

Figure 2 Oscilloscope trace showing the laser output of the  $\text{Nd}^{3+}$  doped glass-ceramic laser rod No. 3 pumped at 169 joules (scan = 100  $\mu\text{sec}/\text{div}$ ).

was detected. The oscillogram in Fig. 2 shows the spiking characteristics in the output of the glass-ceramic laser rod No. 3 pumped at 169 joules (about twice the threshold). With an output mirror reflectivity of 74.5%, the threshold for the glass-ceramic laser rods was found to be about two to three times as high as that of the glass laser rods; that is, about 90 joules for the glass-ceramic as compared to about 40 joules for the glass. The measured thresholds for the glass-ceramic and glass laser rods are given in Table II. The lasing efficiencies of the glass-ceramic rod No. 3 and the glass rod No. 2 were measured with an output mirror reflectivity of 83.5%. Output energy measurements were made with a TRG model 101 thermopile. Fig. 3 shows a plot of the energy output versus the pump energy for these two laser rods. As can be seen, the lasing efficiency of the glass-ceramic laser rod is lower by at least an order of magnitude relative to that of the glass. This is a considerable decrease in the efficiency considering the fact that the thresholds

\*With Owens-Illinois Inc, Corporate Research Labs, Technical Center, Toledo, Ohio, USA.

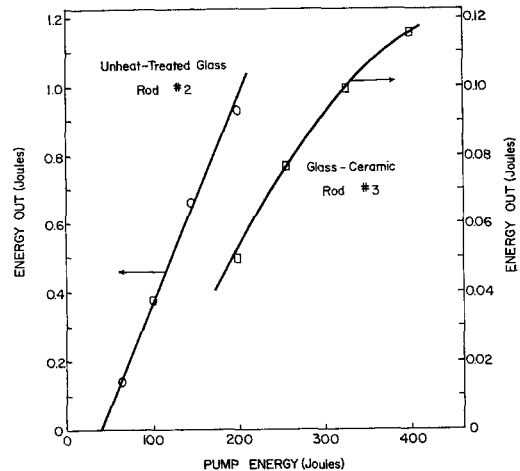


Figure 3 Plot of laser energy out versus pump energy for glass and glass-ceramic laser rods.

for these two rods differed by about a factor of 2.

Subsequent publications will treat the spectroscopic properties of the active ions in this host and the influence of the microstructure on the properties of this laser host.

## References

1. T. H. MAIMAN, *Nature* **187** (1960) 493.
2. S. M. OHLBERG and D. W. STRICKLER, *J. Amer. Ceram. Soc.* **45** (1962) 170.
3. S. RAY and G. M. MUCHOW, *ibid* **51** (1968) 678.
4. R. ROY, *Z. Krist.* **111** (1959) 185.

Received 4 April  
and accepted 18 April 1972

C. F. RAPP\*  
J. CHRYSOCHOOS  
Department of Chemistry  
University of Toledo  
Toledo, Ohio, USA

## Surface effects before and after the aragonite-type to calcite-like transformation in potassium nitrate in relation to mechanism

In  $\text{KNO}_3$  the aragonite structure II is known to change above  $128^\circ\text{C}$  to a calcite-like structure I with anions essentially coplanar but orientations disordered within the plane [1]. In the structure of II, symmetry  $Pmcn$ , the arrangement of cations

is approximately as in hexagonal close-packing: the anions are in distorted simple hexagonal array. The arrangement of the ions in I (S.G.  $R\bar{3}m$ ) is a rhombohedral distortion of that in  $\text{NaCl}$  [2], related to cubic close-packing.

The transformation  $\text{II} \rightarrow \text{I}$  has been considered to produce no surface effects, except that recently Asadov and Nasirov [3] briefly reported traces parallel to the interface. Cahn [4] has mentioned the possible relevance of twinning of the

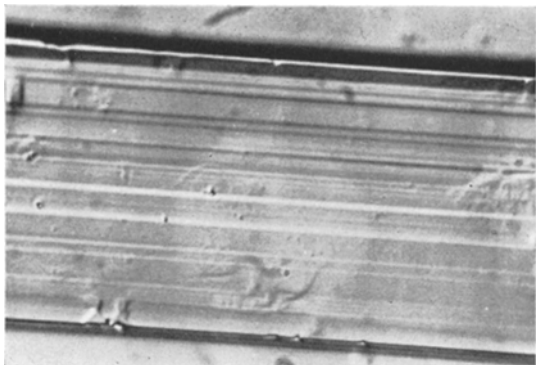


Figure 1 Striations  $\parallel[001]$  formed on 010 face of  $\text{KNO}_3$  II by heating to  $105^\circ\text{C}$ . (Interference contrast, incident light,  $\times 480$ ).

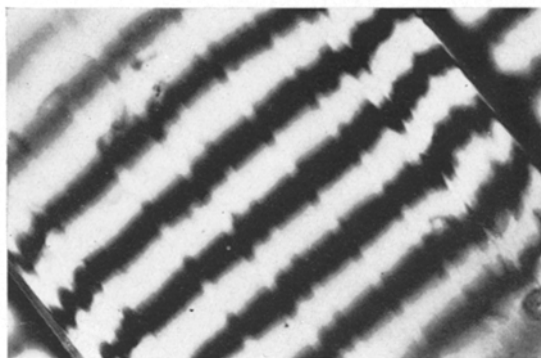


Figure 2 Interferogram of striations  $\parallel[001]$  on form II when heated ( $\times 450$ ).

pseudo-hexagonal aragonite structure in  $\text{CaCO}_3$ , and it occurred in  $\text{KNO}_3$  cycled through the sequence II-I-II [5]. In  $\text{KNO}_3$  the angle  $(110)-(1\bar{1}0)$  is  $61.14$  degrees.

Observations of surfaces, shape change, and fast extinction directions have been made on numerous elongated prismatic crystals lying on 010, about  $0.1$  mm wide, grown from solution on a coverslip, and well dried. Most batches were thinly gold-coated for Nomarski interference contrast microscopy. Extinction directions were measured with transmitted light. The fast extinction direction indicates the projection of the  $c$ -axis on to the stage.

Many unheated crystals showed a few lines (fine bands) similar in appearance to  $(110)$  pressure twin lamellae which we had produced and examined by X-rays. On heating at about  $1^\circ\text{C}/\text{min}$  additional lines appeared at  $76^\circ\text{C}$ , the number increasing with temperature (Fig. 1). That these fine narrow bands were surface displacements was shown both by their persistence after transformation and by polarization interferometry (Fig. 2). No corresponding surface effects were observable on  $C$  cleavage surfaces. The effect was reversible, the longitudinal bands produced by heating disappearing on cooling form II again, whilst the few originally present remained. Twin reflections, however, were not found on  $c^*$  projections in corresponding heating experiments on the X-ray precession camera, possibly because thermal stresses differed. The longitudinal striations nevertheless strongly suggest thermal twinning. Such twinning would increase the apparent number of orientation options in transformation if the unique axis is not

maintained.

The transformation interface was commonly  $\parallel(001)_{\text{II}}$ , but sometimes curved. Striations of two main types resulted. Firstly, traces of  $(001)_{\text{II}}$  appeared on all faces (Fig. 3), as earlier observed in this laboratory by Odlyha [6]. They always occurred when the extinction direction was maintained, but were also usual with other orientations of I. Whilst many of these traces appeared to be slip lines, consistent with the  $(001)_{\text{II}}$  slip plane, polarization interferometry and direct observation of edges also showed that the surface was tilted through angles up to  $14^\circ$  between the prominent traces. This tilting on the  $(010)_{\text{II}}$  face was more evident when the extinction direction was maintained. It indicates a component of macroscopic shear on  $(001)_{\text{II}}$ .

Traces less sharply defined, less common, and inclined to the edge and to the extinction direction are shown in Fig. 4. Fig. 5 shows other

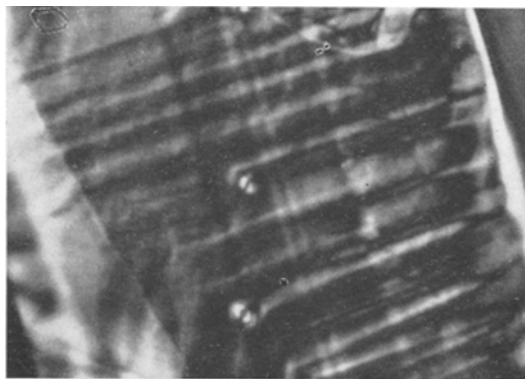


Figure 3 Traces  $\parallel(001)_{\text{II}}$  on  $010_{\text{II}}$  face after transformation to I, (interface contrast,  $\times 680$ ).

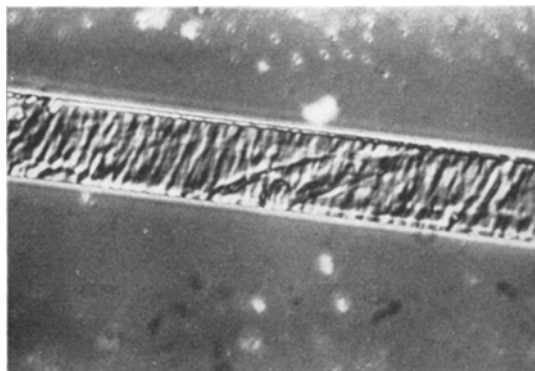


Figure 4 Oblique striations on crystal with extinction at  $32^\circ$  to crystal edge (interference contrast  $\times 450$ ).

types including faint closely spaced lines which in general were very common and crossed  $(001)_{II}$  traces, indicating that they were an additional, not alternative, effect. Since there were in some specimens lamellae of two orientations of product, seemingly twins, and the fine surface traces aligned with these, it appears that fine inclined traces can be related most directly to the product structure. Some crystals transformed instantaneously. They showed only very faint striations, often at  $44^\circ$  to  $[001]_{II}$ , and diffuse extinction suggesting finely mixed orientations.

Filamentary crystals developed a slightly zig-zag shape and some crystals kinked markedly (Fig. 6), both without rotating the  $(001)_{II}$  traces. The original extinction direction could be maintained across the kinked region.

There are various orientations of product [6], but the present authors, by taking X-ray

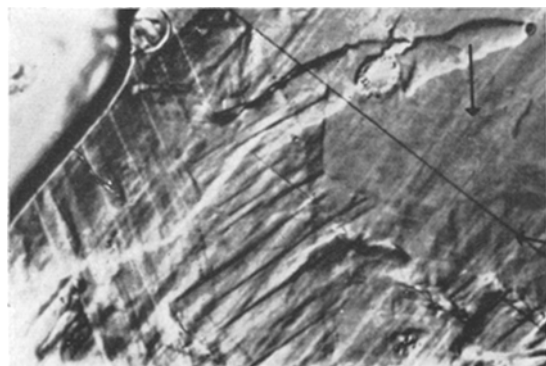


Figure 5 Prominent and faint traces on  $KNO_3$  I (interference contrast,  $\times 450$ ). The arrows are parallel to the faint traces.

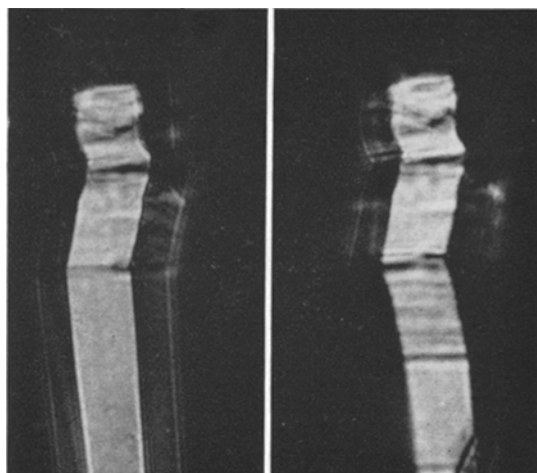


Figure 6 Successive stages of transformation producing kinking which has taken parts of the specimen out of focus. Extinction direction maintained. (Transmitted light,  $\times 280$ , further enlarged  $\times 2$ ).

precession photographs below and above the transformation temperature [7] found the relation  $(0001)_I/(001)_{II}$ ,  $[a]_I/[b]_{II}$ , with the  $(001)_{II}$  traces also present. This orientation relation and the tilts and  $(001)_{II}$  traces that accompanied both it and other examples of persistence of the extinction direction together suggest a mechanism which changes the stacking sequence and includes translation of close-packed layers [8]. A small resultant shape change could be a consequence of translation in equivalent directions, apparently in addition to slip. This is a topotactic [9, 10] or "military" mechanism. (As in iron and thallous nitrate [11], a topotactic mechanism does not necessarily exclude an alternative reconstructive mechanism with relatively random orientations to which traces, if any, would be related.) In this relation the planes of the anions are not rotated. This does not seem to be a necessary condition for a reasonable lattice correspondence. The anions readily tilt in other topotactic transformations [11, 12] and in the twinning of calcite. Accordingly, further analysis of regular surface effects in relation to lattice orientation may reveal other topotactic relations.

#### Acknowledgement

This work is supported by the Australian Research Grants Committee.

## References

1. K. O. STRØMME, *Acta. Chem. Scand.* **23** (1969) 1625.
2. A. F. WELLS, "Structural Inorganic Chemistry" (Oxford University Press, 1962) 83.
3. Y. G. ASADOV and V. I. NASIROV, *Soviet Physics-Doklady* **15** (1970) 324.
4. R. W. CAHN, *Adv. Phys.* **3** (1954) 202.
5. S. W. KENNEDY, A. R. UBBELOHDE, and I. WOODWARD, *Proc. Roy. Soc.* **A219** (1953) 303.
6. M. ODLYHA, Thesis, University of Adelaide (1970).
7. S. W. KENNEDY, W. M. KRIVEN, and M. ODLYHA, to be published.
8. J. W. CHRISTIAN, "The Theory of Transformations in Metals and Alloys" (Pergamon, Oxford, 1965) Ch. XXI.
9. J. D. BERNAL, *Schweizer Arch. angew. Wiss. Tech.* **26** (1960) 69.
10. L. S. DENT GLASSER, F. P. GLASSER, and H. F. W. TAYLOR, *Quart. Rev. Chem. Soc.* **16** (1962) 343.
11. S. W. KENNEDY and J. H. PATTERSON, *Proc. Roy. Soc. A283* (1965) 498.
12. S. W. KENNEDY, *Phys. Stat. Sol.* **2** (1970) 415.

Received 18 April  
and accepted 24 April 1972

S. W. KENNEDY  
W. M. KRIVEN

Physical and Inorganic Chemistry Dept  
University of Adelaide, Adelaide  
South Australia 5001

### Fracture surface of siliconated pyrolytic graphite

Optical microscopic observations of a cross-section of pyrolytic graphite (PG) prepared at deposition temperatures ( $T_{\text{dep}}$ ) of 1440 to 2025°C revealed three typical structures; fine regenerative (F; at high temperatures), string (S) and coarse (C; at low temperatures) structures which depend on preparation conditions [1]. In the case of siliconated pyrolytic graphite [PG(Si)] prepared by pyrolysis of a mixture of propane gas and silicon tetrachloride vapour, it was found that PG(Si) obtained at  $T_{\text{dep}} = 1730^\circ\text{C}$  had still the fine regenerative structure while in PG(Si) at  $T_{\text{dep}} = 1440^\circ\text{C}$  the primary cone boundaries lacked clearness the and

secondary cone boundaries were barely detectable [2]. From the results of optical microscopic observations, it seems that PG(Si) at  $T_{\text{dep}} = 1440^\circ\text{C}$  and PG at  $T_{\text{dep}} = 1440$  and  $1730^\circ\text{C}$  are glass-like structures.

On the other hand, X-ray studies showed that PG and PG(Si) except for PG at  $T_{\text{dep}} = 1730^\circ\text{C}$  had relatively well developed crystalline structures [3]. The crystallinity of PG and PG(Si) is shown in Table I in which the interlayer spacing ( $c_0/2$ ) [3], preferred orientation parameter ( $\beta$ ) [3, 4] and density ( $d$ ) [1, 2] are included.

It is generally assumed that the microscopic structures have a large influence on the properties of PG. However, there seems to be no detailed information on the effect of microscopic and X-ray structures on mechanical properties

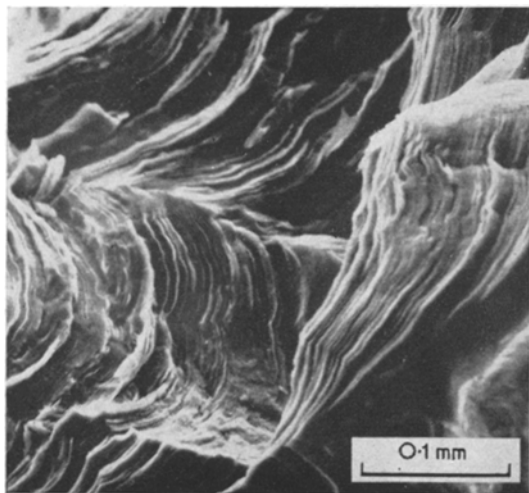


Figure 1 Fracture surface of PG prepared at 1440°C.

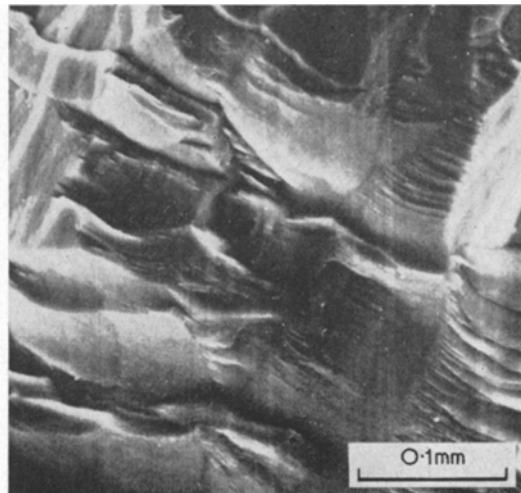


Figure 2 Fracture surface of PG prepared at 1730°C.