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Phenomenological description of the diffuse phase transition in ferroelectrics

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Abstract

Features of the diffuse phase transition in lead magnesium niobate and strontium barium niobate, typical relaxor ferroelectric materials, were studied as a function of temperature and frequency. A new empirical equation for a phenomenological description of the temperature dependence of the dielectric permittivity (ε') peak is proposed. In fact, the proposed equation provides an excellent fitting of the experimental curves at temperatures into and above the dielectric dispersion region, enabling us to calculate some characteristic parameters of the phase transitions in ferroelectric materials.

Ferroelectric materials with diffuse phase transition (DPT) characteristics and/or relaxor properties have been extensively studied in the last few decades mainly due to their very interesting and still not completely explained physical properties [1]. The diffuse phase transition in ferroelectrics is characterized by extending the phase transition in a wide temperature interval around the temperature (T_m) where the dielectric permittivity assumes its maximum value (ε'_m). This temperature interval is commonly refered to as the Curie range. Within the Curie range, the dielectric permittivity achieves its highest values and the ferroelectric material displays its most remarkable relaxor features, which are a large frequency dispersion, at temperatures lower than T_m, with a practically frequency independent dielectric permittivity at temperatures slightly above this temperature. Furthermore, the Curie–Weiss law is only observed at temperatures far above T_m (typically hundreds of degrees) [2]. In despite of their controversial physical behaviour, relaxor ferroelectrics with DPTs had found applications in a variety of devices, like piezoelectric actuators, multilayer capacitors, non-volatile memories and pyroelectric detectors [3].

In this way, the characterization of the temperature dependence of the dielectric permittivity, at temperatures above T_m, has been widely studied as an important feature to determine the character of the phase transition in ferroelectrics with DPTs [4–8]. In fact, the dielectric dispersion is not observed in this temperature range. The ferroelectric phase transition diffuseness has been determined by different methods [5]. One of them, which sometimes has been utilized by many authors, is shown to be in good agreement with the general approach of Kirilov and Isupov [4]. In this model, the material compositional

fluctuations give rise to the diffuse phase transition, considering micro-regions that present a slightly different phase transition temperature. A semi-quantitative treatment based on a Gaussian distribution of local polar micro-regions (that were considered to be not correlated) was evolved to parametrize the broadening of the phase transition. In this way, after some assumptions, a phase transition diffuseness parameter can be determined from the fitting of the dielectric permittivity curve as a function of temperature with the equation

$$\varepsilon' = \frac{\dot{\varepsilon}_m}{1 + \frac{1}{2}((T - T_m)/\delta)^2} \tag{1}$$

where ε'_m is the maximum of the real part of the dielectric permittivity, T_m the temperature of maximum dielectric permittivity and δ the diffuseness parameter related to the peak broadening of the phase transition. In other words, δ indicates the degree of the DPT. However, the quadratic law proposed in equation (1) deals only with ferroelectric materials that are considered as ferroelectrics with a so-called 'complete' DPT (see discussion below). Nevertheless, it does not apply in many works found in the literature reporting deviations from the Curie–Weiss law [5]. Furthermore, the ε'_m and T_m parameters brought about by the fitting process of the ε'–T curves with equation (1) are generally in disagreement with those observed experimentally.

Beaing in mind this important aspect, where ferroelectric materials with diffuse phase transition and/or relaxor characteristics do not necessarily present a 'complete' DPT, the following empirical power relation expression was proposed to parametrize the phase transition diffuseness [6]:

$$\varepsilon' = \frac{\dot{\varepsilon}_m}{1 + (T - T_m)^\gamma / 2\delta^2}\,. \tag{2}$$

In equation (2) the same parameters as for equation (1) are considered; however the exponent 2 is substituted by another adjustable parameter γ that is the diffuseness exponent of the phase transition, δ being only an adjustable parameter. In equation (2), $\gamma = 1$ should represent 'normal' Curie–Weiss behaviour, while $\gamma = 2$ corresponds to a 'complete' diffuse phase transition. As can be observed, a simple dimensional analysis shows that equation (2) is valid only for $\gamma = 2$, once the δ parameter needs to have a temperature dimension.

Some other attempts have been employed to characterise the DPT in ferroelectrics. Among them, an exponential relation that appears valid at temperatures much higher than T_m [7], as well as a quadratic relation [8], can be pointed out. However, in spite of their shortcomings (non-correlated polar clusters in equation (1) and dimensional incorrectness in equation (2)), the expressions (1) and (2) still have been commonly used to analyse the dielectric permittivity peak temperature behaviour in ferroelectrics with DPT. Nevertheless, none of the attempts cited above can describe the dielectric behaviour of any ferroelectric materials in the dielectric dispersion region, i.e. at temperatures around T_m.

Beaing in mind the important practical applications of relaxor ferroelectrics, and the great interest of haveing a simple and direct formula describing qualitatively and quantitatively the temperature dependence of the dielectric permittivity at temperatures around and above T_m, we propose a new empirical formula that fulfils these requirements.

In this work, a phenomenological description of the temperature dependence of dielectric permittivity is developed and tested in two distinct ferroelectric materials, lead magnesium niobate (PMN) and strontium barium niobate (SBN). The new proposed phenomenological equation is written as

$$\varepsilon' = \frac{\varepsilon'_m}{1 + ((T - T_m)/\Delta)^\xi} \tag{3}$$

where ε'_m is the maximum of the dielectric permittivity and T_m its related temperature. In equation (3), ξ indicates the character of the phase transition. In fact, $\xi = 1$ indicates a 'normal' ferroelectric phase transition, which is described by the approach proposed in Landau–Devonshire theory for ferroelectric phase transitions (first or second order phase transitions). $\xi = 2$ represents a so-called 'complete' DPT, verified in the theoretical limit of the Kirilov–Isupov approximation [4]. On the other hand, ξ between these limits, i.e. 1 and 2, indicates a so-called 'incomplete' DPT, where the interaction between ferroelectric clusters is considered. In addition, Δ is considered as an empirical diffuseness parameter that indicates the degree of the DPT, being certainly related to the dielectric permittivity peak broadening.

Three distinct scenarios for ferroelectric phase transitions must be considered in the PT feature description with equation (3), as well as for the physical interpretation of the ξ and Δ parameters in each specified case.

When a relaxor ferroelectric material is cooled from the paraelectric to ferroelectric region, polar regions (ferroelectric clusters) start to be formed at temperatures far above T_m, as extensively reported. When the interactions between them are neglected as proposed in [4] (or frustrated), $\xi \to 2$, characterizing a so-called 'complete' DPT. In this limit, equations (3) and (1) become identical.

On the other hand, when a ferroelectric material presenting the Curie–Weiss behaviour is cooled from the paraelectric to the ferroelectric region, the polar regions start to be formed at temperatures closer to T_c, with a consequent stronger interaction between these polar clusters. In this way, $\xi \to 1$, and the Δ parameter is necessarily proportional to the Curie–Weiss constant. In this situation, the analysed material behaves like a 'normal' ferroelectric.

It is very interesting to analyse the situation where a ferroelectric material shows a so-called 'incomplete' diffuse phase transition, as in the majority of the relaxor ferroelectrics. In this situation, when the material is cooled from the paraelectric to the ferroelectric region, the interacting ferroelectric clusters start to be formed at temperature values more elevated than T_m. Furthermore, due to the interaction between them other micro-regions are induced to be formed, consequently increasing its number, interaction and creation rate. This scenario seems to be more realistic in ferroelectrics with DPT that the considered to described ferroelectrics with a 'complete' DPT when deriving equation (1), where the interaction between the polar clusters is disregarded. In fact, recent works have shown this important feature of relaxor ferroelectrics and random-field systems [9, 10].

The $PbMg_{1/3}Nb_{2/3}O_6$(PMN) ceramics used in this work were obtained by the conventional columbite method as extensively reported [11]. The computer assisted weak field dielectric response of the PMN ceramics was carefully determined as a function of the temperature and frequency using an HP4194A impedance gain/phase analyser. The measurements were performed in the temperature range of 20 to 450 K by cooling (cryogenic system APD Cryogenics Inc.), at a constant rate of $|2\ \mathrm{K\ min^{-1}}|$, with a measurement precision of 0.1 K in this temperature interval.

The temperature and frequency dependence of PMN dielectric permittivity is shown in figure 1. The typical relaxor characteristics can be observed at temperatures lower than T_m, where strong frequency dispersion takes place. In fact, T_m increases from 270 K at 1 kHz to 290 K at 1 MHz (see table 1). At some temperatures above T_m no frequency dispersion is observed, and the dielectric permittivity curve can be fitted with equations (1) and (3), as shown in figure 2 for the 1 kHz and 1 MHz curves. The PMN measured and fitted parameters are listed in table 1. As can be seen, both equations can fit very well the high temperature region, although only the ε'_m and T_m parameters obtained with equation (3) coincide with the experimental ones, while poor agreement is achieved with equation (1). Furthermore, the

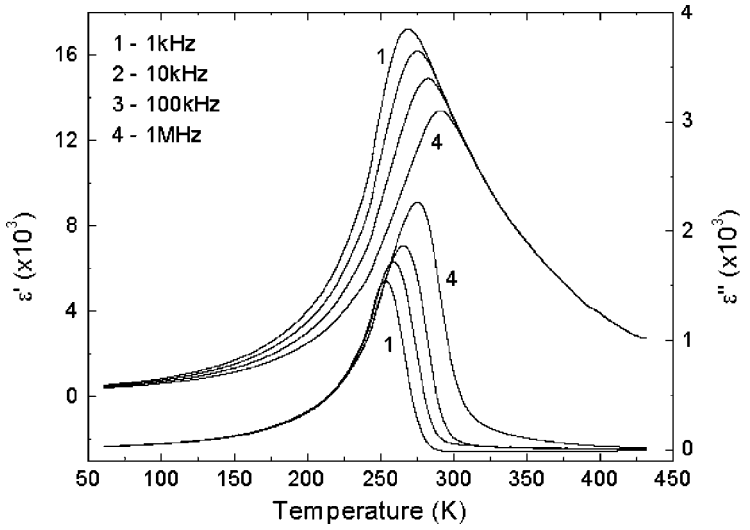

Figure 1. Real and imaginary parts of the dielectric permittivity as a function of temperature and frequency for PMN ceramic.

Table 1. Experimental and fit parameters (equations (1) and (3)) for PMN ceramic.

		ε'_m	T_m (K)	δ (K)	ξ	Δ (K)	Γ_{exp} (K)	Γ_δ (K)	Γ_ξ (K)
Experimental	1 kHz	17 223	270.2	—	—	—	50.1	—	—
	1 MHz	13 390	290.9	—	—	—	50.7	—	—
Equation (1)	1 kHz	18 146	251.2	55.3	—	—	—	65.1	—
	1 MHz	14 198	272.3	55.5	—	—	—	65.3	—
Equation (3)	1 kHz	17 225	270.5	—	1.59	62.5	—	—	49.6
	1 MHz	13 388	290.7	—	1.59	63.0	—	—	50.0

ε'–T curve, generated with the ξ and Δ parameters showed an exceptional accordance with the measured curves into the dielectric dispersion region.

To test the validity of determination of the diffuseness degree of the DPT in ferroelectrics using the suggested empirical equation (equation (3)) the half width at half height in the experimental and generated curves can be compared. For the experimental curves, this procedure consists in measuring the half width at half height only at temperatures higher than T_m, which is the analysed region. In this way, we can determine Γ_{exp} as indicated in figure 2. Similar parameters, i.e. the half width at half height, can be obtained directly from the original Gaussian and power relation distribution functions that give rise to equations (1) and (3). They are defined as $\Gamma_\delta = \delta(2 \ln 2)^{1/2}$, for equation (1), and $\Gamma_\xi = \Delta(\ln 2)^{1/\xi}$ for equation (3). For PMN Γ_{exp}, Γ_δ and Γ_ξ parameters are also listed in table 1. A perfect accordance between Γ_{exp} and Γ_ξ for 1 kHz and 1 MHz curves, as well as the similarities verified in the ε'_m and T_m parameters found experimentally or even in the fitting process, attest to the applicability of equation (3) to describe qualitatively and quantitatively the DPT features of ferroelectrics. Thus, the Δ parameter can be considered as an empirical parameter that is actually related to the degree of the DPT in relaxor ferroelectrics.

Some deviations between the curves generated with equation (3) and the experimental ones, observed at temperatures far above T_m, can be attributed to the so-called low-frequency

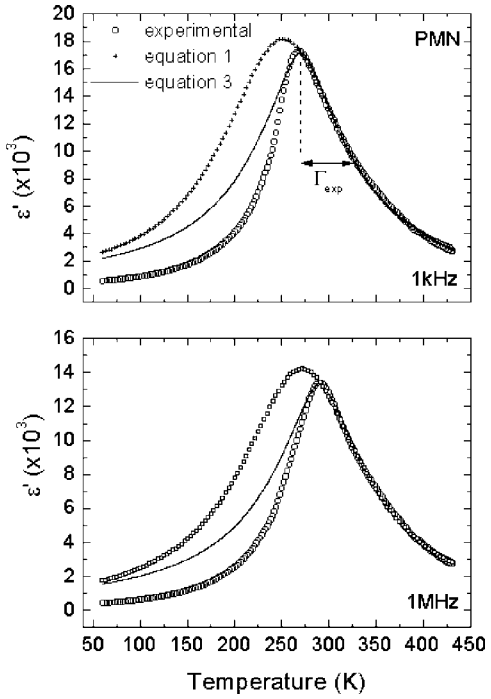

Figure 2. Experimental and fitting curves, generated using equations (1) or (3), for the dielectric permittivity as a function of temperature and frequency for PMN. Γ_{exp}—half width at half height (see text).

dispersion [12]. This effect is not related to the DPT and/or the relaxor behaviour. Nevertheless, at temperatures around T_m, equation (3) can describe correctly the temperature behaviour of the dielectric permittivity curve, considering the same ξ and Δ parameters for all measuring frequencies. In contrast with other phenomenological expressions commonly used to characterise the dielectric permittivity peak temperature [4–8], only equation (3) is able to fit the experimental curves in the dielectric dispersion region. Indeed, this characteristic clearly indicates the frequency independent character of the suggested phenomenological DPT description.

The applicability of equation (3) in the characterization of the diffuseness of the DPT in ferroelectrics was also tested in another typical relaxor ferroelectric—the tungsten-bronze structured strontium barium niobate (SBN). The $Sr_{0.61}Ba_{0.39}Nb_2O_6$ ceramics were prepared through the mixed oxide method, as previously reported [13]. The temperature and frequency dependence of the SBN dielectric permittivity curves is shown in figure 3. The typical relaxor ferroelectric features can be identified in these curves. The α, β and γ relaxation phenomena, extensively discussed by Santos *et al* [14], are also shown in this figure. However, they will not be targets of discussion in this work. As occurs in PMN, an intense dielectric dispersion is observed in the γ region, at temperatures around T_m, and the dielectric permittivity curves are frequency independent at higher temperatures. As can be observed, T_m increases from 304 K at 1 kHz to 339 K at 1 MHz. The experimental and fitted parameters for SBN ceramic are listed in table 2. Once again, a complete agreement between ε'_m and T_m measured or fitted with equation 3 asserts its correctness in the characterization of the DPT in SBN. The generated and measured dielectric permittivity curves (1 kHz and 1 MHz) are shown in figure 4. Once more,

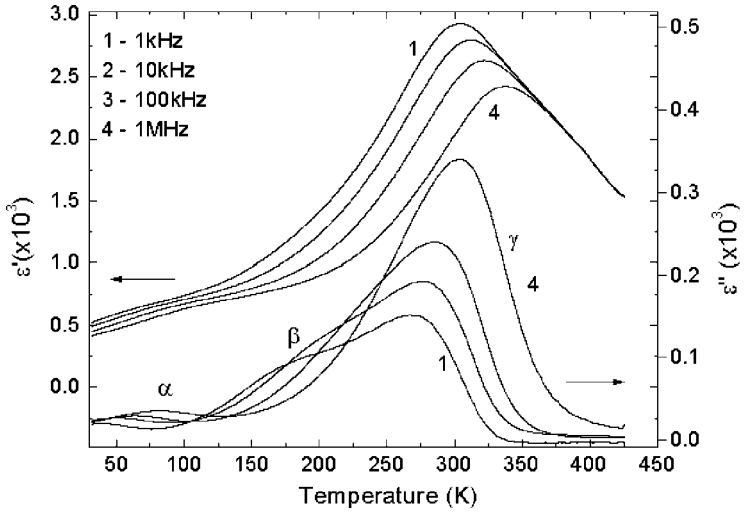

Figure 3. Real and imaginary parts of the dielectric permittivity as a function of temperature and frequency for SBN ceramic. α, β and γ—dielectric relaxation phenomena are discussed in detail in [14].

Table 2. Experimental and fit parameters (equations (1) and (3)) for SBN ceramic.

		ε'_m	T_m (K)	δ (K)	ξ	Δ (K)	Γ_{exp} (K)	Γ_δ (K)	Γ_ξ (K)
Experimental	1 kHz	2927	304.3	—	—	—	104.2	—	—
	1 MHz	2419	339.2	—	—	—	98.1	—	—
Equation (1)	1 kHz	3047	276.5	106.8	—	—	—	125.7	—
	1 MHz	2414	333.4	85.3	—	—	—	100.4	—
Equation (3)	1 kHz	2928	304.1	—	1.62	131.3	—	—	104.7
	1 MHz	2419	339.2	—	1.62	122.4	—	—	97.6

the equation (1) generated curves, as well as the half width at half height obtained through the parameter Δ, showed strong deviations from that obtained experimentally. On the other hand, the equation (3) generated curves and the Γ_ξ parameter show an excellent agreement with their corresponding experimental parameters. In addition, the measured and equation (3) generated curves also showed an exceptional accordance in the dielectric dispersion region.

Also in this case, the deviations between the curves generated with equation (3) and the experimental ones, observed at temperatures far above T_m, are attributed to a low-frequency dispersion [15]. In addition, the ξ value determined in the SBN ceramic from the fit procedure with equation (3) assumes the occurrence of the polar regions at temperatures far above T_m, as previously reported [16]. The higher Δ suggests a higher diffusivity in SBN compared to PMN. Indeed, incommensurations in SBN are known to exist until temperatures far above T_m [17–18]. This superlattice structure can give origin to the additional random field sources that certainly act to destroy the long range interaction between the polar clusters in this ferroelectric system (see [19]).

In summary, we have proposed a phenomenological equation to describe the temperature dependence of the dielectric permitivitty, at temperatures around and above T_m, for ferroelectrics with diffuse phase transition and/or relaxor features. The applicability of the

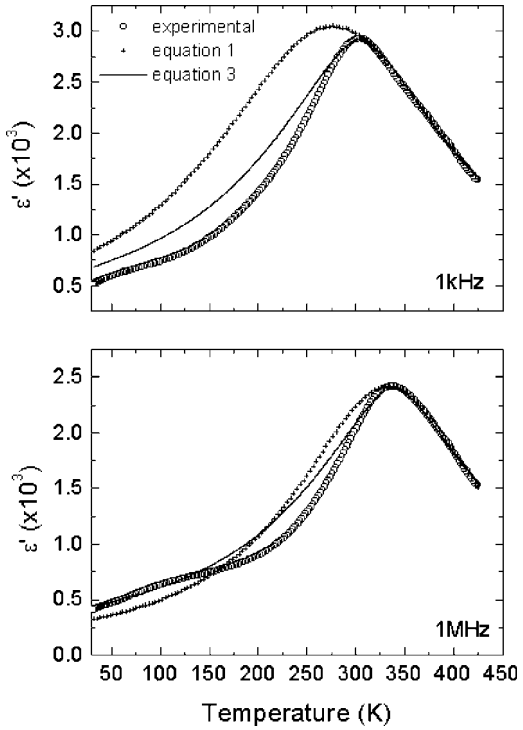

Figure 4. Experimental and fitting curves, generated using equations (1) or (3) for the dielectric permittivity as a function of temperature and frequency for SBN.

proposed equation was tested in two distinct-relaxor ferroelectric systems, lead magnesium niobate and strontium barium niobate. In contrast to other attempts employed to describe quantitatively the peak broadening in ferroelectrics with DPT, the suggested phenomenological equation is the only one able to fit the frequency dispersion region (in the investigated frequency range) of these materials, maintaining the fitting parameters (Δ and ξ) as frequency independent.

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