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In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

THERMODYNAMIC CONSIDERATIONS OF THE GRAIN SIZE DEPENDENCY OF MATERIAL PROPERTIES

A new approach to explain the variation of the dielectric permittivity of BaTiO3 with grain size

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Abstract

Phase transitions which depend on grain size induce very interesting properties in materials such as zirconia or barium titanate. A new and rigorous thermodynamic treatment of this type of phase transition is proposed with consideration of the surface phenomena. An interpretation is given of the observed differences when the material – particularly $BaTiO_3$ – under consideration is a fine grain powder or is a fine grain ceramic.

Keywords: $BaTiO_3$, ZrO_2, fine grained ceramics, fine grained powders, phase transition

Introduction

Fine grained materials with a precise control of the grain size distribution are increasingly in demand for specific purposes.

Two well known examples can be given:

– Zirconia, for increasing both the strength and toughness of ceramics by increasing the resistance to crack propagation [1].

– Barium titanate, as the main component of the dielectric of type II multilayer ceramic capacitors [2].

In both examples a phase transition is induced in the material, at room temperature, when the grain size is lower than a critical value. The special behav-

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iour of these two very interesting materials originates in this particular phase transition.

The aim of the paper is to review this behaviour and the interpretations which have been given. Then a new and full thermodynamic treatment of the problem is proposed.

The grain size dependency of a material behaviour: cases of $BaTiO_3$ and ZrO_2

Barium titanate

The dielectric properties of $BaTiO_3$ have long been known to be grain size dependent [3–6]. The most important property for the use of $BaTiO_3$ as fine grained dielectric material has been evidenced by Arlt *et al.* [7] (Fig. 1); the dielectric constant of $BaTiO_3$, at room temperature, exhibits a maximum value for a grain size in ceramics of ~0.8 μm which is approximately six times the normal value in large grain ceramics.

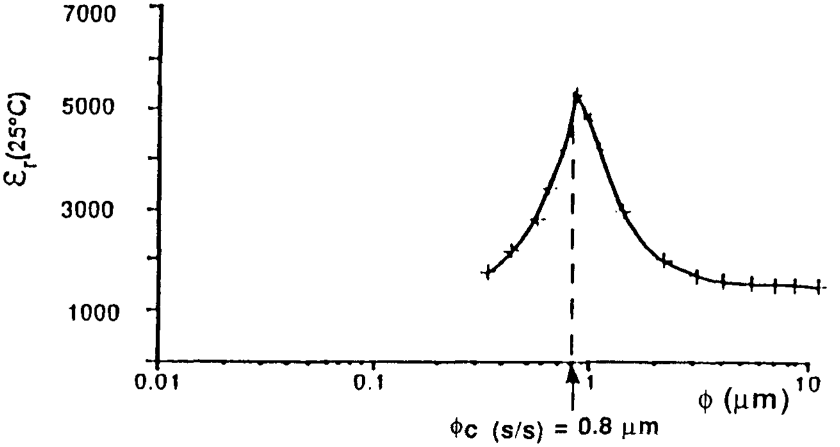

Fig. 1 The relative dielectric constant ε_r (25°) as a function of the mean grain diameter Φ in $BaTiO_3$ ceramics (Ref. [7])

Various explanations have been proposed for this behaviour [5, 7, 8]. None of them suggested a correlation with the variation of the $BaTiO_3$ crystalline lattice with grain size which has also been known for a long time [9], but which has been experimentally better characterized recently [10–12]. The latest contribution [13] suggests that the $\varepsilon_r(RT)$ maximum of Fig. 1 might be associated with the cubic-paraelectric to tetragonal-ferroelectric phase transition of $BaTiO_3$ when the grain size increases progressively (Figs 2 and 3). Such an interpretation would be coherent with the classical interpretation of the drastic increase of ε_r observed in coarse grain $BaTiO_3$ in the temperature range 120–130°C which is associated with the ferroelectric-paraelectric phase transition of $BaTiO_3$

However, an important question remains:

– in $BaTiO_3$ ceramics, the maximum of the dielectric constant is observed, at room temperature, for grain size ≈0.8 μm.

– while, in $BaTiO_3$ powders, the phase change, at room temperature, is observed for grain size ≈ 0.08 μm (Figs 2 and 3).

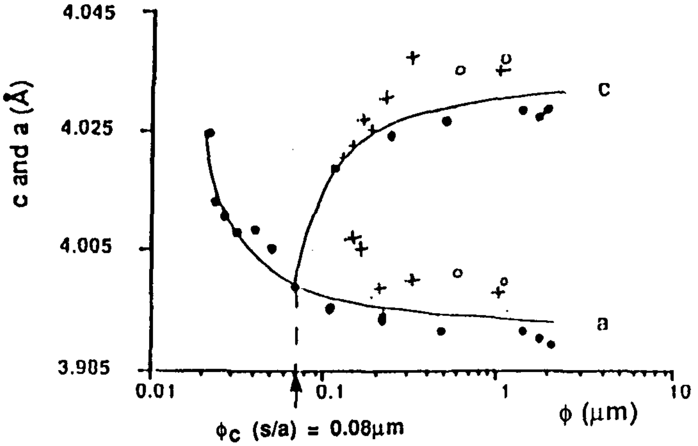

Fig. 2 The cell parameters of $BaTiO_3$, at room temperature, as a function of the mean grain diameter Φ in powders • • •[13] + + +[10] o o o[11]

Without a full experimental study (crystallographic and dielectric) on the same samples is it possible to validate the above suggestion?

Zirconia

In contrast to the case of $BaTiO_3$, the phenomenon which underlies the use of zirconia as a toughening agent in various ceramics has been well known for a long time [1] and [15–19].

Coarse-grained zirconia exhibits a phase transition between a high temperature tetragonal form and a low temperature monoclinic form, in the 950–1200°C temperature range [1]. The important variation in relative volume, +3 to +5%, which is associated with this tetragonal to monoclinic phase transition does not allow the use of pure coarse-grained zirconia ceramics. However, the transition temperature is very grain-size dependent [20] (Fig. 4); the grain-size influence is so large that the tetragonal high-temperature form is stable at room temperature when the grain size is lower than 10 nm [20]. The term 'metastable' was used originally [1, 15, 17]; we will see later, according to [15] and [20], that 'stable' has to be used in place of 'metastable'.

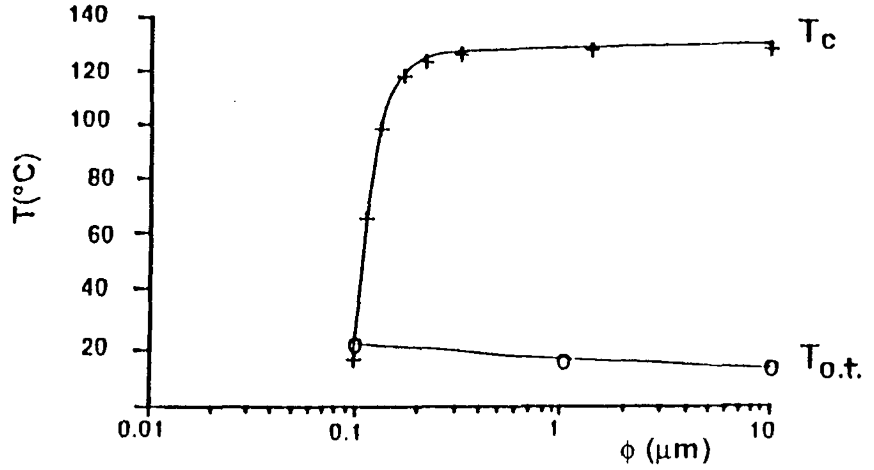

Fig. 3 The transition temperatures of barium titanate as a function of grain size in powders (+ + +[10] for T_C) (o o o mean values for orthorhombic/tetragonal transition [14])

The important volume change associated with the phase transition, on the one hand, and, on the other hand, the important shift of the transition temperature with varying grain sizes both underly the use of well-adapted grain-sized zirconia for increasing the resistance of a ceramic to crack propagation. The practical aspects and phenomena of transformation toughening have been reviewed by Clausen *et al.* [18, 19].

Previous thermodynamic interpretation

In the framework of classical thermodynamics, some theories have been proposed to explain the grain-size dependency of phase stability [21, 22] in finely divided materials. Such models have been applied to ZrO_2 to describe the tetragonal/monoclinic transition [15, 16, 20] which is grain-size dependent.

The authors describe a phase transition between two phases, α and β, using the following two classical relations:

– at equilibrium, at given T and P, the molar Gibbs free energy G of the two phases are equal:

$$G_\alpha = G_\beta \tag{1}$$

– the expression for G is:

$$G = \mu^o(T) \cdot n + \gamma \cdot A \tag{2}$$

where A is the surface area and n is the number of moles in each grain; μ^o is the standard chemical potential (which depends only on temperature) and γ is the surface tension (see below).

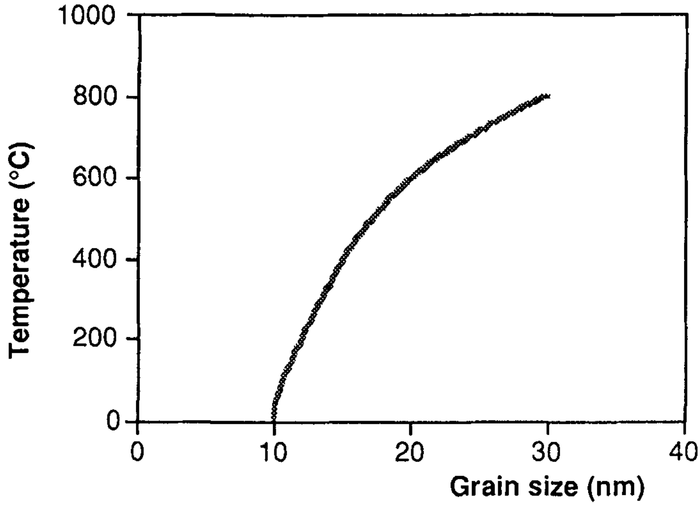

Fig. 4 The monoclinic/tetragonal transition of zirconia as a function of grain size [20]

Both n and A depend on the grain size, consequently the free energy is a function of the grain diameter Φ. At a given temperature and a given pressure, it is then possible to draw a diagram of $G_\alpha(\Phi)$ and $G_\beta(\Phi)$ for the two phases, α and β. The intersection of the plots defines the critical diameter, Φ_c, for the phase transition. The expression for the critical diameter has been calculated:

$$\Phi_c = -\lambda V \frac{\gamma_\alpha - \gamma_\beta}{\mu_\alpha^o - \mu_\beta^o} \tag{3}$$

$V \approx V_\alpha \approx V_\beta$ is the molar volume of the phases α and β and λ is a numerical coefficient equal to 4 or 6 depending on the authors.

This expression, obtained by balancing the surface and the volume contribution to the free energy, is interesting because it explains the experimental phenomenon of a size-dependent phase transition. Particularly, the role of the quality of the surface, through the surface tension, is clearly shown by this relation. Consequently, the large difference observed between $\Phi_{c(s/a)} \approx 0.08$ µm in $BaTiO_3$ powders (Fig. 2) and $\Phi_{c(s/s)} \approx 0.8$ µm in pure $BaTiO_3$ ceramics (Fig. 1) is probably due to the difference between the values of the surface tensions of the tetragonal and of the cubic forms whether $BaTiO_3$ is considered as a powder or as a ceramic.

However, with respect to basic thermodynamics, the above theory is not completely satisfactory because both relation (1) and relation (2) are not correct in the present situation.

Thermodynamic approach to the influence of the grain size upon the phase transition

General considerations

By applying only the two first principles of thermodynamics rigorously, a more satisfactory theory for the prediction of the phase stability in fine-grained materials is proposed. The main difference is the correct definition of the equilibrium condition when taking into account the surface phenomena: the usual minimization of the Gibbs free energy is no longer able to give the equilibrium equation.

The behaviour of a grain, with radius R, which undergoes a phase transition from α to β is described here. It is clear that the phase transition temperature must depend on the grain size because the stability conditions are determined by the total energy (we will see below what kind of energy), which contains both volume and surface contributions which are size dependent.

The following assumption will be made: the considered grain contains only one component, α or β. This is justified by the fact that, when the two phases coexists in the same grain, there is an important elastic energy, associated with the stresses generated by the difference in density between the two phases. This assumption is rigorous when the Young's modulus of the grain is infinite.

According to Gibbs (see for example [21]), the free energy, F, of a grain is equal to:

$$F(V, T, n, A) = F_V(V, T, n) + F_A(T, A)$$

where F_A is the excess energy due to the surface compared with the volume contribution, F_V, which would be F if the surface did not exist, T is the temperature, V the volume, A the surface area and n the number of moles inside the grain.

In a similar way, the internal energy $U(V, S, n, A)$, obtained by the classical Legendre transformation of F, has the additive form:

$$U(V, S, n, A) = F(V, T, n, A) + TS(V, T, n, A) = U_V(V, S_V, n) + U_A(S_A, A)$$

where: $S_V = \left|\frac{\partial F_V}{\partial T}\right|_{V,n}$, $S_A = \left|\frac{\partial F_A}{\partial T}\right|_{A}$, $S = \left|\frac{\partial F}{\partial T}\right|_{V,n,A} = S_V + S_A$, are the volume, surface and total entropies, respectively. $U_V = F_V + TS_V$ and $U_A = F_A + TS_A$ are the volume and surface internal energies.

The two first principles of the thermodynamics can be now applied to the system composed of the grain under consideration.

Application of the first principle

For any transformation (reversible or not), the following relation can be written:

$$dU = -P_{int}dV + TdS + \mu dn + \gamma dA = -P_{ext}dV + \delta Q$$

where P_{int} is the pressure inside the grain, P_{ext} the external pressure, μ the chemical potential of the considered phase and γ a parameter equal by definition to: $\gamma = \left|\frac{\partial U}{\partial A}\right|_{V,S,n}$ (a physical interpretation of γ will be given latter).

The first relation: $dU = -P_{int}dV + TdS + \mu dn + \gamma dA$ expresses the fact that $U(V,S,n,A)$ is an exact differential (i.e. a state function), whereas the second relation: $dU = -P_{ext}dV + \delta Q$ corresponds to the well-known relation: $dU = \delta W_{ext} + \delta Q$ with $\delta W_{ext} = -P_{ext}dV$.

Application of the second principle

The following relation expresses this second principle:

$$TdS = \delta Q + TdS_i$$

where dS_i is the irreversible entropy production.

Fundamental equation and calculation of the free energy

The two principles of thermodynamics lead immediately to the fundamental equation for the free energy:

$$dF = -P_{int}dV - SdT + \mu dn + \gamma dA = -P_{ext}dV - SdT - TdS_i$$

Then, considering the homogeneity of the system: $F(\lambda V, T, \lambda n, \lambda A) = \lambda F(V, T, n, A)$, the Euler theorem gives the following expression for the free energy:

$$F(V, T, n, A) = -P_{int}V + \mu n + \gamma A$$

with $F_V(V, T, A) = -P_{int}V + \mu n$ and $F_A(T, A) = \gamma A$.

Interpretation of γ

By definition, $\gamma = \left|\frac{\partial U}{\partial A}\right|_{V,S,n}$. It is also equal to $\left|\frac{\partial F}{\partial A}\right|_{V,T,n} = \left|\frac{\partial F_A}{\partial A}\right|_{T}$ due to the properties of the Legendre transformation.

Since $F_A(T, A) = \gamma A$, the parameter γ must be considered as the free energy per unit surface. That is only true because F_A has been considered as depending on T and A only. In other words, the possible effects of a chemical contribution to the surface free-energy have been neglected.

The two parameters: P_{int} *and* P_{ext}

It is of considerable importance to note the difference between P_{int} and P_{ext}. The parameter P_{int}, which is equal to $\left|\frac{\partial U}{\partial V}\right|_{S,n,A}$, is a state parameter defined from state functions: it corresponds then to the local pressure inside the grain. On the other hand, P_{ext} is the external applied pressure.

In classical thermodynamics (without surface considerations), P_{int} and P_{ext} are the same at equilibrium ($TdS_i = 0$). However, when we consider surface phenomena, these two quantities are different. It is easy to obtain from the fundamental free-energy equation that the equilibrium ($TdS_i = 0$) of a grain which does not exchange matter with the universe ($dn = 0$), satisfies the following relation:

$$P_{int} = P_{ext} + \frac{dA}{dV}\gamma$$

Due to the spherical geometry of the grain, the following well-known Laplace relation can be obtained:

$$P_{\text{int}} = P_{\text{ext}} + \frac{2\gamma}{R} \tag{4}$$

This expression, which could also be derived from the principle of virtual work, means that the internal pressure must equilibrate both the external pressure and the surface tension.

What is the energy which describes the system?

In thermodynamics, it is usual to determine the energy (generally obtained by an adequate Legendre transformation from the internal energy) which is minimal at equilibrium. This is the energy which takes into account the interactions with the external universe and then correctly describes the system.

For the usual systems (without surface phenomena) that undergo changes at P_{ext} and T constant, the correct energy is the Gibbs free-energy: $G_V(P_{\text{int}}, T, n) = F_V + P_{\text{int}}V$. In this standard situation:

$$\mathrm{d}G_V = V\mathrm{d}P_{\text{int}} - S\mathrm{d}T + \mu\mathrm{d}n = (P_{\text{int}} - P_{\text{ext}})\mathrm{d}V - S\mathrm{d}T + V\mathrm{d}P_{\text{int}} - T\mathrm{d}S_i$$

The equilibrium condition is: $\mathrm{d}G_V = 0$ ($P_{\text{int}} = P_{\text{ext}}$ because of the mechanical equilibrium, $T\mathrm{d}S_i = 0$ since there is reversibility, $\mathrm{d}T = 0$ and $\mathrm{d}P_{\text{int}} = \mathrm{d}P_{\text{ext}} = 0$ because T and P_{ext} are constant. Note that T is here the temperature of the system, which is equal to the external temperature at equilibrium, and that it is this latter quantity which is in fact imposed).

Now, when there are surface phenomena, the Gibbs free-energy is not the right quantity, as one can see by writing the differential $\mathrm{d}G$ of $G(P_{\text{int}}, T, n, A)$:

$$\mathrm{d}G = V\mathrm{d}P_{\text{int}} - S\mathrm{d}T + \mu\mathrm{d}n + \gamma\mathrm{d}A = (P_{\text{int}} - P_{\text{ext}})\mathrm{d}V - S\mathrm{d}T + V\mathrm{d}P_{\text{int}} - T\mathrm{d}S_i$$

At equilibrium: $\mathrm{d}V$ and $\mathrm{d}P_{\text{int}}$ are both different from 0, so that G is not at a minimum.

In fact the energy to consider is $G^* = F + P_{\text{ext}}V$ whose differential is equal to:

$$\mathrm{d}G^* = V\mathrm{d}P_{\text{ext}} - S\mathrm{d}T + \mu\mathrm{d}n + \gamma\mathrm{d}A - (P_{\text{int}} - P_{\text{ext}})\mathrm{d}V = V\mathrm{d}P_{\text{ext}} - S\mathrm{d}T - T\mathrm{d}S_i$$

At equilibrium, $T\mathrm{d}S_i = 0$, and as $\mathrm{d}T = 0$ and $\mathrm{d}P_{\text{ext}} = 0$: $\mathrm{d}G^* = 0$.

The energy which describes the system is then G^* and not G as it is generally considered. The reason being that G^* and not G is at a minimum at equilibrium.

Interpretation of G^* as the chemical/mechanical free energy

By definition: $G^*=F+P_{ext}V$ so that at equilibrium

$$G^* = G - \frac{2\gamma}{R}V \tag{5}$$

G^* is then the sum of the usual Gibbs free-energy which is a chemical energy and of an additional mechanical term which corresponds to the elastic energy due to the surface tension. For this reason, we call G^* the chemical/ mechanical free energy.

A small difficulty is that the energy G^* cannot be obtained from a Legendre transformation of the classical energies, such as U or F, so that a large number of the classical thermodynamic relations which are direct consequences of the properties of the Legendre transformations are not available here. In particular, it is not possible to decide which is the correct set of independent variables, necessary to express easily the energy G^*.

Calculation of G^*

It is necessary to calculate the chemical potential $\mu(P_{int}, T)= G_V(P_{int}, T, n = 1)$. Using the Maxwell relation:

$$\left|\frac{\partial\mu}{\partial P_{int.}}\right|_{T,n} = \left|\frac{\partial V}{\partial n}\right|_{P_{int.},T} = \bar{V}.$$

where $\bar{V}$ is the partial molar volume of the constituent of the grain, and assuming moreover that the material is incompressible ($\bar{V}$ does not depend on P_{int}), the following relation is obtained:

$$\mu(P_{int}, T) = \mu^o(T) + P_{int}\bar{V}$$

Then $G^* = F + P_{int}V = G + (P_{ext} - P_{int})V$:

and $G^* = \mu^o n + \gamma A + P_{ext}V = n(\mu^o + \frac{3\gamma\bar{V}}{R} + P_{ext}\bar{V})$

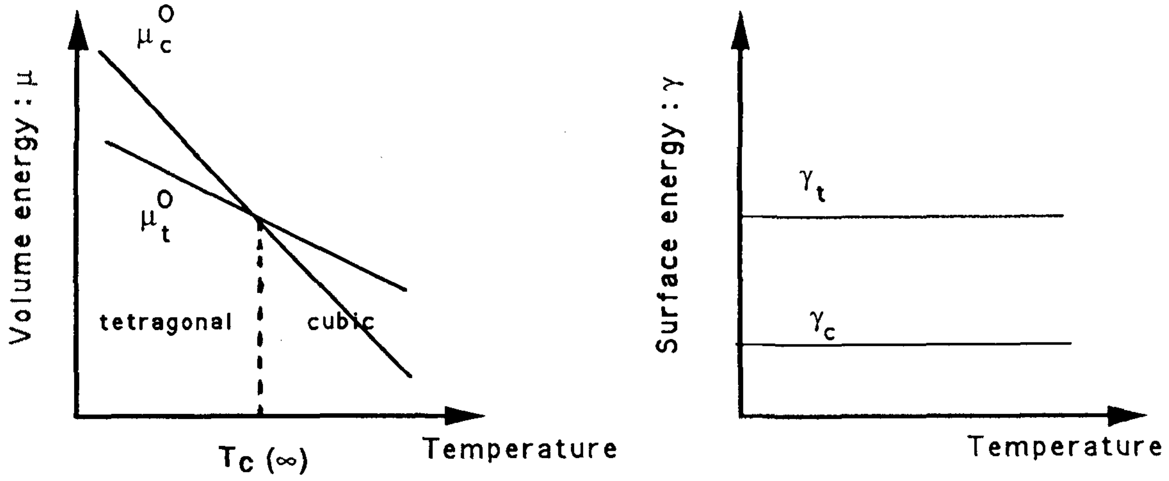

Fig. 5 Diagrammatic representation of the chemical potentials and of the surface free-energies of $BaTiO_3$ given as a function of temperature for the cubic (*c*) and the tetragonal (*t*) phases

The quantity $g^* = \mu^o + \frac{3\gamma V}{R}$ is the chemical/mechanical potential which generalizes the usual chemical potential without surface phenomena. It differs from the generalized potential proposed by Turnbull which was equal to $\mu^o + \frac{2\gamma V}{R}$ [21].

Study of phase stability

At T and P_{ext} constant, there is a phase transition between the two phases α and β when $G_\alpha{}^* = G_\beta{}^*$. The transition condition is then:

$$\mu^o_\alpha + \frac{3\gamma_\alpha V_\alpha}{R} + P_{ext}V_\alpha = \mu_\beta + \frac{3\gamma_\beta V_\beta}{R} + P_{ext}V_\beta$$

This equality is satisfied for a critical radius R_c which depends on the surface free-energies, on the chemical potentials and on the external pressure:

$$R_C = -3\frac{\gamma_\alpha V_\alpha - \gamma_\beta V_\beta}{(\mu^o_\alpha + P_{ext}V_\alpha) - (\mu^o_\beta + P_{ext}V_\beta)} \tag{6}$$

When the difference between the density of the two phases is very small ($V_\alpha \approx V_\beta \approx V$) the critical diameter $\Phi_c = 2R_c$ becomes:

$$\Phi_C = -6\frac{V(\gamma_\alpha - \gamma_\beta)}{\mu^o_\alpha - \mu^o_\beta} \tag{7}$$

Comparing relations (3) and (7), the numerical coefficient λ has now te be equal to 6.

Discussion: application to BaTiO3

For $BaTiO_3$, which undergoes a cubic/tetragonal transformation, Fig. 5 shows the respective variations of the surface energy, γ, and of the chemical potential, μ. As usual, the chemical potentials are assumed to be linearly dependent on temperature and the surface free energy is assumed to be only slightly dependent on the temperature. Considering only the volume energy, the phase would be tetragonal below $T_c(\infty)$ and cubic above $T_c(\infty)$. This is observed for very large grains when the surface contribution can be neglected. On the contrary, for very small grains (where the volume energy can be neglected), the phase is cubic whatever the temperature. Note that it is necessary to assume $\gamma_c < \gamma_t$ to explain the experimental results.

One can then easily understand the grain-size dependency of the phase transition temperature. Figure 6 gives the chemical/mechanical free energy per mole, g^*, of both phases, $BaTiO_3$ tetragonal and cubic, as a function of temperature for two different grain sizes. g^* is the sum of the volume and surface energies per mole. The figure clearly shows a phase transition temperature increasing with grain size.

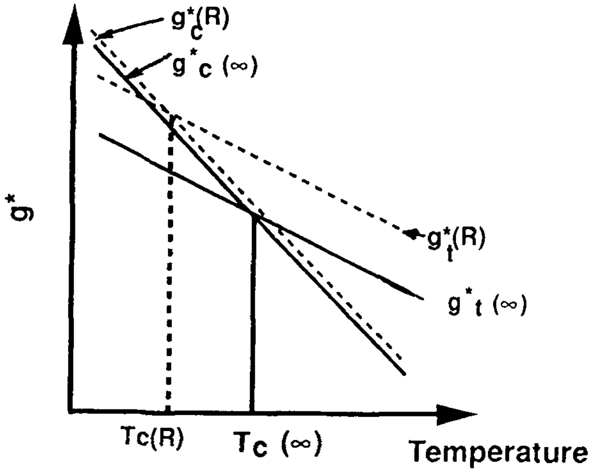

Fig. 6 Grain-size dependency of the phase transition temperature of $BaTiO_3$. The chemical/mechanical free-energy per mole of both phases, g^*: tetragonal (t) and cubic (c) is given as a function of temperature. R is the radius of the grain under consideration: when $R = \infty$, only the volume properties have to be considered

This result is consistent with the direct calculation of the variation of the critical radius R_c with temperature:

$$\frac{d}{dT_c}\left(\frac{1}{R_c}\right)=\frac{1}{3}\frac{S_c^0-S_t^0}{(\gamma_c-\gamma_t)V}$$

where S_c^0 and S_t^0 are the molar entropies of both phases, cubic and tetragonal. As $\gamma_c < \gamma_t$ (see above) and $S_t^0 < S_c^0$ (the phase with the greater entropy is stable at high temperature), $\frac{d}{dT_c}\left(\frac{1}{R_c}\right) \leq 0$, so that as R_c increases T_c increases.

The difference between the grain size corresponding to the drastic increase of ε_r for $BaTiO_3$ ceramics ($\Phi_{c(s/s)} = 0.8$ µm) and the critical grain size relative to the phase transition for $BaTiO_3$ powders ($\Phi_{c(s/a)} = 0.08$ µm) can be understood using the above thermodynamic treatment. There would always be an exact correspondence between the maximum permittivity and the phase transition, but the critical grain size, which depends on the surface free energies of the two phases, cubic and tetragonal, is different for ceramics and for powders: for ceramics, the surface under consideration is a solid/solid interface, whereas it is a solid/air interface in the case of powders. When the stresses relative to the polycrystalline nature of ceramic materials are neglected, relation (7) predicts the ratio of the surface free energies between ceramics $(\gamma_c - \gamma_t)_{s/s}$ and powders $(\gamma_c - \gamma_t)_{s/a}$ as a function of the critical grain sizes $\Phi_{c(s/s)}$ and $\Phi_{c(s/a)}$:

$$\frac{(\gamma_c - \gamma_t)_{s/s}}{(\gamma_c - \gamma_t)_{s/a}} = \frac{\Phi_{c(s/s)}}{\Phi_{c(s/a)}} \approx 10$$

Conclusion

The grain-size dependency of a phase transition is a general phenomenon; the example of Fe_2O_3 has been given more recently [23], and the expression 'size driven phase transition' has been used [24].

The difference in behaviour of $BaTiO_3$ powders and $BaTiO_3$ ceramics with respect to grain size has been explained by surface considerations. This interpretation, which has been validated qualitatively, would have to be confirmed by both a full experimental study (crystallographic and dielectric) and direct measurements of the surface free-energies for ceramics and for powders.

Such surface considerations have already been used to explain the grain-size dependency of some phase transitions. However, the usual thermodynamic models have some small errors which have been avoided by using rigorous basic thermodynamics. The main idea is that, as a consequence of the difference between the external and the internal pressure in the grains, the Gibbs free energy is no longer able to describe the equilibrium condition.

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Zusammenfassung — Korngrößenabhängige Phasenumwandlungen verursachen bei Materialien wie Zirkonerde oder Bariumtitanat sehr interessante Eigenschaften. Unter Berücksichtigung der Oberflächenerscheinungen wurde ein neue und gründliche thermodynamische Behandlung dieses Typs von Phasenumwandlungen vorgeschlagen. Es wird eine Erörterung der beobachteten Differenzen in Abhängigkeit davon angestellt, ab das untersuchte Material – hier $BaTiO_3$ – ein feingekörntes Pulver oder eine feingekörnte Keramik ist.