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Size effects on Curie temperature of ferroelectric particles

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ABSTRACT A model for the size dependence of the Curie temperature T_c of perovskite ferroelectric particles without any free adjustable parameters has been developed. The model predicts that T_c decreases with decreasing particle size. The predictions of the model are in agreement with experimental results for $PbTiO_3$ and $BaTiO_3$.

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1 Introduction

As ferroelectric device elements become smaller and smaller, with the dimensions of the ferroelectric material in the sub-micrometer range or even lower, the physical properties are size-dependent, and this must be taken into consideration in optimizing the properties [1, 2]. One of the most important properties is the size dependence of the Curie temperature. A quantitative model for T_c of $PbTiO_3$ particles has been established on the basis of mechanical and thermodynamic considerations using the Landau–Ginzburg–Devonshire (LGD) phenomenological theory [3]. The model prediction corresponds well to the experimental results for $PbTiO_3$ particles. However, the model cannot be extended to predict T_c of $BaTiO_3$ particles even though both have the same octahedral structure. Therefore, a general model to predict the size dependence of T_c is needed.

Recently, a thermodynamic model for the solid–liquid transition (a first-order transition) has been developed for crystals of finite size for metals [4], semiconductors [5], organics [6] and molecules [7]. The model has also been extended to the glass–liquid transition (a second-order transition) of polymers [8] and organics [9]. Since the model is suitable for predicting transitions of both the first and the second order and the Curie transition of a ferroelectric is also a first-order phase transition, finite-size effects on the Curie temperature T_c of perovskite ferroelectric particles may be related to the corresponding effects on the melting temperature of nanocrystals. In this contribution, the size-dependent crystal–liquid transition model will be generalized to predict finite-size effects on the Curie temperature of ferroelectrics. This extension of the model is found to be consistent with the experimental results for $PbTiO_3$ and $BaTiO_3$ particles.

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2 Model

The size-dependent melting temperature $T_m(D)$ of a crystal with diameter D is given by [4–7]

$$\frac{T_m(D)}{T_{m0}} = \exp\left(-\frac{2S_m}{3R}\frac{1}{D/D_0 - 1}\right), \quad (1)$$

where T_{m0} is the melting temperature of the corresponding bulk crystal. S_m denotes the bulk melting entropy and R is the ideal gas constant. D_0 denotes a critical radius where a crystal particle and a liquid particle are indistinguishable.

To extend the above model to the size-dependent Curie transition temperature T_c, S_m is substituted by the transition entropy S_0 and D_0 is defined as a critical particle size where the ferroelectric phase cannot exist or the Curie transition is absent. D_0 is determined by [10]

$$D_0 = \sigma_{90} / \left(2k\alpha\beta^2\right), \quad (2)$$

where σ_{90} denotes the density of 90° domain walls, k is a coefficient, α is the elastic stiffness of the material and $\beta = (c/a) - 1$, with c and a being the lattice constants of the material. With the above definitions, (1) can be rewritten as

$$\frac{T_c}{T_{c0}} = \exp\left(-\frac{2S_0}{3R}\frac{1}{D/D_0 - 1}\right), \quad (3)$$

where T_{c0} is the bulk Curie temperature.

3 Results and discussion

The T_c functions of $BaTiO_3$ and $PbTiO_3$ have been predicted using (3) and compared with experimental results. The predictions and experimental results are shown for $BaTiO_3$ and $PbTiO_3$ in Figs. 1 and 2, respectively. In the figures and in the predictions from (3), T_c decreases as D decreases. The predicted T_c functions of $BaTiO_3$ and $PbTiO_3$ are in agreement with the corresponding experimental results. Comparing Figs. 1 and 2, it is evident that the drops of T_c of the two compounds with decreasing D have different tendencies, since $BaTiO_3$ has a larger D_0 value and a smaller S_0

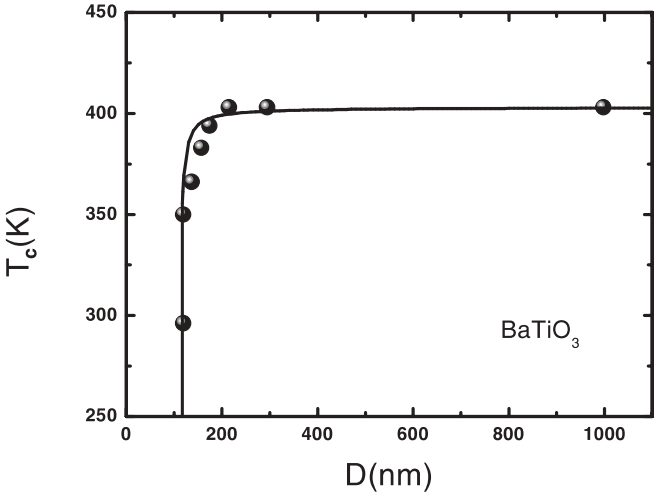

FIGURE 1 Comparison between theoretical predictions of (3) (*solid line*) and experimental results (•) [11] for T_c of $BaTiO_3$ particles. $S_0 = 0.1$ J g-atom^{-1} K^{-1} [12], $T_{c0} = 403$ K [13]. D_0 has been determined to be 40 nm [10]. However, the value of the tetragonality c/a in (2) decreases with decreasing particle size. Taking account of this consideration, D_0 has been redetermined as 110 nm [11]

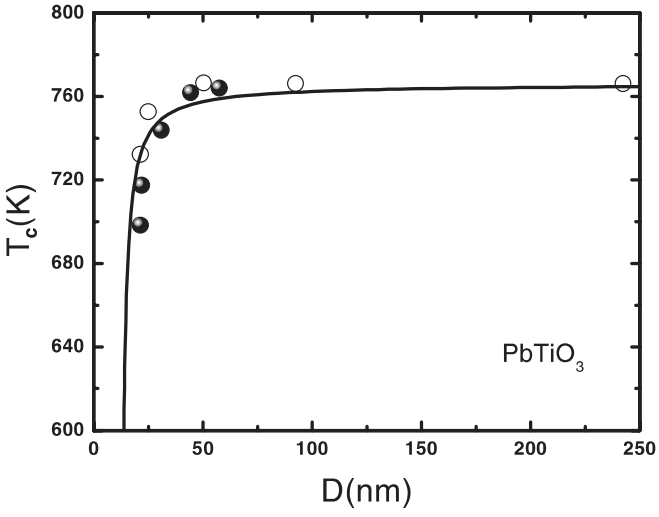

FIGURE 2 Comparison between theoretical predictions of (3) (*solid line*) and experimental results (• [14] and ∘ [15]) for T_c of $PbTiO_3$ particles. $S_0 = 0.46$ J g-atom^{-1} K^{-1} [16], $T_{c0} = 765.1$ K [17]. $D_0 = 11.8$ nm has been determined from (2) using the following parameters: $\sigma_{90} = 0.05$ J/m^2 [18]; $\beta = (c/a) - 1 = 0.065$, where $c = 0.4156$ nm and $a = 0.3902$ nm [17]; and $k\alpha = 0.5 \times 10^9$ N m^{-2} [10]

value than has $PbTiO_3$. The two effects of D_0 and S_0 on T_c lead to the result that the size effect in $BaTiO_3$ is weaker than that in $PbTiO_3$ in terms of (3). This difference could be due to the fact that $BaTiO_3$ has a higher domain wall energy density and a lower tetragonality c/a in comparison with $PbTiO_3$. Thus, the Curie transition of $BaTiO_3$ can proceed easily, and a large-sized domain may be formed easily also.

Note that the Curie transition model [3], in terms of the LGD phenomenological theory, has the form

$$\frac{T_c}{T_{c0}} = 1 - \frac{C}{D}, \tag{4}$$

where C is a material constant. Equation 4 in fact is the same as (3) when D is at least one order magnitude larger than D_0, owing to the mathematical relationship $\exp(-x) \approx 1 - x$. In this case, (3) can be rewritten as $T_c/T_{c0} = 1 - C/D$, where $C = 2S_0D_0/3R$. However, as D approaches D_0, (3) becomes more suitable for predicting the size-dependent Curie transition temperature. This could be the reason why (4) may predict the transition behavior of $PbTiO_3$, with a smaller D_0, satisfactorily but fails to predict the behavior of $BaTiO_3$, which has a larger D_0.

4 Conclusion

Our model for the size dependence of melting has been generalized to describe the size dependence of the Curie temperature of $PbTiO_3$ and $BaTiO_3$ particles by making use of the common feature of a first-order transition in these problems. It was found that the results predicted by the model for the size-dependent Curie temperature of the above compounds were in agreement with the experimental results.

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