

## CRYSTALLOGRAPHY

### Infra-red Transmittance of $Ba_5Ta_4O_{15}$ Crystals Grown by the Czochralski Method

AN investigation of the barium oxide-tantalum pentoxide phase diagram revealed the existence of several phases,  $Ba_{0.44}TaO_{2.94}$ , a hexagonal phase<sup>1</sup>,  $Ba_{0.5}TaO_3$  with the tetragonal tungsten-bronze structure<sup>2</sup>,  $Ba_5Ta_4O_{15}$  with a novel hexagonal structure<sup>3</sup> and  $Ba(Ba_{0.5}Ta_{0.5})O_{2.75}$  with an ordered cubic perovskite structure<sup>4,5</sup>. The stability of one of these compounds,  $Ba_5Ta_4O_{15}$ , has been noted in several papers, in which it was reported to be the high temperature decomposition product of several complex oxides containing barium and tantalum as two of the constituents<sup>6-8</sup>. Because of the need for stable high temperature material for infra-red optical applications, attempts were made to grow single crystals of  $Ba_5Ta_4O_{15}$  so that their infra-red transmission characteristics could be measured and evaluated.

Crystals of  $Ba_5Ta_4O_{15}$  produced previously, using a PbO flux, were small and suitable only for X-ray diffraction examinations. Since much larger crystals were required for the optical measurements, attempts were made to grow them using the Czochralski technique. In this process, a mixture of reagent grade barium carbonate and tantalum pentoxide was placed in an iridium crucible, 1.5 in. diam. by 1.5 in. high, obtained from Engelhard Industries, Newark, New Jersey. The crucible and contents were heated inductively in air to the melting point of the compound. Pulling was performed using an iridium wire as a seed at a melt surface temperature of approximately 1,675° C as sensed by an iridium-iridium/rhodium thermocouple. Best results were obtained using draw rates of 0.6 to 0.9 cm/h while rotating the crystal at 5½ r.p.m. Attempts to increase the rate of growth resulted in inclusions in the crystals. The most satisfactory single crystals of  $Ba_5Ta_4O_{15}$  for infra-red optical measurements were 1 in. long and 3/8 in. in diameter.

The crystals were found to grow preferentially along the 001 direction and exhibited (001) and (110) cleavage. This agrees well with the structure as reported in ref. 3. The structure of  $Ba_5Ta_4O_{15}$  can be described as a five-layer repeat closest packing of oxygens with a barium replacing one oxygen in each layer in the hexagonal unit cell,  $a = 5.79 \text{ \AA}$ ,  $c = 11.75 \text{ \AA}$ . The tantalum ions are in octahedral co-ordination with oxygen, and the octahedra share corners except for the third and fourth layers of oxygens, which are not shared. The absence of metal atoms between these layers makes the crystals vulnerable to cleavage parallel to this plane. All the metal atoms are included in the other cleavage plane.

Spectral transmittance measurements were made on crystals cut perpendicular to the  $c$  direction of a  $Ba_5Ta_4O_{15}$  crystal using a Perkin-Elmer Model 13 Ratio-Recording Infra-red Spectrophotometer. The data are presented in Fig. 1. Note that a specimen of  $Ba_5Ta_4O_{15}$  0.035 in. thick has a long wave-length cut-off limit of 6.14 $\mu$ , which is

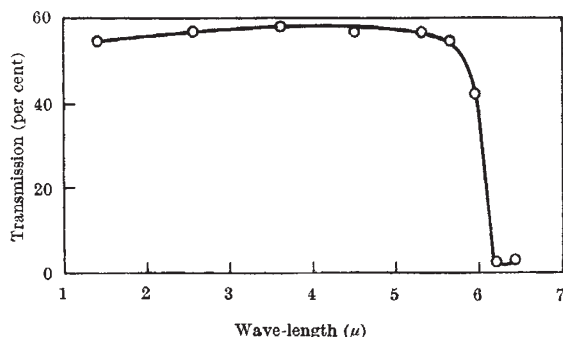


Fig. 1. Transmittance of a sample of  $Ba_5Ta_4O_{15}$ , 0.035 in. thick

larger than that of fused silica and slightly less than that of sapphire of comparable thickness. Because  $Ba_5Ta_4O_{15}$  also is stable to temperatures up to its melting point, resistant to atmospheric attack, and easily grown as a single crystal, it can be considered to be a new high-temperature infra-red material, which may prove useful in infra-red applications.

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### Order-Disorder Transformations in Graphite Nitrates

GRAPHITE nitrates, in which the layers are intercalated in first, second and third sequences, all show an anomaly in thermal expansion around  $-20^\circ \text{C}$ , attributed to a lambda transformation from form I to form II on cooling these solids<sup>1</sup>. Structural investigations by X-ray methods have now confirmed that order-disorder transformations occur in each of these crystal compounds. Moreover, some of the findings indicate that this thermal transformation exhibits several unusual features. It has been shown that:

(1) In form II, the layers of intercalated molecules ( $\text{HNO}_3$  and  $\text{NO}_3^-$ ) assume a two-dimensional crystalline arrangement. On warming to give form I, these crystalline layers 'melt', that is, they pass into a much more disordered two-dimensional assembly, akin to a liquid or glass (cf. Figs. 1a and 1b). Transformations between forms I and II occur quite readily on cycling the temperature around the transformation point. Little is yet known regarding the symmetry and cell dimensions of form II, except that the  $c$ -axis repeat distance doubles in all cases.

(2) Although the four compounds show lambda transformations at effectively the same temperature, suggesting that each intercalate layer undergoes transformation independently, in fact the  $hkl$  superlattice reflexions indicate that in the first sequence compound (Fig. 1b) the sites occupied by the intercalate molecules are ordered in three principal directions. Furthermore, an interesting finding of the present research is that some (although not all) of the  $hkl$  superlattice reflexions are also sharp in compounds of sequences 2, 3 and 4 (Fig. 1c). The simultaneous occurrence of sharp and 'streaked' reflexions (diffuse in one dimension) suggests that the ideal three-dimensional order is perturbed by stacking faults. Even so, considerable three-dimensional order persists between intercalate layers in form II of any of these three sequences. This contrasts markedly with the behaviour reported for the bromine layers in  $\text{C}_8\text{Br}$  (ref. 2). Conceivably, positional correlation between different layers may appear at a lower temperature than the two-dimensional crystallization referred to in (1), but, if so, the temperature interval cannot be greater than a few degrees.

(3) The distances  $d(\text{\AA})$  between layers which show such correlations of position in the ordered structures of form II are as follows:

Sequence	1	2	3	4
$d(\text{\AA})$	7.82	11.15	14.48	17.83