phase may transform into a nonergodic glassy phase (the well-known example is $PbMg_{1/3}Nb_{2/3}O_3$) or to a normal ferroelectric phase, e.g., in $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ solid solutions or $PbSc_{1/2}Nb_{1/2}O_3$. At temperatures significantly above T_m the behavior resembles that of the paraelectric phase in normal ferroelectrics with the temperature variation of the permittivity following the Curie-Weiss law. It was recently discovered that the dielectric Curie-Weiss law in relaxors is related to the displacive-type ferroelectric soft mode.[2] At $T<T_d$ (T_d is typically hundreds of degrees higher than T_m) the soft mode becomes overdamped and the Curie-Weiss law is violated.

The nature of the dielectric peak and other properties of relaxors are under extensive discussion now. It was proposed that the peak originates from the relaxation reorientation of the polar regions of a few dozens nanometers size existing in the corresponding temperature range, or from the relaxation of the boundaries of these polar regions.[3] Experimental evidences were later found to support both hypotheses,[4,5] but do not allow us to unambiguously adopt any particular one.

In the normal ferroelectrics, the Curie-Weiss law $1/\varepsilon = (T-T_C)/C$ is known to describe the high-temperature slope of the sharp permittivity peak with a single shape parameter C. This law can be derived from general theories of ferroelectric phase transitions. For relaxor ferroelectrics the existing theories do not propose such a universal formula to describe the dielectric behavior; therefore it is rewarding to find it out experimentally to provide the basis for further theoretical investigations.

There were several attempts to describe the relaxor permittivity peak empirically (see Ref. 6 for a brief review). The most popular formula[7,8]

$$\frac{\varepsilon_m}{\varepsilon} = 1 + B(T-T_m)^\gamma \tag{1}$$

contains frequency-dependent quantities, T_m and ε_m (the value of the maximum permittivity). As a result, the parameters defining the shape of the function, γ and B, also depend on frequency and thereby are not fully appropriate for describing the frequency-independent high-temperature slope of the permittivity peak. Furthermore, these parameters appear to be different not only in different materials, but sometimes also in different temperature intervals of the same material.[9]

It was recently[6] found that in $0.75PbMg_{1/3}Nb_{2/3}O_3$-$0.25PbTiO_3$ relaxor ceramics a single shape parameter, δ, is good enough to describe the permittivity in a wide temperature range above T_m using the expression

$$\frac{\varepsilon_A}{\varepsilon} = 1 + \frac{(T-T_A)^\gamma}{2\delta^2}, \tag{2}$$

where T_A ($<T_m$) and ε_A ($>\varepsilon_m$) are the parameters defining the temperature position of the peak and the extrapolated value of ε at $T=T_A$, respectively, and γ is a diffuseness exponent which was found to be exactly equal to 2. It was also shown that Eq. (2) with $\gamma=2$ may be approximated within certain temperature intervals by Eq. (1) with the parameters B and γ which had been reported in the literature for some other relaxors. Thus, one can expect that the new quadratic formula (2) is the universal expression for many relaxor ferroelectrics. In this paper we show that it is indeed so. The data for a large number of materials with different broadness of $\varepsilon(T)$ maximum can be collapsed perfectly onto a single scaling line derived from Eq. (2) with the diffuseness exponent $\gamma=2$.

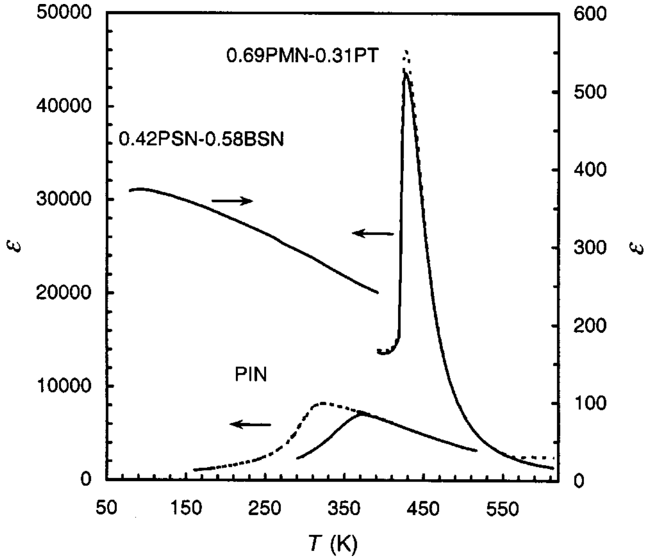

FIG. 1. Dielectric permittivity vs temperature for some of the crystals studied. The solid and dashed lines represent the data for high and low frequencies, respectively (100 kHz and 10 Hz for 0.69PMN-0.31PT, 1 MHz and 100 Hz for PIN, and 1 kHz for 0.42PSN-0.58BSN).

We have studied different perovskite relaxors: lead-containing ternary single crystals and ceramics of 1:1 type [$PbSc_{1/2}Nb_{1/2}O_3$ (PSN), $PbIn_{1/2}Nb_{1/2}O_3$ (PIN), $(1-x)$PSN-xBSN (BSN stands for $BaSc_{1/2}Nb_{1/2}O_3$), $PbFe_{1/2}Ta_{1/2}O_3$] and 1:2 type [$PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $(1-x)$PMN-xPT (PT stands for $PbTiO_3$), $PbZn_{1/3}Nb_{2/3}O_3$ (PZN), $(1-x)$PZN-xPT, $(1-x)$PMN-xPSN], as well as lead-free relaxor ceramics of $0.85NaNbO_3$-$0.15SrCu_{1/3}Nb_{2/3}O_3$. Sample preparation, measurement procedures, and properties of the materials were described in Refs. 10 and 11.

The materials selected for the investigation show very different degrees of dielectric peak diffusion ranging from very broad peak in 0.42PSN-0.58BSN to comparatively sharp one in $(1-x)$PMN-xPT, which looks almost like in normal ferroelectrics (see Fig. 1). We measured the real part of permittivity at different frequencies and temperatures around and above T_m for more than 30 samples of 26 different compositions [in addition to the compositions presented in Table I, $(1-x)$PMN-xPT, $(1-x)$PZN-xPT, $(1-x)$PSN-xPT, and $(1-x)$PSN-xBSN solid solutions with different x were also studied]. The data from the high-temperature slope of $\varepsilon(T)$ maximum (starting from temperatures several degrees higher than T_m) were fitted to Eq. (2) by means of least-squares procedure with adjusting parameters T_A, ε_A, δ, and γ (the criteria for choosing the appropriate measurement frequencies for fitting will be discussed below). No correlation between γ and composition has been noticed. The average value of γ was found to be equal to 2.00 ± 0.03, indicating that the dependence of $1/\varepsilon$ on $T-T_A$ is indeed quadratic. The same data were then fitted to Eq. (2) with fixed $\gamma=2$. The resultant parameters and the frequencies at which the fitting were performed are summarized in Table I. Using the best-fit values of T_A, ε_A, and δ, we plotted in Fig. 2 the data for different compounds as $[\log_{10}(\varepsilon_A/\varepsilon-1)+2\log_{10}\delta]$ vs $\log_{10}(T-T_A)$. In such a presentation, all data points satisfying Eq. (2) should lie on a single straight line.[12] As one can see, for all compounds studied the scaling is valid in a wide temperature interval ΔT_s (the values of ΔT_s are presented in Table I). At higher temperatures the Curie-Weiss law is known to hold (the high-temperature data points which fall apart from the scaling line are not shown in Fig. 2). For some materials the scaling works up to the highest temperatures measured.

At temperatures below $T=T_m+\Delta T_r$, the scaling also becomes violated. The interval ΔT_r varies from 2 to 9 K in different materials. This violation is due to the characteristic dielectric dispersion, which exists around and below T_m [the so-called conventional relaxor dispersion,[10] (CRD)]. Upon heating at $T=T_m+\Delta T_r$, this dispersion disappears and the

TABLE I. Characteristic scaling parameters of selected relaxor ferroelectric materials.

No.	Compound	f (kHz)	T_m (K)	$10^{-2}\varepsilon_m$	T_A (K)	δ (K)	$10^{-2}\varepsilon_A$	ΔT_s (K)
1	$PbMg_{1/3}Nb_{2/3}O_3$[a]	100	276	190	262	41	206	200
2	$PbMg_{1/3}Nb_{2/3}O_3$[b]	100	280	102	264	46	105	190
3	$PbZn_{1/3}Nb_{2/3}O_3$[a]	100	424	358	416	28	419	>190
4	$PbSc_{1/2}Nb_{1/2}O_3$[a]	1	380	377	348	36	567	130
5	$PbIn_{1/2}Nb_{1/2}O_3$[a]	1000	370	73.1	338	109	77.1	>150
6	$PbFe_{1/2}Ta_{1/2}O_3$[a]	100	251	288	248	20	294	60
7	0.69 $PbMg_{1/3}Nb_{2/3}O_3$-0.31 $PbTiO_3$[a]	100	427	444	425	22	458	150
8	0.65 $PbMg_{1/3}Nb_{2/3}O_3$-0.35 $PbTiO_3$[b]	100	451	360	426	20	549	120
9	0.77 $PbMg_{1/3}Nb_{2/3}O_3$-0.23 $PbSc_{1/2}Nb_{1/2}O_3$[a]	10	278	151	243	57	189	>80
10	0.955 $PbZn_{1/3}Nb_{2/3}O_3$-0.04 $PbTiO_3$[a]	100	439	311	425	31	360	>130
11	0.92 $PbSc_{1/2}Nb_{1/2}O_3$-0.08 $BaSc_{1/2}Nb_{1/2}O_3$[a]	1	321	108	294	81	115	>100
12	0.42 $PbSc_{1/2}Nb_{1/2}O_3$-0.58 $BaSc_{1/2}Nb_{1/2}O_3$[a]	1	92	3.73	39	332	3.79	>300
13	0.85 $NaNbO_3$-0.15 $SrCu_{1/3}Nb_{2/3}O_3$[b]	1	133	8.34	132	200	8.34	180

[a] Single crystals.

[b] Ceramics.

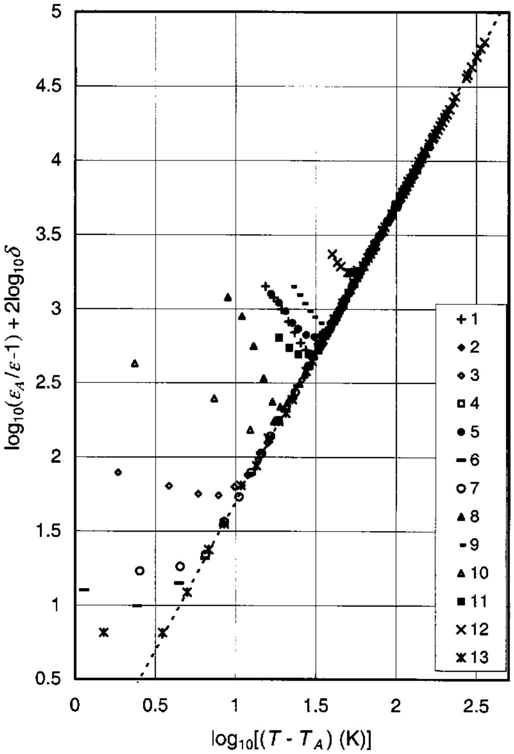

FIG. 2. Scaling plot for the data related to different compositions. The curves are numbered in accordance with the numbering of the compositions in Table I.

conventional relaxor permittivity reaches its low-frequency limit, ε_{R0}. At higher temperatures ε ($=\varepsilon_{R0}$) follows Eqs. (2) with $\gamma=2$. Such a conclusion has been drawn on the basis of our investigation of 0.75PMN-0.25PT ceramics.[13] We have shown that it is just the static conventional relaxor permittivity, ε_{R0}, that follows Eq. (2) at $T>T_m+\Delta T_r$. We can also hypothesize that at lower temperatures ε_{R0} continues holding Eq. (2) and thus T_A and ε_A have the meaning of the temperature and the magnitude of the $\varepsilon_{R0}(T)$ maximum, respectively. But it is not easy to check this hypothesis experimentally, because CRD is observed in relaxors down to the lowest practically available measurement frequencies so that the static permittivity cannot be measured at T_A using conventional dielectric techniques.

It should be underlined that as long as the high-temperature slope of the permittivity peak is independent of frequency, the parameters of Eq. (2), obtained by fitting to this slope, will also be necessarily frequency-independent. But in relaxor ferroelectrics (as well as in any dielectrics) there often exist more than one polarization mechanism contributing to the dielectric permittivity. Clearly, these additional contributions to the permittivity do not follow Eq. (2) and they could disturb scaling. For instance, in PMN and PMN-PT comparatively small but appreciable universal relaxor susceptibility, χ_U, has been found in addition to the conventional relaxor contribution, so that the total permittivity at $T>T_m(f)+\Delta T_r$ can be written as $\varepsilon(T,f)=\varepsilon_{R0}(T)+\chi_U(T,f)$.[10,14] In the whole frequency range accessible for measurements χ_U decreases with frequency as $\chi_U \propto f^{n-1}$ (n is close to but smaller than unity). This dispersion can clearly be seen in Fig. 1 for 0.69PMN-0.31PT crystal around and above the maximum. Upon heating, the universal contribution rapidly diminishes according to the relation $\chi_U=C_\chi(T-T_0)^{-2}$, where C_χ and T_0 ($<T_m$) are frequency-dependent parameters. According to the analysis of the data measured on 0.75PMN-0.25PT (Ref. 6) and our estimations for some other compounds, the universal contribution can perceptibly influence T_A and ε_A parameters determined from the experimental $\varepsilon(T)$ at low frequencies, but its influence on δ is minute. An additional parasitic contribution to the permittivity of 0.69PMN-0.31PT (and some other materials studied) appears at high temperatures and low frequencies. This contribution gives rise to the so-called low-frequency dispersion[14] (compare the curves for different frequencies at $T>550$ K in Fig. 1) and can fully destroy the low-frequency scaling.

To avoid any undesirable effects on the scaling of the above-discussed (and probable other) dielectric contributions, one should perform measurements at high enough frequencies, where these contributions are negligible. Another possible way is to determine and extract the parasitic dielectric susceptibilities (as was done in Refs. 10 and 13). For all the compounds studied in the present work, at the frequencies used for scaling, we have not observed (at temperatures around or higher than T_m) any dispersions pointing to significant additional susceptibilities other than the CRD, which is the only strong dispersion in that frequency range. It gives rise to the Vogel-Fulcher frequency shift of T_m and disturbs the scaling at low temperatures.

It is worth mentioning that alongside with the polar nanoregions, the nanoregions of the other type are often observed in relaxors. Although the structure of these materials is mainly compositionally disordered (i.e., there is no long-range order in the arrangement of different cations, e.g., Mg^{2+} and Nb^{5+} in PMN, on the equivalent lattice sites), the compositionally ordered regions having the size of several dozens nanometers were revealed by means of transmission electron microscopy (TEM).[15] In some of the materials studied in our work the compositionally ordered regions have been reported (e.g., in PMN and PZN), while in some others no such regions have been observed by TEM (PFT, PMN-PT, and PZN-PT with high concentration of PT). But in all cases the scaling appears to be applicable. This means that the compositionally ordered regions are not directly involved in the possible mechanisms responsible for the dielectric properties of the relaxors.

In conclusion, we have shown that in a large number of relaxor ferroelectrics the static conventional relaxor permittivity, ε_{R0}, at the high-temperature side of the permittivity peak follows exactly Eq. (2) with $\gamma=2$. At high enough frequencies, where the other contributions to the permittivity are negligible and thus the measured ε equals ε_{R0}, ε can be scaled as shown in Fig. 2. The parameter δ, being practically independent of frequency, can be considered as a convenient measure for the degree of diffuseness of the permittivity peaks in relaxors. It is expected that the scaling behavior discovered in this work is representative for the whole class of relaxor ferroelectrics. When studying the other materials, it is necessary to keep in mind that any additional nonrelaxor polarization process giving rise to a significant contribution to ε can disturb the scaling. Further investigations are under way to understand the fundamental physical mechanisms underlying the scaling behavior.

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