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SOLUTE DISTRIBUTION IN SHAPED SAPPHIRE CRYSTALS OBTAINED BY EFG METHOD

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One of the specific defects that affect the optical properties of shaped sapphire crystals obtained by Edge-defined Film-fed Growth (EFG) method is the so-called "voids", the trapped gas bubbles. The origin and the distribution of these trapped voids are not yet clarified. In order to study the bubbles and solute distribution sapphire rods and ribbons were obtained by EFG method. The voids and solute distribution were studied by optical microscopy and a quite regular distribution of bubbles was observed in both the rods and ribbons sapphire crystals. The solute distribution was also studied by SIMS analysis and the results show a strong correlation with the optical microscopy observations.

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1. Introduction

Sapphire single crystals present interesting physical and chemical properties like the mechanical hardness or special optical properties. These properties are essential for the use of sapphire for optical applications in extreme environments.

When the aluminum oxide is doped with specific doping agents, the obtained materials are used especially in laser applications. Aluminum oxide doped with titanium Ti^{3+} is used with success as laser material. Doped aluminum oxide is also used in jewelry.

Sapphire shaped crystals (white or doped sapphire) contain as typical defects, the gas bubbles, with dimensions of 1-30 μm. These defects have a bad influence on the sapphire single crystals properties. Bubbles degraded the optical properties by reduction of the transparency or the laser efficiency. In microelectronic applications, the gas bubbles induce other defects during the substrates polishing process.

All the above considerations prove the importance of the knowledge of the gas bubbles formation mechanisms and also the gas bubbles and solute distribution in shaped sapphire single crystals.

2. Experimental procedure

Two types of doped crystals have been obtained using the EFG method [1-3]: ribbons (in the industrial crystal growth set-up from the Le Rubis Society - RSA) and rods (in the crystal growth set-up from the West University of Timisoara - UVT) [2]. The geometrical and growth characteristics of these crystals are given in Table 1.

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Table 1. Geometrical and growth characteristics of the obtained shaped crystals.

Crystal shape	Shaper type	Dimension	Crystal growth set-up	Pulling rate (mm/min)
Rod	Annular	Diameter–length (mm)	UVT	
C 3		4.5 - 200		2
C 4				2.8
Ribbon	Central	Thickness – width -length (mm)	RSA	0.8
R 5		3 – 30 - 300		

3. Results and discussions

It was shown by different authors [2-4] that the void distribution in shaped sapphire strongly depends on the shaper geometry.

In the case of sapphire rods obtained using a annular capillary die – Fig. 1 C – the gas bubbles are present on the core and on the periphery of the crystal, the rest of the crystal being free of bubbles [3]. If a solute is added in the raw material (Ti^{3+} - 450 ppm, Fe^{3+} - 3000 ppm, V – 100 ppm), the obtained rods always present gas bubbles which are distributed exactly in the same way than in white sapphire rods. By optical microscopy it is easy to observe that the gas bubbles are accompanied by solid precipitates (the solute which was added in the raw material) which are not homogeneously distributed. The gas bubbles and the solute are distributed on the periphery and in the core of the crystal (Fig. 1 A-a and B-b).

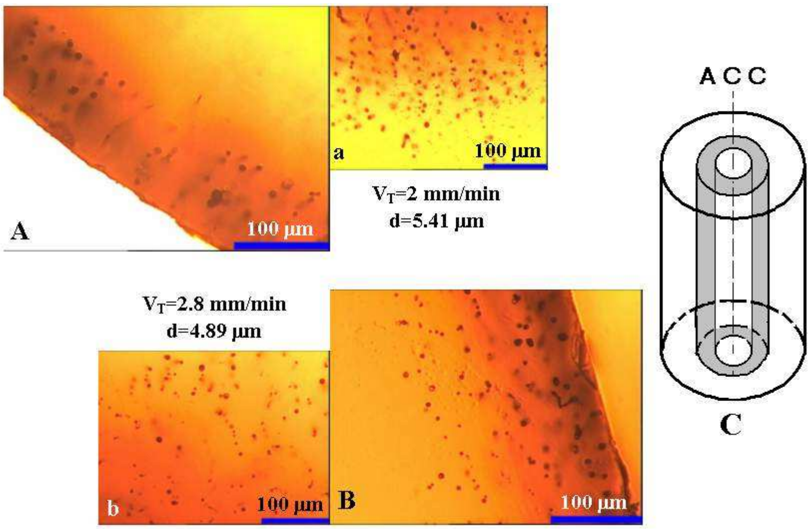


Fig. 1. Bubbles and solute distribution in doped sapphire rods obtained using a annular shaper. A-a, B-b – bubbles and solute distribution in a cross section of the rods C3 and C4 described in Table 1; C – shaper with annular capillary channel.

For the doped crystals, the pulling rate has the same influence on the bubble diameter variation, as in the case of the white sapphire rods [2]: when the pulling rate increases the bubble diameter decreases (Fig. 1A-a and B-b).

Fig. 2 shows the solute distribution in the sapphire rods doped with titanium and vanadium. These results were obtained by SIMS analysis.

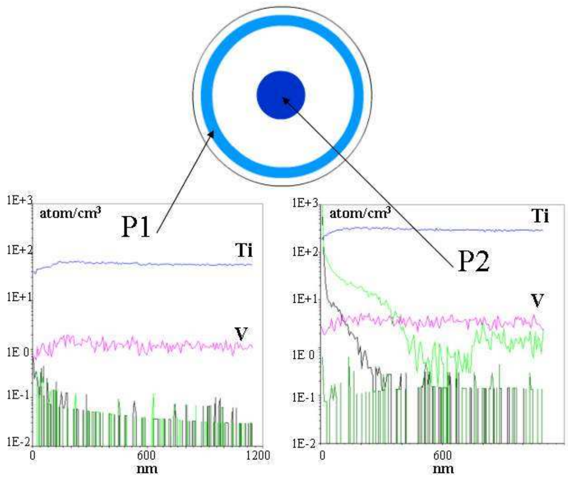


Fig. 2. Solute distribution in sapphire rods obtained from a shaper with an annular capillary channel (concentration is plotted as a function of the depth below the analyzed surface). SIMS analysis made at CEA – Grenoble.

The examined samples present two distinct dark zones on the cross section of the crystal (P1 on the periphery of the sample and P2 in the core of the sample). The optical microscopy observations showed that these two zones, P1 and P2, correspond to the places where the gas bubbles are present (see the Fig. 1). These two zones were analyzed by SIMS technique and the results show that the solute present a stronger concentration in the zones P1 and P2, with a higher concentration in the P2 zone

- Titanium in the clear zone P1 - 60 atoms/cm^3, in the dark zone P2 - 300 atoms/cm^3, so a concentration 5 times larger in the P2 zone;
- Vanadium in the clear zone P1 ~1 atom/cm^3, in the dark zone P2 - 3 atoms/cm^3, so a concentration 3 times larger in the P2 zone.

In the case of sapphire ribbons obtained using a central capillary die – Fig. 3 B – the gas bubbles are present only on the periphery of the crystal, the rest of the crystal being free of bubbles [2]. If a solute is added in the raw material (Cr^{3+} - 6000 ppm; Ti^{3+} - 40 ppm), the obtained ribbons always present gas bubbles which are distributed exactly in the same way like in the white sapphire ribbons. By optical microscopy it was observed that the gas bubbles are accompanied by the solid precipitates (the solute which was added in the raw material) which are not homogeneously distributed. The gas bubbles and the solute are distributed on the periphery of the ruby ribbon (Fig. 3 A).

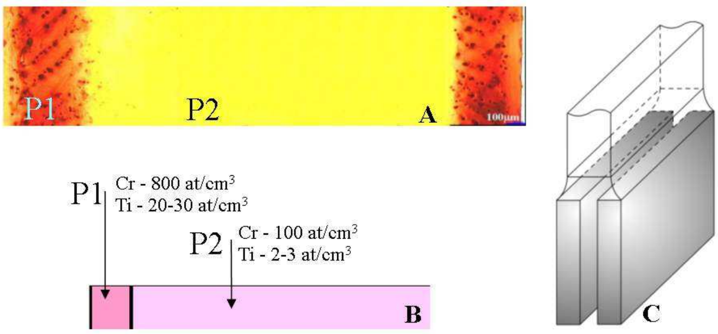
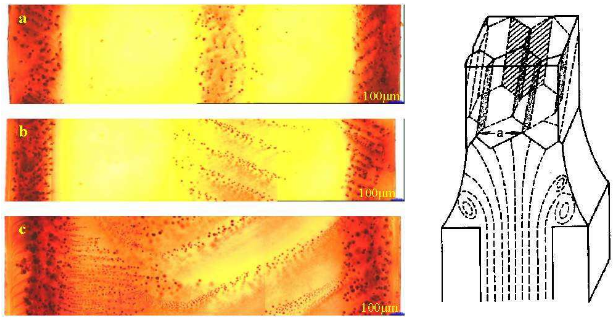


Fig. 3. Bubbles and solute distribution in a ruby ribbon obtained using a central shaper. A – bubbles and solute distribution in a cross section of the ruby ribbon described in Table 1; B – chromium and titanium concentrations obtained by SIMS analysis; C – shaper with a central capillary channel used to obtain the ruby ribbon.

The solute distribution was analysed also in this case by SIMS technique, and the results were published somewhere else [5]. Fig. 3B shows a summary of these results, in the case of a high concentration of chromium and titanium on the ruby ribbon periphery.

In the ruby ribbon, it was also observed the appearance of gas bubbles and of the solute in the core of the crystal. Along the length of the crystal, there are several types of distributions of the gas bubbles and of the solute but they are not dependent on a specified area of the crystal (beginning, middle or the end of the crystal) (Fig. 4 A).



A B

Fig. 4. A - Bubbles and solute distribution in ruby ribbon when the solidification interface is perturbed. B – Model for the formation of the cellular solidification interface formation [3].

Some authors put forth the assumption that the gas bubbles are generated in the vicinity of the solidification interface when this one is destabilized or faceted [3, 6]: the inter - dendritic, or inter - cellular, or inter – faceting regions would be the places where the gas concentration increases. The cellular structure is one of the most often defects that occur at high pulling rates and for high concentration of impurities. In this case, the crystal is divided into parallel areas with a very high concentration of impurities near the borders. In certain cases, the cells take the shape of parallel bands. The cellular structure is caused by the supercooling which depends on the concentration of the impurities which accumulate below the crystallization interface. Such a model, represented in Fig. 4 B by Nicoara [3], is now experimentally confirmed by the gas bubbles and solute distribution in ruby ribbon, Fig. 4 A.

Fig. 4 A shows that there are cells which move laterally during the growth process, which gives the lines of bubbles in skew. It is possible to calculate the lateral movement of the cells. Roughly, if the angle between the cells and the horizontal plane is 45°, this means that the rate of lateral cell movement is the same with the interface rate.

4. Conclusions

The results presented in the previous section are in excellent agreement with the numerical simulations [7] and with the microscopic observations made on the same crystals. It seems that a die with annular capillary channel, even if it is easier to process, is not desirable because in this case the obtained crystals contain bubbles not only on the crystal periphery but also in the core of the crystal. The obtained experimental results can be used in the numerical simulation in order to imagine shaper designs which allow the control of the bubbles and solute distribution.

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References

[1] B. Chalmers, H. E. LaBelle Jr., A. J. Mlavsky, J. Crystal Growth **13/14**, 84 (1972).
[2] O. Bunoiu, Ph. D. Thesis, INP Grenoble, UV Timisoara, (2003).
[3] I. Nicoara, D. Nicoara, V. Sofonea, J. Crystal Growth **104**, 169 (1990).
[4] V. Borodin, T. Steriopolo, V. Tatarchenko, T. Yalovets, Cryst. Res. Tech. **20**, 301 (1983).
[5] O. Bunoiu, I. Nicoara, T. Duffar – Procedings of the ICNPAA 2004, to be published.
[6] I. Berezina, S. Tsivinskii, L. Zatulovskii, Izv. Akad. Nauk, Ser. Fiz. **49**(12), 2398 (1985).
[7] O. Bunoiu T. Duffar, F. Theodore, J. L. Santailler, I. Nicoara, Crystal Research and Technology **36**(7), 707 (2001).