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Abstract. Bismuth tetratitanate, $Bi_2Ti_4O_{11}$, undergoes a paraelectric-to-antiferroelectric phase transition at about 233 °C. The integrated intensities of selected x-ray reflections and the linear optical excess birefringence have been measured as a function of temperature for $Bi_2Ti_4O_{11}$ to characterize the transformation. Both methods indicate a continuous transition with a critical exponent of $\frac{1}{4}$. From the change of the lattice constants with temperature the scalar spontaneous strain, ϵ_s, can be calculated. In the present case of a zone boundary transformation, ϵ_s couples quadratically with the primary order parameter. The observed linear dependence of ϵ_s^2 on the temperature T points once again to the tricritical nature of the transition. Despite the mean field behaviour of the transition inferred from these results, diffuse intensities at the positions of superlattice reflections just above T_c may be attributed to the existence of non-classical order parameter fluctuations. Taking this observation into account the transformation can be designated as almost tricritical.

1. Introduction

The structural phase transition in bismuth tetratitanate at about 250 °C was first reported by Subbarao [1] who investigated the transformation using dielectric and dilatational measurements. The space groups $C2/m$ and $C2/c$ for the high- and the low-temperature phases, respectively, were suggested in [2]. The x-ray powder diffraction pattern for the β phase was presented in an article of Mitrovich and Blinov [3]. The transition temperature given by these authors is 240 °C. Raman scattering experiments were carried out by Hisano and Toda [4]. According to their results the transition at 238 °C is reflected in the Raman spectrum by a considerable softening of a mode near 38 cm^{-1}. The theoretical studies of Tolédano and Tolédano [5] on non-ferroic phase transformations revealed first information about the character of the α-to-β transition in $Bi_2Ti_4O_{11}$ based on the dielectric data of Subbarao. The close resemblance between their predicted temperature dependence of the dielectric susceptibility for a continuous transition and the experimental variation of $\chi(T)$, as well as the absence of a dielectric hysteresis loop, are consistent with a second-order transition.

A structural description of the transformation was given in [6] as the symmetry breaking of the high-temperature phase with space group $C2/m$ to $C2/c$ and the critical point $A = (0\,0\,\frac{1}{2})$ on the surface of the Brillouin zone of $C2/m$. The transition at $T_c = 233$ °C is induced by a displacement of the cations in the tunnels of the TiO_6 octahedral network. The Bi shifts parallel and antiparallel to the b axis were taken as the primary order parameter η. From projection operator methods it became obvious that η transforms as the A_2^+ irreducible representation (notation of Stokes and Hatch [7]) fulfilling the group theoretical conditions for a continuous transformation. The lattice parameters of the high-temperature structure in

the setting used for group theoretical considerations are as follows: $a \simeq 14.6$ Å, $b \simeq 4.0$ Å, $c \simeq 10.8$ Å and $\beta \simeq 136°$. In this case the transition is indicated by a cell doubling in the [0 0 1] direction. The indexing of the reflections and the evaluation of the spontaneous strain in this investigation are referred to a different setting with a pseudotetragonal cell ($a \simeq 14.6$ Å, $b \simeq 4.0$ Å, $c \simeq 14.9$ Å and $\beta \simeq 93°$). Using this setting leads to the non-standard space group $F2/m$ for the β phase but offers the possibility of describing the metric of both phases in cells of equal dimensions. Further details of the metrical relations of these cells are discussed in [6].

The aim of this paper is to show that the approach to describe the transition in the terms of the Landau theory is a very good approximation and one justified by experimental results of high-temperature single-crystal x-ray diffraction and optical investigations.

2. Experimental details

The $Bi_2Ti_4O_{11}$ single crystals used in our experiments were synthesized by the flux method. A single-crystal sphere (0.2 mm diameter) was prepared using an Enraf & Nonius sphere grinder. All x-ray diffraction measurements were carried out on a CAD-4 four-circle diffractometer (graphite monochromator; Mo Kα radiation) equipped with a gas flow furnace capable of reaching 1100 °C as described in [8]. The temperature stability was in the range of $\pm$ 0.3 °C. The furnace was fastened to the collimator allowing an almost unrestricted movement of the goniometer head with the crystal. The nitrogen gas flow was regulated through a flow valve at the rate of 0.5 l min^{-1}. For the temperature measurement a multimeter in combination with a chromel–alumel thermocouple mounted on an x–y stage was employed. The crystal was mounted with a ceramic cement on the tip of a silica glass capillary (0.2 mm diameter) cemented into a stainless steel rod. A second capillary (0.5 mm diameter) was slid over the first one.

Diffraction intensities of the ($0\bar{2}1$) reflection were recorded using ω–2θ scans covering $1.33°$ ω with a scan speed of $0.01°$ s^{-1}. The background scattering was measured for one half of the scan time on either side of the scan; the total background was subtracted to obtain the net intensity. The scan was repeated three times for each temperature and the integrated intensities were averaged; a reproducibility of 1% was reached.

The unit cell dimensions were determined by least-squares refinement of the 2θ values of 23 reflections within the 2θ range between 36° and 64°. Each reflection was centred with positive and negative 2θ values to eliminate the zero-point error of the detector.

Linear optical birefringence was measured using a heating stage mounted on a Zeiss polarizing microscope with a calcite compensator and a sodium lamp as a light source†.

3. Determination of the critical exponent

The critical exponent of the transformation was derived from two independent methods: the temperature change of selected Bragg reflections and the variation of the linear optical birefringence with increasing temperature across the transition point.

The temperature dependence of the intensity of the reflection ($0\bar{2}1$) is shown in figure 1. The Laue indices refer to the pseudotetragonal unit cell of the α phase. This reflection was chosen because its integrated intensity decreases rapidly on approaching the transition from below T_c. No indication of a discontinuity was found. However, the reflection which

† This experiment was carried out courtesy of Dr J Hensler and Dr U Bismayer (University of Hanover).

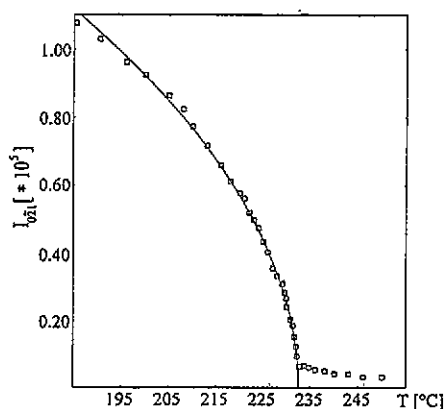should be extinct in the high-temperature phase shows a very weak diffuse scattering also above T_c.

Figure 1. Integrated intensity of the $(0\bar{2}1)$ reflection as a function of temperature; a non-vanishing weak intensity just above T_c is evident.
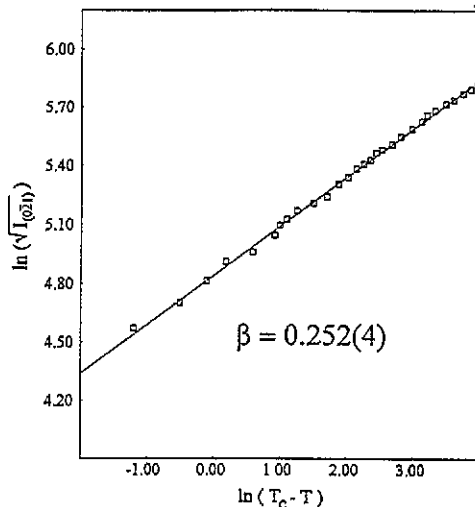

Figure 2. A plot of $\ln(\sqrt{I_{(0\bar{2}1)}})$ versus $\ln(T_c - T)$; the critical exponent is 0.252(4).

The Bragg intensity of a superlattice reflection is proportional to the square of the order parameter of the transition, i.e. $I \propto \eta^2$ [9]. The critical exponent β is related to the order parameter as

$$\eta = \eta_0(T_c - T)^\beta.$$

From a plot of $\ln(\sqrt{I_{(0\bar{2}1')}})$ versus $\ln(T_c - T)$, β can be calculated as the slope of a least-squares linear regression function (see figure 2). The resulting value of 0.252(4) is equal to $\frac{1}{4}$ within one standard deviation implying that the transition is of a tricritical nature.
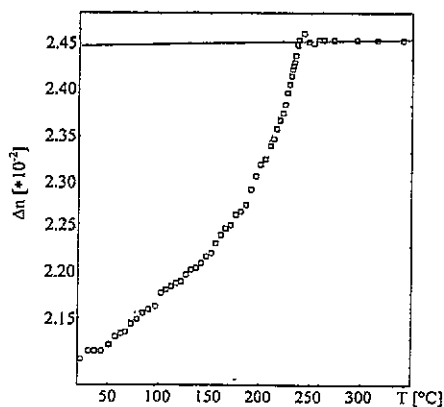

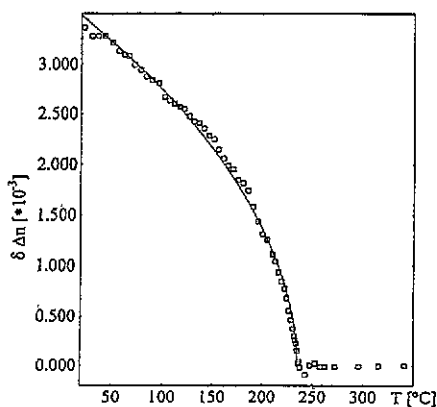**Figure 3.** Thermal dependence of the linear optical birefringence Δn.

Figure 4. Excess birefringence $\delta \Delta n$; the determined critical exponent is 0.258(9).

Figure 3 shows the linear optical birefringence Δn at $\lambda_{Na} = 589.3$ nm as a function of temperature. The curve exhibits a distinct increase in Δn on heating until 235.2 °C

where the birefringence becomes linear on heating. This value for T_c is in good agreement with the results of DSC measurements (233.48 °C) and high-temperature x-ray investigations (233 °C). The excess birefringence $\delta\Delta n$ can be obtained by subtracting the observed value of Δn from a baseline representing the extrapolation of the linear temperature change of Δn in the β phase (figure 4). For a zone boundary transition a relation $\delta\Delta n \propto \eta^2$ must hold. So β can be determined from a least-squares fit using the relation $\delta\Delta n \propto (T_c - T)^{2\beta}$. The calculations lead to a critical exponent of $\beta = 0.258(9)$ which corresponds very well with the x-ray intensity studies.

4. Lattice constants and spontaneous deformation

The cell constants measured on heating from 23 °C to 650 °C are plotted in figures 5–8. The diagrams reveal a significant change in the temperature dependence of all four metrical parameters at the phase transformation. The b-axis value decreases with increasing temperature until T_c is reached whereas a and c show an opposite change with temperature. This thermal behaviour is consistent with our structural model of the transition. The contraction in the [0 1 0] direction is due to the shifts of the cations from the positions in 8(f) of the α phase onto the mirror planes (site 4(i)) of the β phase requiring a coupled expansion in the a–c plane.
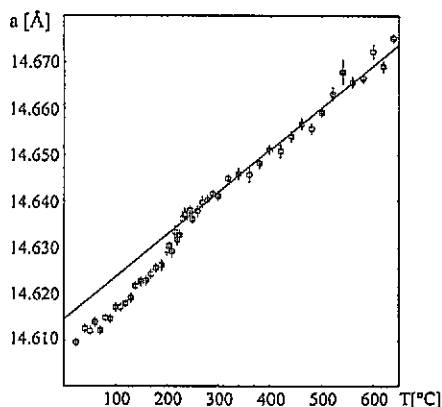

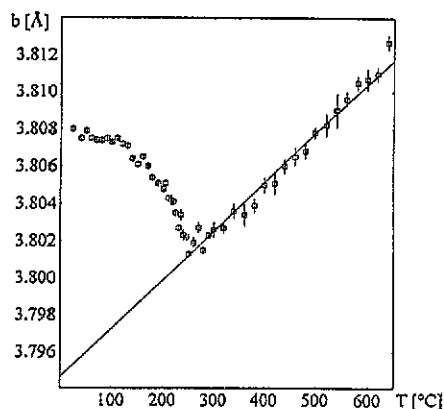**Figure 5.** Lattice constant a as a function of temperature.

Figure 6. Lattice constant c as a function of temperature.

The pronounced non-linear dependence of the lattice parameters below T_c is a common feature of many structural phase transitions and can be attributed to the spontaneous deformation. This physical property is a symmetric second-rank tensor describing that part of the macroscopic distortion in a material which results from a phase transition alone and not from the thermal expansion. Salje [10] discussed several methods for the determination of the spontaneous deformation from the temperature variation of the lattice constants. In the present study the calculation of the tensor components was accomplished by measuring the lattice parameters over a large temperature interval in the high-symmetry phase to warrant a reliable extrapolation into the stability field of the phase with lower symmetry. The relations for obtaining the tensor components from the actual and the extrapolated parameters for general triclinic symmetry were given in [11]. For the monoclinic case the

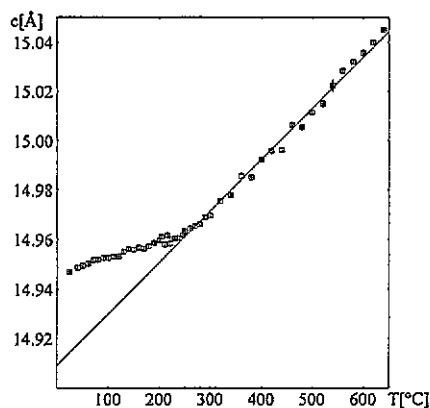four independent components in the standard tensor notation can be calculated using the following equations:

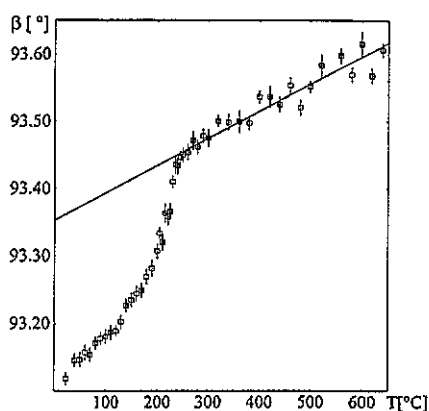**Figure 7.** Lattice constant *b* as a function of temperature.

Figure 8. Monoclinic angle β as a function of temperature.

$$x_1 = x_{11} = \frac{a}{a_0} - 1 \qquad x_2 = x_{22} = \frac{b}{b_0} - 1 \qquad x_3 = x_{33} = \frac{c \sin \beta^*}{c_0 \sin \beta_0^*} - 1$$

$$x_4 = x_{13} = \frac{1}{2}\left(\frac{a \cos \beta_0^*}{a_0 \sin \beta_0^*} - \frac{c \cos \beta^*}{c_0 \sin \beta_0^*}\right). \tag{4.1}$$

The values *a*, *b*, *c* and β belong to the low-symmetry phase whereas the parameters a_0, b_0, c_0 and β_0 describe the metric of the higher-symmetric structure; the parameters labelled with a star represent the corresponding reciprocal lattice constants. The orthogonal coordinate system g_1, g_2, g_3 used for the description of the tensor components was defined in such a way that g_2 is parallel to the *b* axis (the common direction of both cells), g_3 is parallel to c^* and g_1 is perpendicular to g_2 and g_3. The change of the four components with temperature is shown in figures 9 and 10. The strain tensor can be transformed to its principal axis giving the principal strains. The diagonalization process for each tensor was carried out using the Mohr circle construction as described in [12]. Figure 11 depicts the principal strain elements ϵ_1, ϵ_2 and ϵ_3. It is interesting to note that the components ϵ_2 and ϵ_3 are almost equal in magnitude although there is no corresponding symmetry constraint in the monoclinic system. The associated representation quadric of this second-rank tensor is a hyperboloid of revolution of one sheet. In order to compare the lattice deformations in different crystal systems a scalar spontaneous strain, ϵ_s, is used in the literature. According to the definition given in [13] ϵ_s can be calculated from the diagonal elements by the formula

$$\epsilon_s = \sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2}. \tag{4.2}$$

At 23 °C, the scalar spontaneous strain in Bi$_2$Ti$_4$O$_{11}$ is approximately 51×10^{-3}. This value is comparable with the results for the zone boundary transformation in NaNO$_3$ (55×10^{-3} [14]) and can be considered large with respect to other non-ferroic or improper ferroelastic transitions, for example in anorthite, with an ϵ_s of about 5×10^{-3} [13].
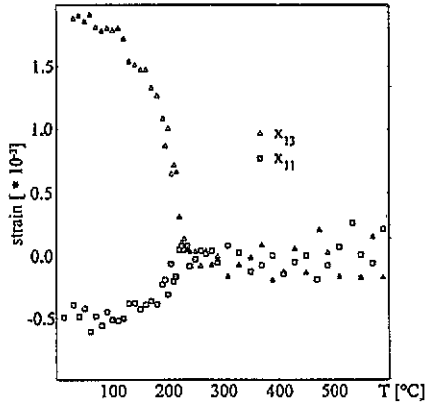
Figure 9. Temperature dependence of the strain tensor components x_{11} and x_{13}.
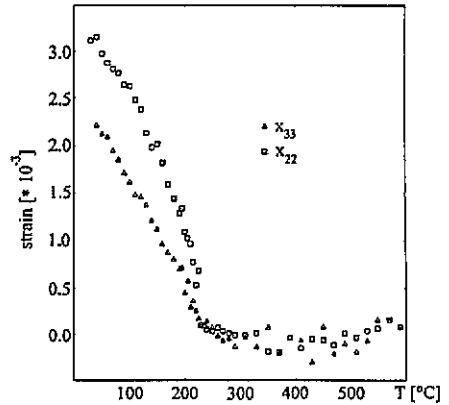
Figure 10. Temperature dependence of the strain tensor components x_{22} and x_{33}.

5. Order parameter coupling

The primary order parameter η can couple to other second-order parameters, which onset at the transformation but do not cause any further symmetry reduction. For the α-to-β transition in $Bi_2Ti_4O_{11}$ a second-order parameter has to be consistent with the symmetry loss caused by the primary order parameter of A_2^+. Due to the fact that the crystal point group is the same for both phases, a possible secondary order parameter has to transform necessarily according to an identical representation associated with the Γ point of $C2/m$. As can be seen in [7] only the Γ_1^+ representation satisfies the condition of leaving the point group invariant. In the present case the spontaneous strain plays the role of such a second-order parameter.

It can be shown that, for a transition with a critical point on the boundary of the first Brillouin zone, like the $C2/m$ to $C2/c$ transformation in $Bi_2Ti_4O_{11}$, linear coupling between η and the spontaneous strain is not allowed by symmetry [15]. However, the order parameter can couple with the elastic strain via a coupling energy that is linear in the strain and quadratic in η, i.e. $\epsilon_s \propto \eta^2$[10]. On the other hand η should be proportional to $(T_c - T)^{1/4}$ for a tricritical transition. The combination of the two relations leads to the expression $\epsilon_s^2 \propto (T_c - T)$. The relationship between ϵ_s^2 and T is shown in figure 12. A linear dependence is evident which once again confirms the tricritical nature of the transition.

6. Discussion and summary

An effective free energy for a system such as $Bi_2Ti_4O_{11}$ with interacting η and the spontaneous strain as one of the important structural parameters can be formulated as

$$G = \tfrac{1}{2}A(T_c - T)\eta^2 + \tfrac{1}{4}B\eta^4 + \tfrac{1}{6}C\eta^6 + D\epsilon\eta^2 + E\epsilon^2.$$

The first three terms in this equation represent the classical 2-4-6 Landau potential of the primary order parameter. A, B and C are coefficients which do not depend explicitly on temperature. The coefficient A is always positive. For a second-order transformation, B is positive too and the η^6 term can be dropped. When B has a negative value the transformation is of first order and the η^6 term is needed again with a positive C for stability reasons. A
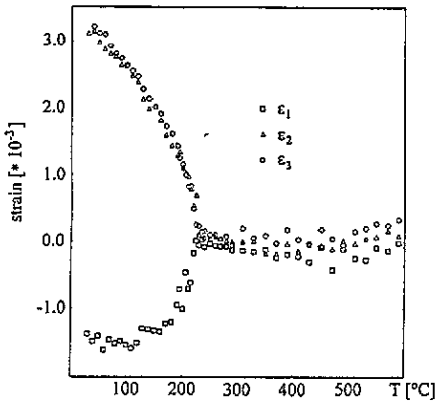
Figure 11. Temperature evolution of the principal strain components ϵ_1, ϵ_2 and ϵ_3.
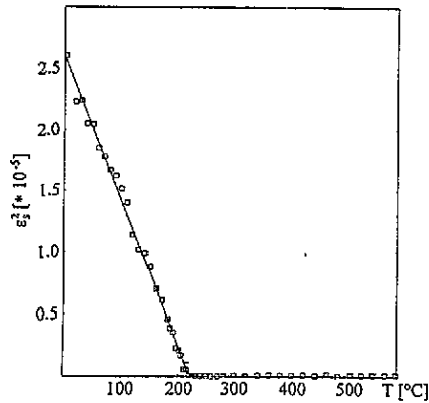
Figure 12. Variation with temperature of the square of the scalar spontaneous strain, which is proportional to η^4. The observed linear dependence reflects the tricritical character of the transformation.

special situation arises when $B = 0$. This point terminates the line of continuous transitions in the B–T space and is called the tricritical point. The η^6 term is needed again $(C > 0)$. For the tricritical and the second-order case η continuously goes to zero when approaching T_c while, in the first-order case, there is a jump for $\eta = 0$ to $\eta \neq 0$.

The other two terms $E\epsilon^2$ and $D\epsilon\eta^2$ account for the elastic energy due to the relaxation of the unit cell and the interaction energy between η and the spontaneous strain for a linear quadratic coupling, respectively. Strictly speaking this expression for the excess energy is an abbreviated notation of a relation reflecting the fact that for the description of the macroscopic spontaneous strain, in the present case, four tensorial components are needed. In the exact formulation $E\epsilon^2$ should be replaced by $\frac{1}{2}\sum_{i,k} C_{ik}x_i x_k$ where the C_{ik} are the elastic constants, the spontaneous strain ϵ must be replaced by $\sum_i x_i$ and the coupling constant D by $D_{t,i=1...4}$.

Minimization of G with respect to ϵ in the simplified form leads to a relation

$$\epsilon = -\frac{D}{2E}\eta^2.$$

Substituting this new expression for ϵ results in a renormalization of the quartic term in the Landau free energy which becomes $B' = (B - D^2/E)$. Our present data show that bismuth tetratitanate has a continuous phase transition that can be interpreted in terms of an order parameter η that varies as $(T_c - T)^{1/4}$ indicating a tricritical phase transition where the quartic term in the energy expansion vanishes. This absence of a quartic term could be attributed to the cancellation of B and D^2/E.

Our measurements of the linear birefringence and the spontaneous strain do not reveal any deviation from a mean field behaviour. Neither conspicuous extra contributions in form of characteristic tails above T_c in Δn or the strain nor any crossover effects were observed, though we determined a weak diffuse intensity at or near to the position of the superlattice reflection $(0\bar{2}1)$. From this finding the question arises of whether the Bi atom positions in the high-temperature phase represent an average of two Bi positions or a single position with a large anisotropic thermal component in the $[010]$ direction. In our

structure refinement of the β phase at 300 °C, which is about 65 °C above the transition temperature, the single-site model leads to a significantly better R factor than the split model. However, the diffuse scattering reveals the existence of non-classical fluctuations very close to T_c. Since the phase transition in $Bi_2Ti_4O_{11}$ is associated with the development of antiphase domains due to the loss in translational symmetry, the $C2/m$ phase could then be interpreted as a statistical average of dynamic $C2/c$ domains with fluctuating domain walls. In this respect the transition would be similar to the $A2/a$-to-$P2_1/a$ transformation in titanite or the $I\bar{1}$-to-$P\bar{1}$ transition in anorthite [16, 17]. It might initially be driven by a soft mode with the Bi displacements as the primary order parameter η transforming as the irreducible representation A_2^+ and then followed by an order–disorder process very close to T_c.

High-temperature transmission electron microscopy investigations on $Bi_2Ti_4O_{11}$ and further high-temperature single-crystal studies in the temperature region of the transition are currently in progress and will help to establish the detailed transformation mechanism which seems to have only a little deviation from an ideal tricritical character.

Acknowledgments

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