

## Letters

### Note on inclusions in yttrium vanadate crystals

Yttrium orthovanadate ( $\text{YVO}_4$ ) is a water-white, tetragonal material of current interest for various optical applications.

The system  $\text{Y}_2\text{O}_3\text{-V}_2\text{O}_5$  has been described by Levin [1]. Single crystals have been grown by flux [2-5], modified floating zone [6], hydrothermal [7], Verneuil [8] and Czochralski techniques [9-10]. Pure yttrium vanadate, YVAN, shows promise as a polarizing prism material [11]. With various rare earth dopants, it has proven to be both an efficient phosphor [12] and an efficient low threshold laser host crystal [13]. The usefulness of single crystal yttrium vanadate in optical systems has been limited: first, by the small size of crystals produced by other than the Czochralski method: and second, by the optical quality of Czochralski material. Although large single crystal boules, up to  $> 1.25$  cm diameter  $\times$  10 cm long, are now easily grown by the Czochralski technique, light scattering and optical damage are experienced due to inclusions of extraneous phases. The figures presented here are from a current effort to reduce or eliminate the inclusions.

Crystals of YVAN are pulled from melts in iridium crucibles in RF heated stations. Typical boules are shown in Fig. 1. In an effort to eliminate the inclusions, various pull and rotation rates, thermal gradients, and oxidizing, inert, and reducing atmospheres have been evaluated. None of these appeared to influence significantly the character or concentration of the inclusions. The original seeds were cut from

polycrystalline boules which had been nucleated on an iridium tube. All subsequent crystals were grown along the  $c$ -axis. The seeds were oriented using the preferred "a" cleavage surfaces. Two different starting materials have been used: pre-reacted Sylvania yttrium vanadate powder, and Molycorp 5-9s  $\text{Y}_2\text{O}_3$  plus Johnson Matthey Puratronic Grade I  $\text{V}_2\text{O}_5$ . Spectrographic analyses of the starting materials are given in Table I.

Qualitative electron probe analyses were made of crystal matrix and inclusions. The matrix varied, within the limits of detection, from pure to slightly calcium contaminated  $\text{YVO}_4$ . The major constituents of the inclusions were calcium silicon and chlorine; and the minor constituents, potassium, nickel, and copper.

Typical crystals were examined under the petrographic microscope. Crystals grown from the two pure oxides contain few inclusions while crystals prepared using the pre-reacted  $\text{YVO}_4$  contain many.

Three kinds of inclusions have been observed in  $\text{YVO}_4$  crystals. The crystals grown from high purity oxides generally contain  $< 5$  randomly scattered impurity dendrites per cubic millimeter up to  $5 \times 10^{-2}$  mm in size and occasional triangular iridium platelets approximately  $5 \times 10^{-4}$  mm across. Crystals prepared using the less pure pre-reacted  $\text{YVO}_4$  contain bubbles and many, up to  $10^4$  per cubic millimeter, dendrites. All the figures are photographs of crystals grown from the Sylvania  $\text{YVO}_4$ . The bubbles, Fig. 2, occur in stringers on the top shoulders of the crystals and along the sides. They are typical of inclusions in crystals grown under constitutional

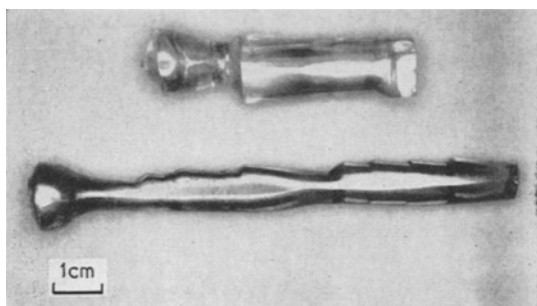


Figure 1 Typical  $\text{YVO}_4$  boules. The step faceting is a result of off-axis growth.

TABLE I Impurities in starting materials (ppm)\*

	Johnson Matthey $\text{V}_2\text{O}_5$	Molycorp $\text{Y}_2\text{O}_3$	Sylvania $\text{YVO}_4$
Ca		8	5-50
Cl		3	50
Cu		1	0.5-5
K		30	
Na		13	
Ni			10
Si	2	4	50-500
Ti	30		

\*All others  $< 1$ .



Figure 2 Bubble inclusions in  $YVO_4$ .

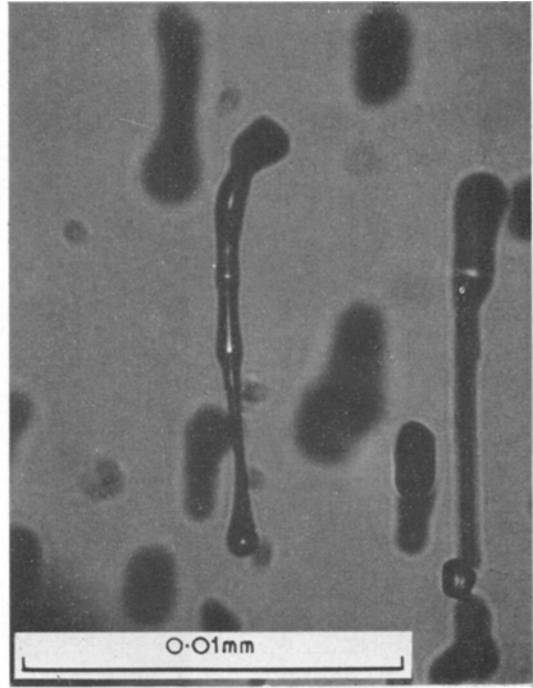


Figure 4 Wandering stringers of uniform size dendrites in YVAN.



Figure 3 Included impurity dendrites in an YVAN crystal.



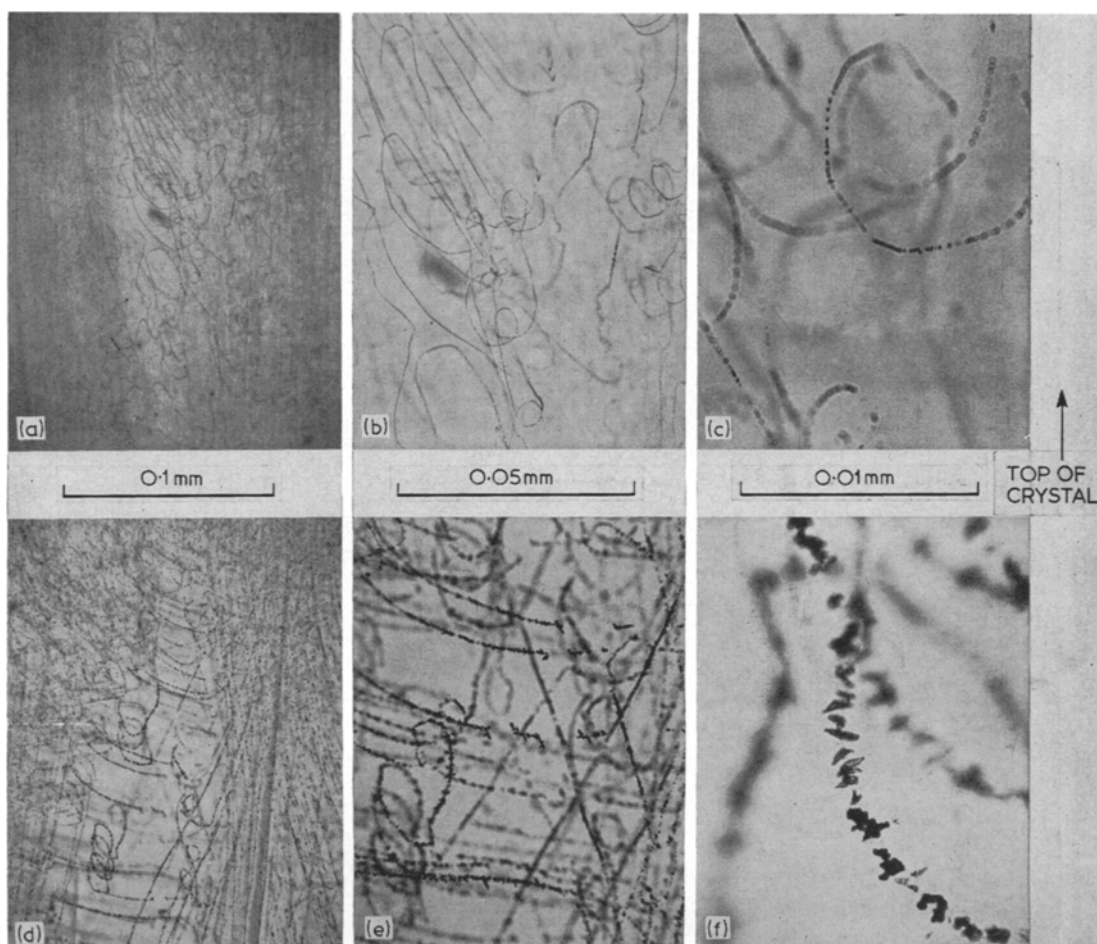


Figure 5 (a) (b) and (c) kinked and coiled stringers of discrete dendritic impurity inclusions in  $\text{YVO}_4$ . (d), (e) and (f) helices and stringers of discrete dendrites.

supercooling conditions. The dendrites, Fig. 3, from  $1 \times 10^{-5}$  to  $2 \times 10^{-3}$  mm in size, occur throughout the crystals. Their size and concentration increase from top (beginning) to bottom (end). Four distinct modes of distribution of the dendrites are observed: random scattering, random stringers, structure controlled stringers, and helices. The stringers and helices are comprised of individual dendritic particles apparently not connected or continuous through the matrix. Not understood at this time is the incorporation of stringers of discrete dendrites which wander in three dimensions without apparent relation to crystal structure, growth direction, or interface morphology, Fig. 4. Even more surprising is the occurrence of helices, which also are formed without any apparent

relevant orientation, Fig. 5. These arrays may be impurity decorated dislocation edges and loops.

Of the three kinds of light scattering inclusions observed in YVAN crystals, iridium platelets, bubbles, and dendrites, neither the iridium platelets nor the bubble inclusions occur in sufficient numbers to be a serious problem. Both can probably be totally eliminated – the iridium by atmosphere control [14] and the bubbles by increasing melt purity and/or by slowing the growth rate. The dendrites appear to be growths of segregated impurities. The composition is chiefly that of the impurities observed in the starting materials and their number varies with the concentration of the impurities. Therefore, it appears that dendrite formation will be avoided by the use of very pure starting materials.

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## References

1. E. M. LEVIN, *J. Amer. Ceram. Soc.* **50** (1967) 381.
2. L. G. VAN UITERT, R. C. LINARES, R. R. SODEN, and A. A. BALLMAN, *J. Chem. Phys.* **36** (1962) 702.
3. L. H. BRIXNER and E. ABRAMSON, *J. Electrochem. Soc.* **112** (1965) 1.
4. A. A. BALLMAN, R. C. LINARES, JUN, and L. G. VAN UITERT, US Patent 3, 152, 085 (1964).
5. W. PHILLIPS and R. J. PRESSLEY, *Amer. Ceram. Soc. Bulletin* **46** (1967) 366.
6. K. MUTO and K. AWAZU, *Japan J. Appl. Phys.* **8** (1969) 1360.
7. R. PUTTBACH, personal communication.

8. V. I. POPOV, KH. S. BAGDASAROV, I. N. BUSEVA, and M. V. MOKHOSOEV, *Sov. Phys. Cryst.* **13** (1969) 974.
9. H. M. DESS and S. R. BOLIN, *Trans. Met. Soc. AIME* **239** (1967) 359.
10. J. J. RUBIN and L. G. VAN UITERT, *J. Appl. Phys.* **37** (1966) 2920.
11. E. A. MAUNDERS and L. G. DESHAZER, *J. Opt. Soc. Amer.* **61** (1971) 684.
12. R. C. PALILLA, A. K. LEVINE, and M. RINKEVIC, *J. Electrochem. Soc.* **8** (1965) 776.
13. J. R. O'CONNOR, *Appl. Phys. Letters* **9** (1966) 407.
14. C. D. BRANDLE, D. C. MILLER, and J. W. NIELSEN, *J. Crystal Growth* **12** (1972) 195.

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## A correlation between thermal and anodic oxide growth behaviour on some metals

A systematic and comprehensive investigation of the comparative thermal oxidation behaviour of the elements of the periodic table has been recently reported by Stone [1]. A parameter,  $T_p$ , was chosen as the measure of the comparative ease of oxidation; this  $T_p$  is the temperature for every element, in °C, at which a weight change of  $1 \text{ mg cm}^{-2} 4\text{h}^{-1}$  was achieved. The parameter  $T_p$  is thus only a *rough* index of the relative oxidation rates of metals because it fails to take into account the differences in the densities of oxides; thus the same rate of weight gain may not correspond to the same *amount* (e.g., in milliequivalent or millimoles) of oxide formed under the same conditions. However, for the purposes of comparison of relative trends of various metals for the thermal oxide growth process,  $T_p$  is indeed a satisfactory index, as shown by Stone [1].

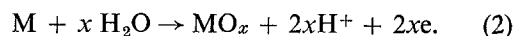
The purpose of the present note is to show that the relative ease (or difficulty) of *thermal* oxidation of various metals is related to their relative ease (or difficulty) of *anodic* oxide growth; the oxide formed in the latter process

results from the electrochemical processes occurring on the anode dipped in an electrolyte solution and placed in an electrolysis configuration [2].

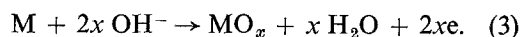
In the thermal oxide growth, the overall process is:



where M is the metal. In the anodic oxide growth, the corresponding reaction in acidic or neutral solutions is:



In the alkaline solutions, the anodic oxide growth occurs by the reaction:



The driving force for oxide growth during the thermal oxidation is the temperature. When one adopts  $T_p$  as the parameter denoting ease of oxidation, after Stone [1], higher  $T_p$  values indicate that larger driving force (i.e., temperature) is needed to force the oxidation; alternatively, lower  $T_p$  values show that the thermal driving force needed is rather low.

In the anodic growth, the driving force (corresponding to the  $T_p$  of thermal growth) is