Short Communications

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Thermal expansivity and spontaneous strain temperature dependence in Tb₂(MoO₄)₃. By S. C. Abrahams, J. L. Bernstein, F. Lissalde* and K. Nassau, Bell Laboratories, Murray Hill, New Jersey 07974, USA

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The lattice constants of Tb₂(MoO₄)₃ have been measured by X-ray diffraction in the temperature range 296 to 505 K, and by dilatometry in the range 296 to 1015 K. The coefficients of thermal expansion for both orthorhombic and tetragonal phases are presented. The c-axis lattice constant in the paraelectric-paraelastic tetragonal phase above the transition temperature Tₜ varies by less than 2 parts in 10⁴, with a shallow minimum at 1.23Tₜ. The temperature dependence of the spontaneous strain is shown to follow that of the spontaneous polarization very closely, confirming their linear proportionality.

Tb₂(MoO₄)₃ is a coupled ferroelectric-ferroelastic crystal, as is isomorphous β-Gd₂(MoO₄)₃, with a transition at 436 K (Tₜ) to the paraelectric-paraelastic phase. The temperature dependence of dielectric constant, heat capacity, spontaneous polarization, and birefringence for TMO has been given by Keve, Abrahams, Nassau & Glass (1970), together with other room-temperature properties. An inelastic neutron scattering study over a wide temperature range by Dorner, Axe & Shirane (1972) shows that the spontaneous polarization arises from the shear strain through piezoelectric coupling. The magnetic moment and heat capacity have been measured by Fisher, Hornung, Brodalen & Giauque (1975) in the range 0-4 to 4.2 K: antiferromagnetism is found to develop gradually below 2 K. In the present paper, the thermal expansivity of TMO between 296 and 1015 K is presented together with the temperature dependence of the spontaneous strain above 296 K.

The lattice constants of TMO between 296 and 505 K were derived from the Bragg angles of 22 different reflections, measured with Mo Kα radiation (λ = 0.7107 Å) on a computer-controlled CAD-4 diffractometer, by the method of least squares. The Bragg-angle range was 34° < 2θ < 42°. The poled crystal was mounted within a microfurnace described previously (Lissalde, Abrahams & Bernstein, 1978). All measured lattice constants were linearly corrected by 0.015 Å, on the basis of the previous room-temperature values (Keve et al., 1970): the measured temperature scale was adjusted to retain Tₜ = 436 K. The expansivity was also measured on an unpoled crystal, with a duPont 943 Thermomechanical Table 1. Coefficients of thermal expansion for Tb₂(MoO₄)₃

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>α (10⁻⁶ deg⁻¹)</th>
<th>β (10⁻⁸ deg⁻²)</th>
<th>γ (10⁻¹⁰ deg⁻³)</th>
<th>Standard deviation in lattice constant (Å)‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (ortho)</td>
<td>4.44</td>
<td>123</td>
<td>6.2</td>
<td>0.0013</td>
</tr>
<tr>
<td>b (ortho)</td>
<td>-13.55</td>
<td>45.8</td>
<td>-21.0</td>
<td>0.0018</td>
</tr>
<tr>
<td>c (ortho)</td>
<td>-7.47</td>
<td>-16.5</td>
<td>12.9</td>
<td>0.0029</td>
</tr>
<tr>
<td></td>
<td>(10⁻⁶ deg⁻¹)</td>
<td>(10⁻⁸ deg⁻²)</td>
<td>(10⁻¹⁰ deg⁻³)</td>
<td></td>
</tr>
<tr>
<td>a (tetrag)</td>
<td>7.06</td>
<td>-3.3</td>
<td>-1.0</td>
<td>0.0004</td>
</tr>
<tr>
<td>c (tetrag)</td>
<td>-2.57</td>
<td>9.4</td>
<td>-8.7</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

† a (ortho)₂ₙₙ = 10.34443 (5), b (ortho)₂ₙₙ = 10.38623 (5), c (ortho)₂ₙₙ = 10.65485 (4) Å; a (tetrag)₄ₙ₄ = 10.4106 (25), c (tetrag)₄ₙ₄ = 10.6274 (25) Å.
‡ Given by \[ \frac{1}{11} \sum d^2 \left( \frac{n-m}{n} \right)^2 \], where d is difference between measured and calculated lattice constants at n = 11 temperatures for m = 3 coefficients.
Analyser (TMA) and a heating rate of 10° min⁻¹. The tetragonal lattice constants at \( T_1 \) were used for calibrating the TMA measurements. The results of both sets of experiments are shown in Fig. 1.

The magnitudes of the expansion coefficients in the expression

\[
a_{T^2} = a_{T_1} \left[ 1 + \alpha \Delta T + \beta (\Delta T)^2 + \gamma (\Delta T)^3 \right],
\]

where \( \Delta T = T_2 - T_1 \) for temperature \( T_2 > T_1 \) and \( T_1 = 296 \) K for the orthorhombic and 436 K for the tetragonal phase, as derived by least-squares fit from the data in Fig. 1, are presented in Table 1. Fig. 1 shows that the TMA results on the unpoled crystal give only two lattice parameters, as expected: one has average value between that of the diffraction \( a \) and \( b \) axial lengths, the other closely follows the diffraction values for the \( c \) axis, below \( T_c \). The diffraction and TMA lattice constants agree well above \( T_c \). The tetragonal \( a \) axis approaches a nearly constant value of 10.440 Å above 900 K. A transition from \( \beta \)-TMO to a phase designated \( \alpha \)-TMO occurs at about 1075 K (Keve et al., 1970). The tetragonal \( c \) axis does not vary by more than about 0.002 Å between \( T_c \) and 1015 K, passing through a shallow minimum at about 600 K.

Small temperature variations in lattice parameter have been reported in a number of ferroelectric crystals, several exhibiting maxima or minima. In the case of LiNbO₃, the total fractional variation in the hexagonal \( c \) axis over a range of 1100 K is less than \( 3 \times 10^{-3} \) with a broad maximum at 0.62 \( T_c \) (Abrahams, Levinstein & Reddy, 1966; Lissalde & Peuzin, 1974): in NaBa₂Nb₅O₁₅, the \( c \)-axis variation in the tetragonal phase is less than 0.7 parts in \( 10^4 \) over a range of 300 K with a shallow minimum at 1.22 \( T_c \) (Ballman, Carruthers & O'Bryan, 1970). In TMO, the \( c \) axis varies by less than 2 parts in \( 10^4 \) with a minimum at 1.23 \( T_c \), see Fig. 1. Minima in lattice parameters occur in materials without a phase change: orthorhombic ThF₄ is reported to exhibit minima in all three axes between 500 and 600 K (Van Uitert, Guggenheim, O'Bryan, Warner, Brownlow, Bernstein, Pasteur & Johnson, 1976), with a total variation less than 4 parts in \( 10^4 \) over a 400 K temperature range.

The spontaneous strain \( e_{12} \) [given by \( \frac{(b-a)}{(b+a)} \)] temperature dependence, based on the diffraction results, is presented in Fig. 2. Since TMO is a completely coupled ferroelectric-ferroelastic crystal (Keve et al., 1970), a proportionality is expected between \( e_{12} \) and \( P_s \) (the spontaneous polarization). Dorner et al. (1972) suggested that both \( e_{12} \) and \( P_s \) are proportional to the square of the zone-boundary soft-mode displacement. The temperature dependence of \( P_s \) (Keve et al., 1970), normalized to the value of \( e_{12} \) at \( T = 333 \) K, is represented in Fig. 2 by the solid line. The linear proportionality between \( e_{12} \) and \( P_s \) is confirmed by the excellent fit over the measured temperature range. The standard deviation in \( e_{12} \) is estimated to be about 0.2 \( \times 10^{-3} \). The coercive stress \( (E_{12}) \) in TMO has been measured only at room temperature with a value of about 1.5 MN m⁻² in the short-circuit case, 50 MN m⁻² in the open-circuit case (Keve et al., 1970). The temperature dependence of \( E_{12} \) in a given crystal is expected to be a function of its defect distribution, as is the case for the coercive field \( E_c \). In a defect-free crystal, \( E_{12} \) is considered likely to be proportional to \( E_c \).

![Fig. 2. Variation of spontaneous strain in \( T_2(MoO_4)_3 \) with temperature. Points are from Fig. 1, solid line from \( P_s/T \) normalized to \( T = 333 \) K (Keve et al., 1970).](image)

References


