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# Landau theory-based analysis of grain-size dependence of ferroelectric-to-paraelectric phase transition and its thermal hysteresis in barium titanate ceramics

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**Abstract.** Ferroelectric barium titanate ceramics with grain sizes in the range (0.5, 20)  $\mu\text{m}$  were used for a comparative study of grain-size influence on the ferro–para phase transition and its thermal hysteresis. The investigations were performed by recording the temperature dependence of the dielectric constant, heat capacity and pyrocharge. The experimental results have been analysed in the framework of Landau–Devonshire theory. The grain-size dependent Landau coefficients of the free energy have been derived from our experimental data and used to compute the grain-size dependence of the theoretical transition interval related to the thermal hysteresis. The good qualitative agreement between theory and experiment recommends the size dependent Landau coefficients as a way to improve the modelling of the size dependent ferro–para phase transition in ceramics.

## 1. Introduction

For all the ferroelectric materials, the physical properties in their ceramic form are different from those of the single crystal and depend on parameters like grain size, density, doping amount and structural defects. The modifications of physical properties of ceramics detected as their grain size decreases are referred to as *grain-size effects*. The study of these phenomena started with the observation by Kniepkamp and Heywang [1] that ferroelectricity in barium titanate (BT) single crystals disappears when decreasing the crystal thickness under 1  $\mu\text{m}$ . Jonker and Noorlander [2] supposed that a similar effect should appear in BT ceramics on decreasing the size of the grains. For a barium titanate ceramic specimen having a grain size of 1  $\mu\text{m}$ , they observed a higher value of the dielectric constant at room temperature ( $\epsilon_r \approx 4000$ ) and a smaller jump at the ferroelectric-to-paraelectric transition point, as compared to a 100  $\mu\text{m}$  grain-sized ceramic sample. Later, Kinoshita and Yamaji [3] studied the grain-size influence on the structural phase transitions in BT ceramics with grain sizes in the range (1.1, 53)  $\mu\text{m}$ , by means of dielectric measurements made on cooling from the Curie temperature. For all the investigated ceramics, they observed very sharp peaks at the transition points and a diminishing of the Curie temperature from 122 to 120 °C as the grain

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size decreases in the mentioned interval. Also the other two structural transition temperatures of rhombohedral-to-orthorhombic and orthorhombic-to-tetragonal transformations increase by about 10 °C. The temperature dependence of the dielectric constant during all the observed structural transformations exhibited thermal hysteresis [3]. Later, Kanata *et al* [4] investigated the dielectric properties of BT ceramics having grain sizes in a wider range, (0.1, 200)  $\mu\text{m}$ . They observed (on cooling) variations of the Curie temperature from 99 to 96 °C. During a heating-cooling cycle, the  $\varepsilon_r(T)$  dependences showed a thermal hysteresis of about 7 °C, with a minimum of 3 °C for a ceramic sample with 1  $\mu\text{m}$  grain size. Unlike the above-mentioned researchers, Uchino and co-workers [5, 6] reported that decreasing the grain size of BT powders or ceramics determines a fast decrease of the ferro-para transition temperature. They observed that the tetragonal phase changes to a cubic one in a powder having grains of 0.12  $\mu\text{m}$ , which was therefore considered as a critical grain size for the existence of ferroelectricity in BT powders. Uchino and co-workers [5, 6] also mentioned that the Curie temperature of a BT ceramic is always lower than the Curie temperature of a powder with the same grain size.

These observations allow one to conclude that the critical grain size for the ferroelectric phase of BT ceramics may lie between 0.2 and 0.1  $\mu\text{m}$ . Further, the ceramics with grain sizes in this range should exhibit a pronounced decrease of their Curie temperature from 100 °C to less than 20 °C. However, recent experiments performed by Frey and Payne [7] revealed a ferro-para transition at 110 °C for a BT ceramic sample with 35 nm grain size. Similar results reported by Wada *et al* [8] and Lobo *et al* [9] suggest that the critical grain size in BT ceramics has not yet been clearly established and the decreasing of their Curie temperature is not so fast as in powders. The ferro-para transition temperatures of fine grained BT ceramics reported by all the researchers mentioned above are contradictory: 110 °C for 35 nm [6], 90 °C for 58 nm [7], 103 °C for 100 nm [4] and 108 °C for 200 nm [9]. There are also disagreements between the dielectric data reported by different authors, concerning the shape of  $\varepsilon_r(T)$  dependences. Some authors observed a sharp maximum at the ferro-para transition temperature [3, 10], while other authors reported curves with smeared peaks, for ceramics with grain sizes in the range from 0.3 to 30  $\mu\text{m}$  [2, 9, 11, 12]. The broadening of the ferro-para phase transition (diffuse character) can be due to different types of defect existing in the ferroelectric material [13], as a consequence of different raw materials and preparation methods employed.

As for explaining and modelling of grain size effects detected on barium titanate ceramics, several hypotheses have been proposed. As summarized in the article of Frey and Payne [7], possible causes for the grain-size dependent behaviour could be the depolarization fields, the absence of long-range cooperative interactions, internal stresses and structural defects. Models based on the presence of high internal stress fields in fine grained ceramics [14] as well as the presence of the free surface that induces a size-driven phase transition have been proposed [15–18].

The aim of our paper is a systematic study of the ferro-para phase transition and its thermal hysteresis in BT ceramics. We investigated BT ceramic samples with four different average grain sizes (0.5, 2.5, 10 and 20  $\mu\text{m}$ ), by three different types of measurement: dielectric, calorimetric and pyroelectric. The measurements have been done on ceramic samples in the well aged state. The experimental results were explained in the frame of Landau-Devonshire theory (LD), using grain-size dependent Landau coefficients of the free energy.

## 2. Barium titanate ceramic samples

A barium titanate fine powder with 50 nm grain size was used to obtain green sheets of 0.5 mm thickness, using a multilayer technique. Discs of 8 mm diameter were cut from the green sheet and subjected to different sintering conditions, in order to obtain ceramics with different

average grain sizes. This preparation method provided good quality BT ceramics with 0.5, 2.5, 10 and 20  $\mu\text{m}$  grain size, with relative densities in the range (95, 98)%. Details concerning preparation and physical properties of these ceramics were given in a previous work [19].

### 3. Experimental results

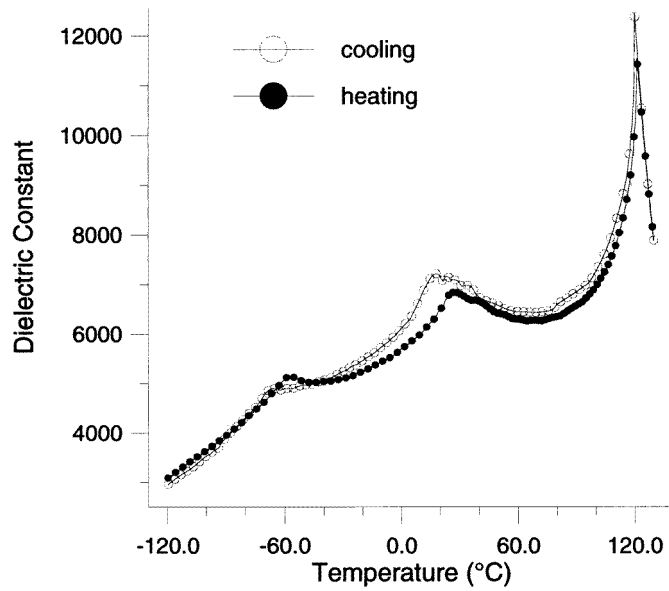
In the above reported papers on grain-size effects in BT [1–11], the authors did not mention the influence of ageing on their experimental results. However, it was proved that the ageing affects the physical properties of BT ceramics, especially during the first 100 minutes after the paraelectric-to-ferroelectric phase transition [20–24]. As the time passes the ceramic evolves towards a very stable well aged state in which changes of the physical properties are virtually non-existent [24]. In order to remove the effects of ageing, heating the ceramic at 180 °C or more, for at least 30 minutes, is required. Subjecting the ceramic to short heat pulses at temperatures lower than 180 °C, or applying an ac electric field (with amplitude higher than the coercive field) for only 1 or 2 cycles, does not affect the natural equilibrium state of the well aged ceramic [21, 22, 25]. As our paper was primarily concerned with the grain-size effects, we studied BT ceramics in the well aged state, in order to minimize the influence of ageing. However, because the stable state of the investigated BT ceramics was reached after ageing, the experimental results obtained here include the final effect of all the mechanisms that have a contribution to ageing, but the ferro–para phase transition was not smeared by time-dependent modification of physical properties due to ageing.

#### 3.1. Dielectric data

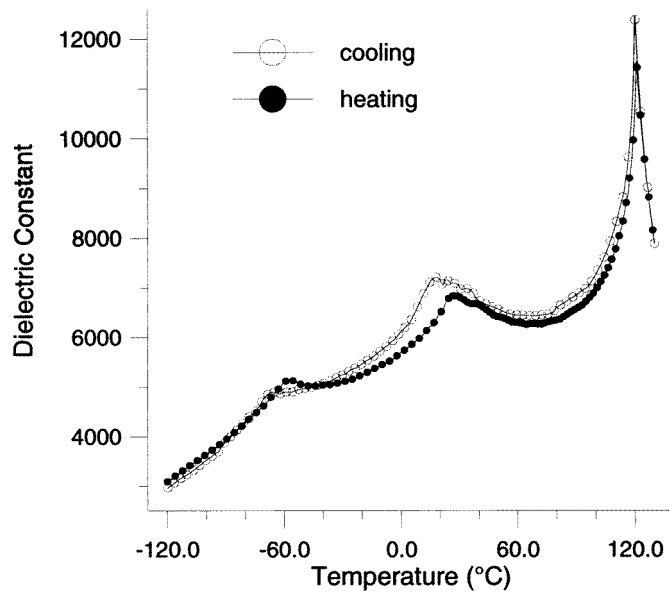
The dielectric study of the ferro–para phase transition in the BT ceramics was performed by recording the temperature dependence of the dielectric constant during a heating–cooling cycle, with a rate of 10 °C h<sup>-1</sup>. The dielectric measurements were performed using a computer controlled HP 4284 LCR precision meter. The temperature variation of the dielectric constant  $\epsilon_r(T)$  for each ceramic sample is shown in figure 1.

The  $\epsilon_r(T)$  curves show local maxima at all the structural phase transition temperatures and a sharp peak at the ferro–para transition point, for all the samples. As curves in figure 1 exhibit quite sharp ferro–para transition peaks, it proves that the investigated ceramics are chemically pure and the structural inhomogeneities are not important enough to induce a diffuse character of the phase transition. In case of diffuse phase transitions, the dielectric constant and loss are frequency dependent in the transition region. No such dependences have been observed in the case of our samples, from measurements made in the frequency range (100 Hz, 1 MHz) [26]. Moreover, diffuse phase transitions are characterized by deviations from the Curie–Weiss law in the paraelectric phase, where a power function for  $\epsilon_r^{-1}(T)$  (close to quadratic) provided a better description of the experimental data [27]. In the case of our ceramics, the reciprocal dielectric constant dependence on temperature is linear (with 0.9999 correlation coefficient), for all grain sizes, in very good agreement with the Curie–Weiss law. All these facts prove that the results of our measurements are not significantly affected by defects or dispersion of grain sizes and therefore do not require to be examined using diffuse phase transition concepts.

The Curie temperature on heating  $T_C^{(h)}$  is always larger than in case of the ferro–para phase transition observed on cooling  $T_C^{(c)}$ . The difference between them  $\Delta T_C = T_C^{(h)} - T_C^{(c)}$  is usually referred to as the ‘thermal hysteresis’ of the ferro–para phase transition. Both the critical temperatures  $T_C^{(h)}$ ,  $T_C^{(c)}$  as well as the thermal hysteresis  $\Delta T_C$  are grain-size dependent.



(a)

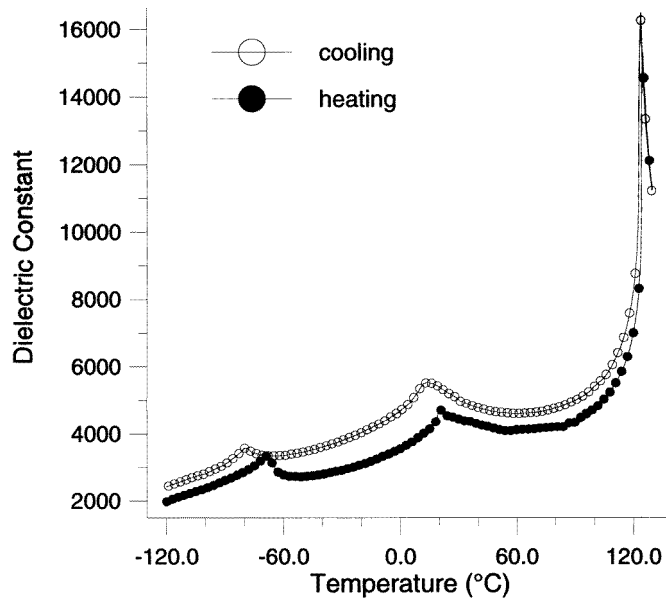


(b)

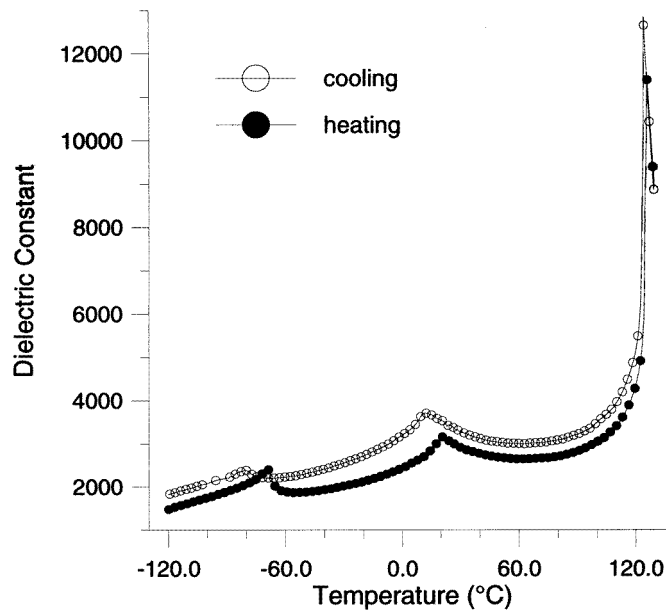
**Figure 1.** Temperature dependences of the dielectric constant for various grain sizes: (a)  $0.5 \mu\text{m}$ , (b)  $2.5 \mu\text{m}$ , (c)  $10 \mu\text{m}$ , (d)  $20 \mu\text{m}$ .

### 3.2. Calorimetric data

The temperature dependences of the heat capacity at constant pressure  $C(T)$  were recorded with an ACC-1 Ulvac Shinku-Riko automatic ac calorimeter. The same heating–cooling rate as in the dielectric measurements ( $10^\circ\text{C h}^{-1}$ ) was ensured. The recorded  $C(T)$  curves are



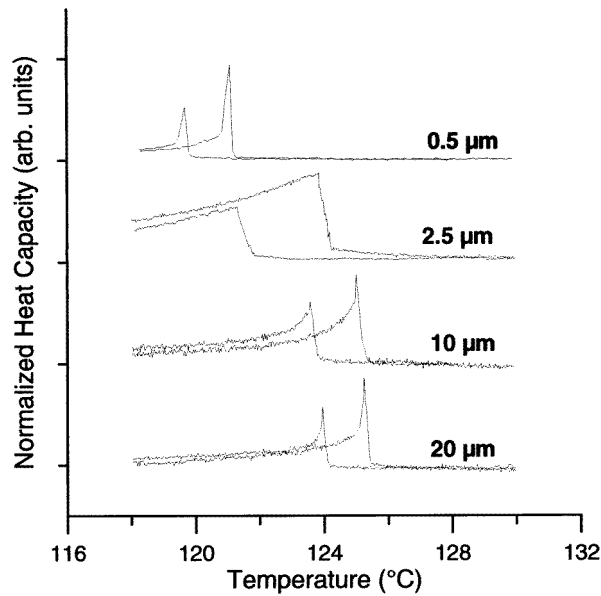
(c)



(d)

Figure 1. (Continued)

presented in figure 2. The heat capacity of each sample exhibits a rapid variation at the transition points. As in the case of dielectric measurements, the Curie temperature and the thermal hysteresis of the heat capacity are grain-size dependent. Due to the particularities of the experimental set-up used in ac calorimetric measurements [10], the values of the heat capacity are given in arbitrary units.



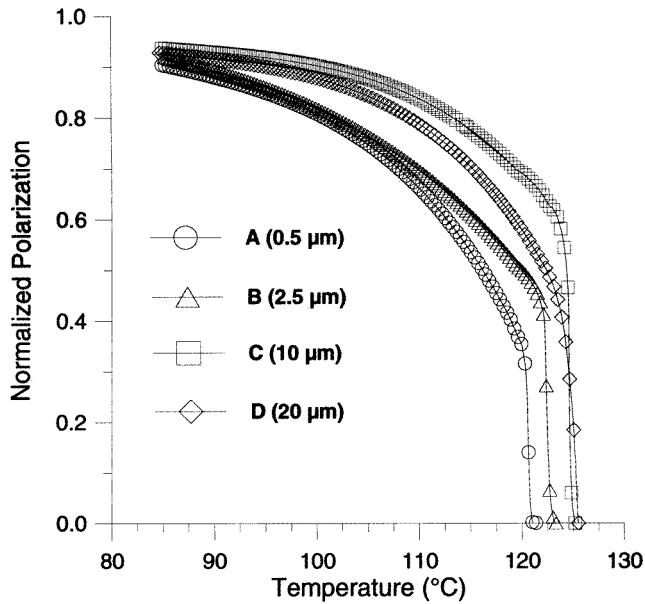
**Figure 2.** Temperature dependences of heat capacity on a complete heating-cooling cycle.

### 3.3. Pyrocharge data

Before the pyrocharge measurements, each ceramic sample was poled just below the Curie temperature, in a  $30 \text{ kV m}^{-1}$  dc electric field. After one hour, the ceramics were cooled under a field at  $10 \text{ }^\circ\text{C h}^{-1}$ , down to room temperature and short-circuited for 24 hours. The pyrocharge study consisted in recording the temperature dependence of the electric charge released by each ceramic sample during heating at  $10 \text{ }^\circ\text{C h}^{-1}$ . The pyrocharge was collected on a reference capacitor, read by a computer controlled TR B401 electrometer and used for computing the remnant polarization  $P_r$ . The normalized experimental  $P_r(T)$  profiles are presented in figure 3. This figure shows the remnant polarization reduction occurs with maximum rate at temperatures near the transition point. Following Lines and Glass [28] and the method of Cerceda *et al* [30], we determined the temperatures at which  $\partial^2 P_r / \partial T^2 = 0$  as being the Curie temperatures in the pyrocharge experiments, for all ceramic samples.

As the thermally stimulated depolarization of a poled ceramic is an irreversible process, one cannot define a thermal hysteresis of the remnant polarization in the same manner as in the case of ac calorimetry and dielectric measurements. However, based on the remark of Lines and Glass [28] we regarded the transition width as being the difference between the temperatures at which  $\partial^2 P_r / \partial T^2 = 0$  and  $P_r = 0$  respectively, as an equivalent thermal hysteresis of the pyrocharge.

Because of poling, in the pyrocharge experiments the ceramics were no longer in the well aged state as in the case of the dielectric and calorimetric experiments. Poled BT ceramics exhibit a nonlinear ageing that seems to accelerate after 10 days and continue for years [29]. In this case, we minimized the influence of ageing on pyrocharge data by performing the measurements immediately after the relaxation of free carriers, i.e. after removing the poling field and a 24 h short-circuit at room temperature.



**Figure 3.** Normalized pyrocharge polarization versus temperature, for various grain sizes: (A) 0.5  $\mu\text{m}$ , (B) 2.5  $\mu\text{m}$ , (C) 10  $\mu\text{m}$ , (D) 20  $\mu\text{m}$ .

#### 4. Discussion

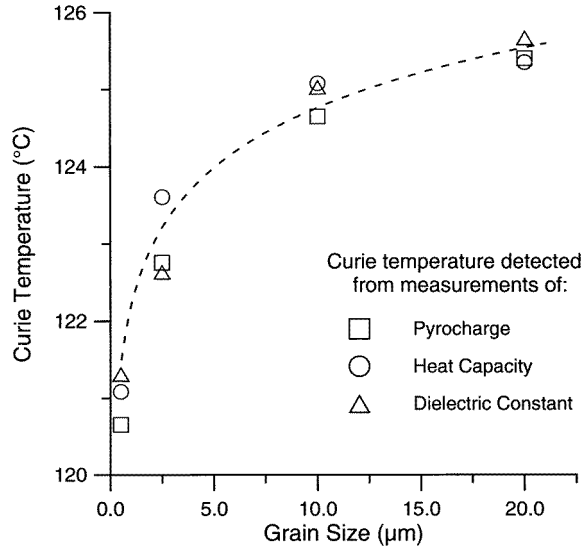
We extracted from figures 1–3 the values of the temperature at which the ferroelectric-to-paraelectric transition occurs and plotted them as function of grain size in figure 4. Irrespective of the measurement technique, the data show that the Curie temperature decrease when grain size decreases, which supports the idea of a unique origin of size dependent effects in BT ceramics. There are slight differences between the  $T_C$  values observed by the three measurement methods. A similar situation was reported in the case of PZT ceramics [30]. Because the differences seem to increase as the grain size decreases, their origin could be the increasing density of  $90^\circ$  domain walls. An accurate explanation of this phenomenon would require a model of ferroelectric domain contribution to each investigated parameter (dielectric constant, heat capacity, pyrocharge), not available at the moment.

The usual method for theoretical description of the ferro–para phase transition is the one provided by the Landau–Devonshire (LD) theory. Although this theory was initially used for modelling the phase transitions of single crystal ferroelectrics, we consider it to be valid in the case of ferroelectric ceramics also. Obviously, the presence of grain boundaries and different orientations in ferroelectric ceramics are not taken into account by the original form of LD theory. However, it is our assumption that LD theory is still valid under these new physical circumstances, as both grain boundary and different orientation effects can be accounted for by merely renormalizing the Landau coefficients. Moreover, the experimental results presented here are obtained under equilibrium conditions, which falls also into the validity range of LD theory.

The appropriate thermodynamic potential of the ferroelectric system is the Gibbs free energy [28]:

$$G = \frac{\alpha_0}{2}(T - T_0)P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + \dots \quad (1)$$





**Figure 4.** Grain-size dependence of the Curie temperature detected from various experiments.

where  $\alpha_0$ ,  $\beta$  and  $\gamma$  are the Landau coefficients. At the Curie point  $T_C$ , barium titanate undergoes a first order phase transition. The latent heat of this process is related to the entropy variation [28] by:

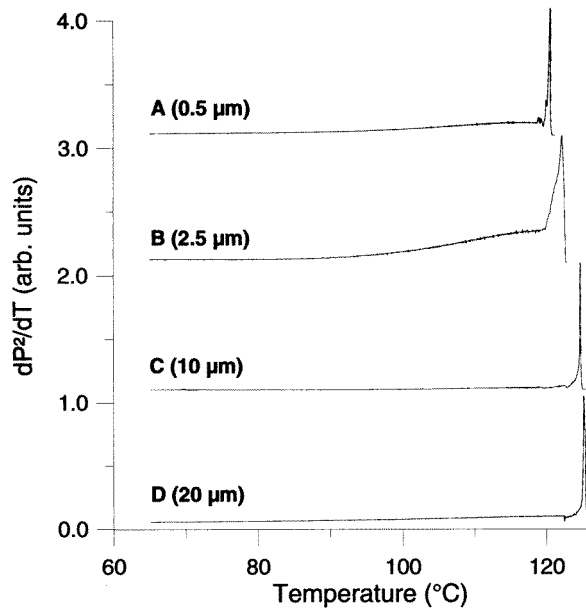
$$Q = T_C \Delta S = T_C (S_{para} - S_{ferro}) = \frac{1}{2} \alpha_0 T_C P_s^2. \quad (2)$$

Equation (2) leads to a simple relation between the heat capacity and the spontaneous polarization:

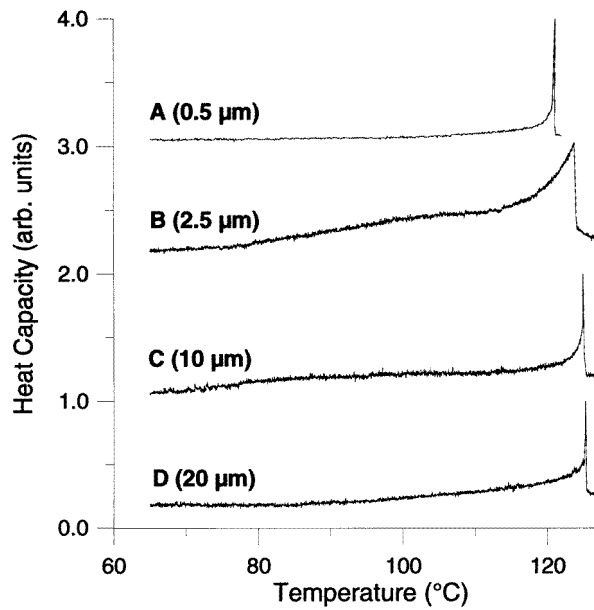
$$C(T) = \frac{1}{2} \alpha_0 T_C \frac{\partial P_s^2}{\partial T}. \quad (3)$$

Equation (3) has been used as a validity test of the LD theory for barium titanate and other ferroelectrics and for a comparison between the values of experimental and theoretical transition heat [31, 32]. We used a similar method in order to test the LD theory predictions, by comparing the experimental calorimetric profiles  $C(T)$  and the  $\partial P_r^2 / \partial T$  curves extracted from the pyrocharge dependences given in figure 3. The remnant polarization of BT ceramics obtained from pyrocharge data is in fact different from the spontaneous polarization and it could be equal only in highly oriented single crystals. However, in spite of this difference, we attempted to perform the qualitative comparison described above, based on equation (3). We numerically derived the normalized values of  $P_r^2$  obtained from pyrocharge measurements, as function of temperature. The results are shown in figure 5, where the temperature dependences of the normalized values of  $\partial P_r^2 / \partial T$  are given. Figure 6 contains a plot of the calorimetric profiles on heating, in the same temperature range as in figure 5. We note in both figures the same grain-size dependent behaviour. The good qualitative agreement between the two sets of curves presented in figures 5 and 6 proves the suitability of the LD theory for explaining the phenomena observed in our experiments.

The grain-size dependence of thermal hysteresis revealed from our experiments is presented in figure 7. The calorimetric measurements provided the highest values of thermal hysteresis (1.5, 2.5) °C, as compared with the electrical measurements. The lowest thermal hysteresis was obtained in the pyrocharge experiment. This result is somewhat expected,

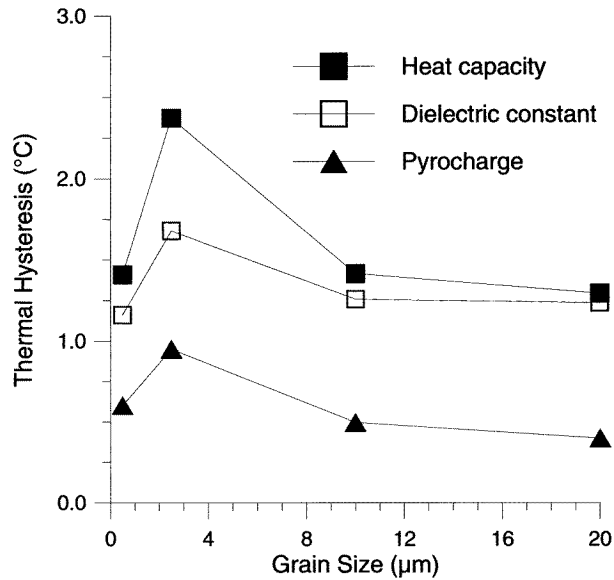


**Figure 5.** Normalized temperature dependences of the derivative  $\partial P_r^2/\partial T$ , where  $P_r$  is the pyrocharge remnant polarization.



**Figure 6.** Representation of temperature dependences of heat capacity measured on heating.

as we needed to reconsider the definition of the thermal hysteresis in the case of ferro–para phase transition occurring during the pyrocharge measurement, thus making an approximation. However, the main trend of the thermal hysteresis dependence of grain size is the same even



**Figure 7.** Grain-size dependences of the thermal hysteresis of ferro–para phase transition, measured from various experiments.

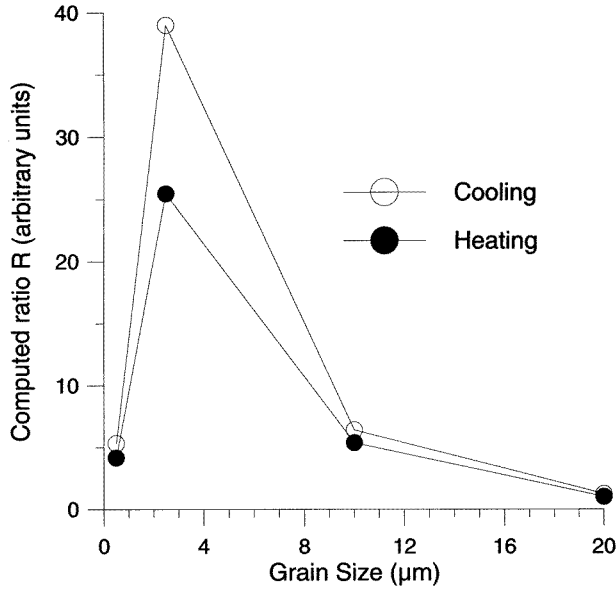
in this case. The thermal hysteresis detected from all the experimental data shows a maximum value for the 2.5 μm grain size sample, confirming the peculiar properties of this ceramic reported before [19, 33].

The theoretical size dependence of the thermal hysteresis was obtained in the framework of LD theory, in order to confirm the size dependence of the thermal hysteresis and the anomaly of the B sample. According to this theory, ferroelectrics undergoing a first order phase transition are characterized by a set of temperatures limiting the metastable regions of the two phases, as follows:  $T_0$ —the Curie–Weiss temperature at which the theoretical dielectric susceptibility becomes infinite;  $T_C$ —the Curie temperature at which the two phases are equally probable, so that  $G_{ferro} = G_{para}$ ;  $T_1$ —the highest temperature for which the ferroelectric phase can exist as a metastable state and  $T_2$ —the temperature above which only the paraelectric phase can exist. The mathematical expressions of these temperatures are written as:

$$T_C = T_0 + \frac{3}{16} \frac{\beta^2}{\alpha_0 \gamma} \quad T_1 = T_0 + \frac{1}{4} \frac{\beta^2}{\alpha_0 \gamma} \quad T_2 = T_0 + \frac{9}{20} \frac{\beta^2}{\alpha_0 \gamma}. \quad (4)$$

Thus, the first order ferro–para phase transition proceeds in a domain of temperatures and not at fixed temperature, as in the case of the second order phase transition. The thermal hysteresis revealed in various experiments is directly related to this phase transition width. The correct evaluation of thermal hysteresis is not possible in a classical thermodynamic theory, but some authors consider that the possible maximum value of thermal hysteresis is the difference  $\Delta T = T_2 - T_0$  [28]. The relations (4) provided a value of the first order transition width  $\Delta T = T_2 - T_0 \propto R$ , where  $R$  is the ratio  $R = \beta^2/\alpha_0\gamma$ .

We consider that a possible verification of the grain-size dependent thermal hysteresis can be obtained in the framework of LD theory, by evaluating the grain-size dependent Landau coefficients (a concept introduced by us in [34])  $\alpha_0$ ,  $\beta$  and  $\gamma$  from experimental data and computing the  $R$  ratio using the above relation.



**Figure 8.** Grain-size dependence of the ratio associated with the theoretical thermal hysteresis ( $R$ ), on heating and cooling.

In order to perform such a qualitative verification, we computed first the coefficient  $\alpha_0$  and the Curie–Weiss temperatures  $T_0$ , using a linear regression analysis of the experimental dielectric constant data, in the paraelectric region, where the temperature dependence of the reciprocal dielectric constant is linear:

$$\frac{1}{\varepsilon_0(\varepsilon_r - 1)} = \alpha_0(T - T_0). \quad (5)$$

Using the experimental jump of the heat capacity at the ferro–para transition, described in the LD theory as [28]:

$$\Delta C = \frac{\alpha_0 T_0}{2\gamma\beta} \quad (6)$$

and the spontaneous polarization jump at the transition point:

$$\Delta P_s(T_0) = P_s(T_0) - 0 = \sqrt{-\frac{\beta}{\gamma}} \quad (7)$$

we evaluated the ratio  $w$ :

$$w = \left| \frac{\Delta C}{\Delta P_s^2(T_0)} \right| = \frac{\alpha_0^2 T_0}{2\beta^2} \quad (8)$$

and then we computed the size dependent Landau coefficients  $\beta$  and  $\gamma$  from the equations:

$$\beta = \sqrt{\frac{\alpha_0^2 T_0}{2w}} \quad \gamma = \frac{1}{\Delta P_s^2(T_0)} \sqrt{\frac{\alpha_0^2 T_0}{2w}}. \quad (9)$$

Because in the calorimetric study [19] the heat capacity data are given in arbitrary units, we mention that our experimental Landau coefficients computed on the basis of (9) are expressed in arbitrary units, too. Another approximation already mentioned above is the difference between

the spontaneous and remnant polarization, found mainly in the case of ceramic materials. Despite these limitations, we tried to verify whether the anomalous behaviour of the sample B can be obtained from the transition width predicted by the LD theory. We computed the Landau coefficients on heating and cooling using the relations (5)–(9) and then the  $R$  ratio, which is proportional to the transition width  $\Delta T$ .

Figure 8 shows the grain-size dependence of the ratio  $R$ , with a pronounced maximum value for sample B, both on heating and on cooling, as obtained in the experiments. Therefore, it became obvious that the relations provided by the LD theory confirm the anomaly of the thermal hysteresis experimentally observed for sample B, as well as its grain-size dependence. We believe that this peculiar behaviour detected in all the experiments and verified in the framework of LD theory is related to the fact that the size of sample B particles is near the critical one of  $1.1 \mu\text{m}$ , around which other authors have reported unusual properties also [12, 35].

## 5. Conclusion

We investigated in this work the ferroelectric-to-paraelectric phase transition in barium titanate ceramics with different average grain sizes, by means of four different techniques: dielectric, calorimetric, pyroelectric and hysteresis loops. The experiments revealed that the Curie temperature decreases from 126 to  $120^\circ\text{C}$  on decreasing the grain size from  $20 \mu\text{m}$  to  $0.5 \mu\text{m}$ . The temperature dependences of the dielectric constant and heat capacity exhibited a grain-size dependent thermal hysteresis, with values between 1 and  $2.5^\circ\text{C}$ . The thermal hysteresis reached a maximum at a  $2.5 \mu\text{m}$  grain-size.

An analysis of the Landau–Devonshire (LD) theory predictions was performed, in an attempt to model the experimental data. Firstly, we compared the experimental temperature dependences of heat capacity with the derivative of the square remnant polarization. Using the LD theory and the experimental data, we estimated the grain-size dependence of the first order phase transition width, which was considered as a measure of its thermal hysteresis. The results of these estimations are in good agreement with the experimental thermal hysteresis, having a maximum value for our sample B with grain size  $2.5 \mu\text{m}$ .

We conclude that the LD theory is a valuable approach for describing the ferroelectric-to-paraelectric phase transition in ferroelectric ceramics. We emphasize the usefulness of estimating the Landau coefficients from experimental data, as many physical properties of the ceramic material can be explained on their basis. Experiments aiming to find Landau coefficients as functions of grain size, temperature and electric field from various types of experiment are in progress in our laboratory.

## Acknowledgments

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## References

- [1] Kniepkamp H and Heywang W 1954 *Z. Angew. Phys.* **6** 385
- [2] Jonker G H and Noorlander W 1962 *Science of Ceramics* (London: Academic)
- [3] Kinoshita K and Yamaji A 1976 *J. Appl. Phys.* **47** 371

- [4] Kanata K, Yoshikawa T and Kubota K 1987 *Solid State Commun.* **62** 765
- [5] Uchino K, Sadanaga E and Hirose T 1989 *J. Am. Ceram. Soc.* **72** 1555
- [6] Uchino K, Sadanaga E, Oonishi K, Morohashi T and Yamamura H 1990 *Ceramic Dielectrics—Ceramic Transactions* (Westerville: American Ceramic Society)
- [7] Frey M H and Payne D A 1996 *Phys. Rev. B* **54** 3158
- [8] Wada S, Suzuki T and Noma T 1995 *J. Mater. Res.* **10** 306
- [9] Lobo R P S M, Mohallem N D S and Moreira R L 1995 *J. Am. Ceram. Soc.* **78** 1343
- [10] Lee B W and Auh K H 1995 *J. Mater. Res.* **10** 1418
- [11] Zhong W, Zhang P, Wang Y and Ren T 1994 *Ferroelectrics* **160** 55
- [12] Arlt G 1990 *Ferroelectrics* **104** 217
- [13] Smolenskii S A, Bokov V A, Isupov V A, Krainik N N, Pasynkov R E and Sokolov A I 1984 *Ferroelectrics and Related Materials* (New York: Gordon and Breach) p 589
- [14] Arlt G 1990 *J. Mater. Sci.* **25** 2655
- [15] Wang Y G, Zhong W L and Zhang P L 1994 *Solid State Commun.* **90** 329
- [16] Schlag S and Eicke H F 1994 *Solid State Commun.* **91** 883
- [17] Zhong W L, Wang Y G and Zhang P L 1994 *Phys. Lett. A* **189** 121
- [18] Wang C L and Smith S R P 1995 *J. Phys.: Condens. Matter* **7** 7163
- [19] Tura V, Mitoseriu L, Papusoi C, Osaka T and Okuyama M 1998 *Japan. J. Appl. Phys.* **37** 1950
- [20] Mason W P 1955 *J. Acoust. Soc. Am.* **27** 73
- [21] Wu K and Schulze A S 1992 *J. Am. Ceram. Soc.* **75** 3385
- [22] Wu K and Schulze A S 1992 *J. Am. Ceram. Soc.* **75** 3390
- [23] Ikegami S and Ueda I 1967 *J. Phys. Soc. Japan* **22** 725
- [24] Okazaki K and Maiwa H 1992 *Japan. J. Appl. Phys.* **31** 3113
- [25] Dederichs H and Arlt G 1986 *Ferroelectrics* **68** 281
- [26] Mitoseriu L, Tura V, Ricinschi D and Okuyama M 1998 *Proc. Conf. on Dielectrics and Related Phenomena DRP'98 (Bielsko-Biala, 1998) SPIE J. Nonlinear Opt.* at press
- [27] Smolenskii S A, Bokov V A, Isupov V A, Krainik N N, Pasynkov R E and Sokolov A I 1984 *Ferroelectrics and Related Materials* (New York: Gordon and Breach) p 601
- [28] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Clarendon) p 78
- [29] Thomas A G and Pearson D L 1986 *Proc. 6th IEEE Int. Symp. on Applications of Ferroelectrics (Lihigh University)* (New York: IEEE) p 111
- [30] Cerceda N, Noheda B and Gonzalo J A 1998 *J. Kor. Phys. Soc.* **32** S241
- [31] Todd S S and Lorenson R E 1952 *J. Am. Chem. Soc.* **74** 2043
- [32] Volger J 1952 *Philips Res. Rep.* **7** 21
- [33] Tura V, Mitoseriu L, Papusoi C, Osaka T and Okuyama M 1998 *J. Electroceram.* **2** 163
- [34] Ricinschi D, Harnagea C, Papusoi C, Mitoseriu L, Tura V and Okuyama M 1998 *J. Phys.: Condens. Matter* **10** 477
- [35] Niepce J C 1994 *Electroceramics 4 (Aachen, 1994)*