THERMAL EXPANSION OF CRYSTALS

Part VII. Barite

BY S. S. SHARMA

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1. INTRODUCTION

Barite or heavy spar is a well-known mineral of which colourless and transparent big-sized crystals are easily obtainable. Hence it is not surprising that it has been a subject of investigation by various workers in different fields of study. Thus, R. S. Krishnan (1946) has studied its Raman spectrum with some thoroughness; while the temperature dependence of Raman frequencies and their width has been investigated by Narayanaswamy (1948). Amongst the directional properties, mention may be made of the elastic constant determinations of Voigt (1910) by static method and of Bergmann (1938) by dynamic method. Bridgman (1928) has measured the linear compressibilities of this crystal along the crystallographic axes. Results of magnetic susceptibility (K. S. Krishnan and others, 1933) and dielectric constant measurements (Rao, 1949) have also been reported in the literature. More recently the thermo-optic behaviour of this crystal has been studied in detail by Radhakrishnan (1951) in this laboratory.

In view of such diverse studies of the properties of this mineral, it is surprising to note that its thermal dilatation has not been studied so far. In I.C.T. (Vol. III, p. 44, 1928) is reported one value for the coefficient of linear expansion which appears to be misquoted. As an accurate knowledge of the directional dependence of thermal expansion is required for an understanding of the relation between thermal behaviour and crystal structure, the author has undertaken the measurements of thermal expansion of this crystal in different directions and the results of study are set forth in the present paper.

2. PROCEDURE OF THE EXPERIMENT

Barite is an ionic crystal belonging to the bipyramidal class of the orthorhombic system. The relevant crystallographic data for identifying the faces are given by Groth (1908) according to whom the axial ratios are
The c-face (001) is a perfect cleavage plane. Cleavage along b (010) is also perfect, while along m (110) it is rather good. The symmetry of the crystal under investigation being orthorhombic, the three axes of the thermal ellipsoid coincide in direction with the crystallographic axes, and thus there are only three independent coefficients of expansion, \( \alpha_{11}, \alpha_{22} \) and \( \alpha_{33} \). Hence, for the purposes of the present investigation, three sets of spacers, in the form of right pyramids, with their altitudes coincident with the crystallographic axes, are needed. Two more sets of pyramids with their altitudes along (i) a direction equally inclined to the three axes and (ii) along a direction perpendicular to the natural cleavage m-face have been employed for verification and a check on the values previously determined.

The thermal expansion coefficient in an arbitrary direction is easily obtained by a transformation of axes to the concerned direction. The new set of axes \( X_1', X_2', X_3' \) are defined with respect to the old ones by the usual direction-cosine scheme:

\[
\begin{array}{ccc}
X_1 & X_2 & X_3 \\
C_{11} & C_{12} & C_{13} \\
C_{21} & C_{22} & C_{23} \\
C_{31} & C_{32} & C_{33}
\end{array}
\]

As usual \( \alpha_{33}' \) indicates the constant in the arbitrary direction, which coincides with the \( X_3' \)-axis. The expression for \( \alpha_{33}' \) is given by (Wooster, 1936)—

\[
\alpha_{33}' = C_{13}'^2 \alpha_{11} + C_{23}'^2 \alpha_{22} + 2C_{13}'C_{23}' \alpha_{12} + 2C_{13}'C_{33}' \alpha_{13} + 2C_{23}'C_{33}' \alpha_{23}
\]

in the orthorhombic system \( \alpha_{ij} (i \neq j) \) vanish. The direction cosines for the arbitrary direction (i) are given by

\[
C_{11} = C_{22} = C_{33} = \frac{1}{\sqrt{3}}
\]

Hence we get

\[
\alpha_{33}' = \frac{1}{3} \sum \alpha_{ii}'.
\]

For the expansion perpendicular to the m-face, the expression (1) further simplifies

\[
\alpha_{3m} = C_{13}'^2 \alpha_{11} + C_{23}'^2 \alpha_{22}.
\]
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The specimen of the crystal of barite at the disposal of the author had its cleavage planes c and m perfectly well marked out. The axes were located with the help of ordinary polaroids. The c-axis was contained in the m-plane, while 'a' and 'b' in the c-plane. The latter were identified by the length of intercepts made by the m-plane with them.

3. Results and Their Discussion

The coefficients of thermal expansion, \( a_a, a_b, a_c \) along the three crystallographic axes a, b and c are entered in Tables I–III. The calculated values of the same from the interpolation formulæ are also put forth in the same tables.

**Table I**

Coefficient of linear expansion for barite parallel to the a-axis

\[
\alpha_a = 0.01362 + 0.01298 t + 0.001192 t^2
\]

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( a_a \times 10^6 ) observed</th>
<th>( a_a \times 10^6 ) calculated</th>
<th>Difference %</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.3</td>
<td>14.23</td>
<td>14.22</td>
<td>..</td>
</tr>
<tr>
<td>78.5</td>
<td>14.67</td>
<td>14.71</td>
<td>-.3</td>
</tr>
<tr>
<td>111.2</td>
<td>15.24</td>
<td>15.21</td>
<td>+ .2</td>
</tr>
<tr>
<td>142.5</td>
<td>15.83</td>
<td>15.71</td>
<td>+ .7</td>
</tr>
<tr>
<td>175.6</td>
<td>16.46</td>
<td>16.58</td>
<td>..</td>
</tr>
<tr>
<td>210.6</td>
<td>16.76</td>
<td>16.88</td>
<td>-.7</td>
</tr>
<tr>
<td>244.3</td>
<td>17.48</td>
<td>17.59</td>
<td>..</td>
</tr>
<tr>
<td>270.4</td>
<td>18.27</td>
<td>18.12</td>
<td>+ .8</td>
</tr>
<tr>
<td>307.3</td>
<td>18.83</td>
<td>18.73</td>
<td>+ .5</td>
</tr>
<tr>
<td>340.8</td>
<td>19.43</td>
<td>19.43</td>
<td>..</td>
</tr>
<tr>
<td>377.1</td>
<td>20.21</td>
<td>20.21</td>
<td>..</td>
</tr>
</tbody>
</table>

**Table II**

Coefficient of linear expansion for barite parallel to the b-axis

\[
\alpha_b = 0.042395 + 0.071256 t + 0.001368 t^2
\]

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( \alpha_b \times 10^6 ) observed</th>
<th>( \alpha_b \times 10^6 ) calculated</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.6</td>
<td>24.58</td>
<td>24.51</td>
<td>+ .3</td>
</tr>
<tr>
<td>74.5</td>
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<td>..</td>
</tr>
<tr>
<td>106.6</td>
<td>25.43</td>
<td>25.43</td>
<td>..</td>
</tr>
<tr>
<td>138.1</td>
<td>25.86</td>
<td>25.91</td>
<td>-.4</td>
</tr>
<tr>
<td>170.9</td>
<td>26.42</td>
<td>26.50</td>
<td>-.5</td>
</tr>
<tr>
<td>202.6</td>
<td>27.18</td>
<td>27.18</td>
<td>..</td>
</tr>
<tr>
<td>247.0</td>
<td>28.01</td>
<td>27.89</td>
<td>+ .4</td>
</tr>
<tr>
<td>283.5</td>
<td>28.68</td>
<td>28.61</td>
<td>+ .2</td>
</tr>
<tr>
<td>319.1</td>
<td>29.20</td>
<td>29.35</td>
<td>-.2</td>
</tr>
<tr>
<td>353.8</td>
<td>30.12</td>
<td>30.08</td>
<td>..</td>
</tr>
<tr>
<td>387.5</td>
<td>31.10</td>
<td>30.87</td>
<td>+ .8</td>
</tr>
</tbody>
</table>
TABLE III
Coefficient of linear expansion for barite parallel to the c-axis

\[
a_c = 0.041407 + 0.071520 t + 0.0101102 t^2
\]

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>(a_c \times 10^5) observed</th>
<th>(a_c \times 10^5) calculated</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.5</td>
<td>14.73</td>
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<td>-0.4</td>
</tr>
<tr>
<td>70.8</td>
<td>15.09</td>
<td>15.20</td>
<td>-0.7</td>
</tr>
<tr>
<td>113.7</td>
<td>16.08</td>
<td>16.08</td>
<td>+0.3</td>
</tr>
<tr>
<td>141.4</td>
<td>16.81</td>
<td>16.57</td>
<td>+0.4</td>
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<td>157.1</td>
<td>17.00</td>
<td>16.92</td>
<td>+0.5</td>
</tr>
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<td>17.44</td>
<td>17.46</td>
<td></td>
</tr>
<tr>
<td>223.2</td>
<td>18.03</td>
<td>18.01</td>
<td></td>
</tr>
<tr>
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<td>18.67</td>
<td>18.55</td>
<td>+0.7</td>
</tr>
<tr>
<td>276.6</td>
<td>19.01</td>
<td>19.08</td>
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</tr>
<tr>
<td>303.7</td>
<td>19.72</td>
<td>19.70</td>
<td></td>
</tr>
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<td>334.1</td>
<td>20.23</td>
<td>19.38</td>
<td>-0.8</td>
</tr>
<tr>
<td>363.6</td>
<td>20.87</td>
<td>21.05</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

The values of \(a_{ab}, c\), the coefficient of expansion along a direction equally inclined to the axes are entered in Table IV. The interpolation formula

\[
a_{ab, c} = 0.011720 + 0.01369 t + 0.01204 t^2
\]

has been derived from the experimental values of \(a_n\), \(a_a\) and \(a_c\) by employing the relation (2) given above. The calculated values of \(a_{ab, c}\) from this formula are entered in the third column of this table. From a perusal of these values it can be seen that the agreement between the experimental and calculated values is quite satisfactory.

TABLE IV
Coefficient of expansion for barite in a direction equally inclined to the axes

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>(a_{ab, c} \times 10^5) (observed)</th>
<th>(a_{ab, c} \times 10^5) = (\frac{1}{2} a_{ij})</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.4</td>
<td>17.91</td>
<td>17.89</td>
</tr>
<tr>
<td>79.2</td>
<td>18.31</td>
<td>18.36</td>
</tr>
<tr>
<td>108.0</td>
<td>18.81</td>
<td>18.84</td>
</tr>
<tr>
<td>138.0</td>
<td>19.28</td>
<td>19.31</td>
</tr>
<tr>
<td>168.1</td>
<td>19.77</td>
<td>19.81</td>
</tr>
<tr>
<td>198.7</td>
<td>20.26</td>
<td>20.26</td>
</tr>
<tr>
<td>228.7</td>
<td>20.94</td>
<td>20.98</td>
</tr>
<tr>
<td>258.6</td>
<td>21.68</td>
<td>21.61</td>
</tr>
<tr>
<td>288.6</td>
<td>22.24</td>
<td>22.24</td>
</tr>
<tr>
<td>318.6</td>
<td>22.80</td>
<td>22.87</td>
</tr>
<tr>
<td>348.9</td>
<td>23.41</td>
<td>23.51</td>
</tr>
</tbody>
</table>
The values of $a_{m}$ are entered in Table V.

**TABLE V**

*Coefficient of expansion for barite perpendicular to m-face*

\[ a = 0.01770 + 0.01254 t + 0.001262 t^2 \]

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$a_{m} \times 10^6$ observed</th>
<th>$a_{m} \times 10^6$ calculated</th>
<th>Difference %</th>
</tr>
</thead>
<tbody>
<tr>
<td>43.4</td>
<td>18.28</td>
<td>18.27</td>
<td>..</td>
</tr>
<tr>
<td>75.1</td>
<td>18.84</td>
<td>18.71</td>
<td>+.7</td>
</tr>
<tr>
<td>105.7</td>
<td>19.28</td>
<td>19.17</td>
<td>+.6</td>
</tr>
<tr>
<td>135.6</td>
<td>19.72</td>
<td>19.63</td>
<td>+.5</td>
</tr>
<tr>
<td>164.6</td>
<td>20.07</td>
<td>20.10</td>
<td>-.3</td>
</tr>
<tr>
<td>195.8</td>
<td>20.59</td>
<td>20.64</td>
<td>-.3</td>
</tr>
<tr>
<td>226.8</td>
<td>21.23</td>
<td>21.23</td>
<td>..</td>
</tr>
<tr>
<td>260.8</td>
<td>21.94</td>
<td>21.83</td>
<td>+.5</td>
</tr>
<tr>
<td>291.8</td>
<td>22.55</td>
<td>22.43</td>
<td>+.5</td>
</tr>
<tr>
<td>321.9</td>
<td>23.04</td>
<td>23.04</td>
<td>..</td>
</tr>
<tr>
<td>355.0</td>
<td>23.62</td>
<td>23.74</td>
<td>-.4</td>
</tr>
</tbody>
</table>

*Fig. 1. Variation of coefficients of expansion of barite with temperature.*
The variation of the various coefficients of expansion with temperature has been depicted by smooth curves in Fig. 1.

\( \sigma_{\perp m} \) can also be evaluated from the observed values of \( \sigma_a \) and \( \sigma_b \) by employing relation (3) given above. Thus if \( \theta \) be the angle between the normal to the \( m \)-plane and \( a \)-axis, the relation (3) reduces to

\[
\sigma = \sigma_a \cos^2 \theta + \sigma_b \sin^2 \theta
\]

where

\[
\theta = \tan^{-1} 0.8152 = 39^\circ 9'.
\]

For the sake of comparison the experimental values of \( \sigma_{\perp m} \) are tabulated below along with those calculated from (4).

**TABLE VI**

| Coefficient of expansion \((\times 10^6)\) perpendicular to \( m \)-face |
|-----------------------------------|---|---|---|---|---|
| Temperature \( ^\circ \text{C.} \) | 0\(^\circ \text{C.} \) | 100\(^\circ \text{C.} \) | 200\(^\circ \text{C.} \) | 300\(^\circ \text{C.} \) | 400\(^\circ \text{C.} \) |
| \( \sigma_{\perp m} \) (observed) | 17.70 | 19.08 | 20.71 | 22.60 | 24.74 |
| \( \sigma_{\perp m} \) (calculated) Equation (4) | 17.74 | 19.14 | 20.80 | 22.72 | 24.80 |

Although there is a systematic deviation between these two sets of values, yet the discrepancy is not very marked and the agreement can be taken to be fairly satisfactory.

The values of the principal coefficients of expansion at 0\(^\circ \text{C.} \) have been calculated and are given below:

\[
\sigma_a = 13.62 \times 10^{-6}; \; \sigma_b = 23.95 \times 10^{-6}; \; \sigma_c = 14.07 \times 10^{-6}.
\]

It is seen that the thermal anisotropy is maximum along the \( b \)-axis, while along the \( a \)- and \( c \)-axes the coefficients are nearly equal. The exact inequality can be represented by \( \sigma_b > \sigma_c > \sigma_a \). It may be mentioned here that in this respect the thermal behaviour of barite is different from its optical behaviour. According to Groth (1908) the principal refractive indices are \( n_a = 1.6491, \; n_b = 1.6381 \) and \( n_c = 1.6369 \). Thus in this case \( n_b > n_a > n_c \).

The optical and thermal ellipsoids are differently oriented in the crystal. But a survey of the literature shows that many other properties of barite, namely dielectric constant, magnetic susceptibility, linear compressibility, etc., exhibit anisotropy in the same sense as the coefficient of thermal expansion, i.e., being maximum along the \( b \)-axis and minimum along the \( a \)-axis.
In conclusion, the author expresses his heart-felt thanks to Professor R. S. Krishnan for his constant interest in the work.

**SUMMARY**

The paper describes the results of study of the thermal expansion of barite and its directional dependence. The principal coefficients of linear expansion along the crystallographic axes are given by

\[
\begin{align*}
\alpha_x &= 0.041362 + 0.071298 t + 0.0101192 t^2 \\
\alpha_y &= 0.042395 + 0.071256 t + 0.0101368 t^2 \\
\alpha_z &= 0.041407 + 0.071520 t + 0.011021 t^2.
\end{align*}
\]

**REFERENCES**

- Bergmann... *Ultrasonics*, 1938.
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