

Estimation of Specific Heat of BaTiO₃ Crystals Derived from Relationship Between Uniaxial Pressure and Electric Field

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Shifting the Curie temperature in dependence on both uniaxial pressure and electric field in BaTiO₃ crystals was studied based on literature data. It was shown that both these dependences perfectly coincide when adjusting the scale. Based on coincidence of these dependencies a relationship between both an uniaxial pressure and an electric field when shifting the Curie temperature was established. The specific heat is calculated using this relationship.

Keywords: Curie temperature, uniaxial pressure, electric field, specific heat.

1. Introduction

Barium titanate, BaTiO₃, is a well-known ferroelectric, has been discovered in 1945 and since is extensively studied. It is well documented that upon heating BaTiO₃ undergoes a structural transition from ferroelectric to paraelectric phase pointed out by sharp peak of dielectric permittivity at the Curie temperature, T_c . An effect of both electric field, E , and mechanical pressure, p , on T_c shift is studied as well.

Shifting the T_c on 8.5°C, detected from the hysteresis loops of BaTiO₃ crystals grown by the Remeika method, was found to be a linear as E enhances up to 6 kV/cm at the fixed temperatures up to 116°C¹. Meanwhile, shifting the T_c on 15°C, detected from the birefringence of BaTiO₃ crystals grown by the Remeika method, was found to be a nonlinear as E enhances up to 12 kV/cm and a linear as E weakens down to 0 kV/cm at the fixed temperatures up to 136°C². However, shifting the T_c on 3°C, detected by the acoustic emission of BaTiO₃ crystals grown by the melt-grown method, was found to be a linear upon heating at the fixed fields up to 2 kV/cm³. Recently, shifting the T_c on 8.5°C, detected from the electrocaloric effect of BaTiO₃ crystals grown by the melt-grown method, was found to be a nonlinear upon heating at the fixed fields up to 10 kV/cm⁴. While the dependencies between T_c and E in Merz¹ and Dul'kin et al.³ coincide well, the dependencies between T_c and E in Meyrhofer² and Bai et al.⁴ are not consistent.

Shifting the T_c on 3°C, detected by the dielectric permittivity of BaTiO₃ crystals grown by the melt-grown method, upon heating up to 410°C at the fixed uniaxial pressures up to 1000 bar was measured previously⁵. Shifting the T_c in dependence on p was approximated to be a linear, but one can clearly see that it is a very rough approximation. In fact the $T_c(p)$ dependence is a nonlinear and visibly trends to saturation as the p enhances. Also a relationship between p and E , p/E one can calculate to be 23.8 bar·cm/kV at room temperature, not at T_c , as it might be expected.

The goal of the present paper to derive the relationship between both p and E within the T_c shifting region based on

comparison the data of above cited works and check it for usefulness in practical application.

2. Material

In this paper a consideration is devoted to comparison the data of BaTiO₃ crystals, used in Bai et al.⁴ and Suchanicz et al.⁵, because they were grown by the same melt-grown method, and exhibit the same $T_c \approx 407$ K, and studied at the same conditions: upon heating under fixed pressure and field up to their higher values, and, thus, can be compared truly.

3. Results and Discussion

Figure 1 presents the T_c shifting in dependence on both p and E reconstructed from the corresponding data of Bai et al.⁴ and Suchanicz et al.⁵, respectively. Accurate reconstructed the T_c shifting in dependence on p is indeed a nonlinear in contrast to that declared in Suchanicz et al.⁵. One can see that both these dependencies perfectly coincide when adjusting the scale. Such the perfect coincidence unambiguously proves that both p and E shift the T_c in the same manner.

Both these $T_c(p)$ and $T_c(E)$ dependencies are approximated the following equations:

for uniaxial pressure

$$T_c^p = 407 + 3.2 \cdot 10^{-3} p - 7.3 \cdot 10^{-7} p^2 \quad (1)$$

for electric field

$$T_c^E = 407 + E - 2.29 \cdot 10^{-2} E^2 \quad (2)$$

From these equations one can establish the relationship between both p and E values at the same T_c . For example, to shift the T_c on 1 K, i.e. up to 408 K one need apply or the equivalent $p = 335$ bar or the equivalent $E = 1$ kV/cm, and, consequently, the relationship between p and E , $\frac{dp}{dE}$ is about 335 bar·cm/kV = $3.35 \cdot 10^2$ N/mV at T_c .

Let's now check this relationship for usefulness in practical application. For example, let us apply it to calculate the specific

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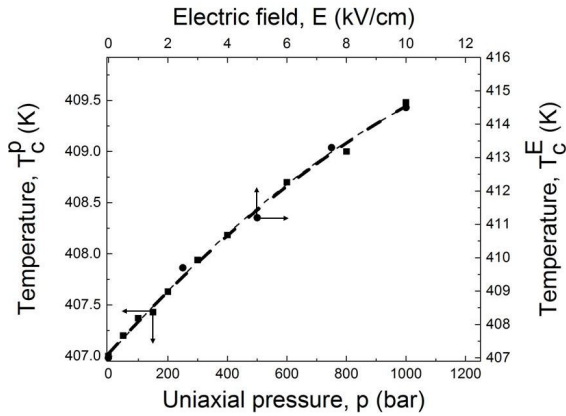


Figure 1. A complex plot of T_c shifting in dependence on an uniaxial pressure, p , (filled squares, thick dash) and on an electric field, E , (filled circles, thin dash).

heat, L , during the phase transition in BaTiO_3 crystals due to essential contradiction in their L values: $\sim 2.37 \text{ J/kg}^4$ and $\sim 0.54 \text{ J/kg}^6$.

For our calculations we will use the Clausius-Clapeyron relations⁷:

$$\frac{dp}{dT_c} = \frac{L}{T_c \Delta v} \quad (3)$$

$$\frac{dT_c}{dE} = \frac{1}{\alpha_0} \sqrt{\frac{16\gamma}{3\beta}} \quad (4)$$

where: p - pressure, T_c - Curie temperature, v - volume, reduced to the mass of the crystal, E - electric field, α_0 , β , γ are the coefficients of the Landau expansion.

It is well-known that in BaTiO_3 crystals the ratio of the $\Delta c/\Delta a$ axes is about $0.014/0.006 \approx 2.33$ at $T_c \approx 407 \text{ K}$ ⁸. The Δc is obviously proportional to $\Delta h \approx 2 \mu\text{m}$, measured at T_c in BaTiO_3 crystals with the sizes: $h = 0.5 \text{ mm}$ and $l = 5 \text{ mm}$ ⁹, and, so, $-\Delta l \approx -0.86 \mu\text{m}$, and, consequently, the volume change during the phase transition is about $4.6 \cdot 10^{-11} \text{ m}^3$. Because the BaTiO_3 density is $6.02 \cdot 10^3 \text{ kg/m}^3$, crystal mass is found to be $75.25 \cdot 10^{-6} \text{ kg}$ and $\Delta v \approx 0.06 \cdot 10^{-3} \text{ m}^3/\text{kg}$. And $\alpha_0 = 3.3 \cdot 10^5 \text{ Jm}^2/\text{C}^2\text{K}$, $\beta = 1.37 \cdot 10^8 \text{ Jm}^5/\text{C}^4$, $\gamma = 2.76 \cdot 10^9 \text{ Jm}^9/\text{C}^6$ ¹⁰.

When multiplying Equation 3 by Equation 4 we obtain the relation:

$$\frac{1}{T_c} \frac{dp}{dE} = \frac{L}{\alpha_0 T_c \Delta v} \sqrt{\frac{16\gamma}{3\beta}} \quad (5)$$

from which the L is calculated to be $\approx 6.42 \text{ J/kg}$. This data is obviously lies closer to $L \approx 2.37 \text{ J/kg}^4$, not to $L \approx 0.54 \text{ J/kg}^6$, and the former is believed to be really true.

Note that our L value is calculated at $\frac{dp}{dE} = 335 \text{ bar}\cdot\text{cm}/\text{kV}$ of $\Delta T=1 \text{ K}$. Unfortunately, L value varies in dependence on ΔT due to some nonlinearity of both $T(p)$ and $T(E)$ dependencies. The error is approximately to be 14% for $\frac{dp}{dE} = 382 \text{ bar}\cdot\text{cm}/\text{kV}$ of $\Delta T=2.5 \text{ K}$ in relation to $\frac{dp}{dE} = 335 \text{ bar}\cdot\text{cm}/\text{kV}$ of $\Delta T=1 \text{ K}$, that is satisfactory for estimation of the specific heat. Thus, this relationship between p and E is proved to be useful for practical applications.

4. Conclusions

In summary, we have compared the Curie temperature shifting in dependence on both uniaxial pressure and electric field based on literature data and found their acting proportionally the same. Based on this proportionality we have established the relationship is equal to be $335 \text{ bar}\cdot\text{cm}/\text{kV}$ between both uniaxial pressure and electric field when shifting the Curie temperature. Using this relationship we estimated the specific heat is equal to be 6.42 J/kg during the phase transition in BaTiO_3 crystals.

5. References

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