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Crystal growth of yttrium vanadate by the EFG technique

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Abstract The applicability of shaped growth of yttrium orthovanadate was approved by successful growth of rod-like single crystals with the rectangular shape. Nd-doped single crystals with content of Nd^{3+} ions of 1,2,3,5 atomic % in the starting melt were grown by the EFG technique with the size up to 10*10 mm in section and up to 85 mm in length. For the testing of the multiple growth of the orthovanadates, two and three Nd- and Yb-doped YVO_4 single crystals were grown by the EFG technique simultaneously up to 110 mm in length.

Key words Edge defined film fed growth, Oxides, Rare-earth, Compounds, Vanadates

1. Introduction

The application of YVO_4 single crystals doped with laser active rare-earth ions is expected to be a compact and efficient laser source with low pumping threshold and high slope performance [1]. However, growth difficulties seriously limit the production of high quality YVO_4 crystals with large size. The main problems are growth instability manifesting itself in typical "stepped" habit and generation of scattering defects in Czochralski grown crystals [2, 3]. The main reason of these defects is the reduction of vanadium valence state from +5 to +3 under low partial pressure of oxygen and melt overheating. In order to improve growth stability for the crystals and to decrease the melt overheating we applied the EFG (edge-defined film-fed growth) technique for Nd- and Yb-doped YVO_4 single crystals. Earlier, the undoped YVO_4 rod-like single crystals with the circle section were grown by the EFG technique up to 5 mm in diameter [4]. The growth pattern of orthovanadate crystal observed along the growth axis in the case of Czochralski growth was closer to a rectangle than to a circle [5]. In present work the attempt to adjust the die shape to the preferable crystal shape was made. Moreover, the possibility of simultaneous growth of few YVO_4 items with a rectangle shape by the EFG technique was investigated. The size of YVO_4 samples for LD pumping usually is 2~3 mm with the rectangular shape. In that case it would be more effective to grow few smaller rectangular crystals simultaneously than one larger size crystal with following cut it to few items.

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2. Experimental: Growth of Rectangular Crystals

The experimental growth arrangement is shown on Fig. 1. Thermal environment was arranged with the use of horizontal ceramic baffle and the set of vertical alumina tubes. The Ir tube was used as a stand for the crucible. The vanadate melt is known as creeping material with the tendency to creep off the crucible along the wall, especially in the case of the melt overheating [6]. In the case of the traditional construction (crucible on the ceramic stand), there is a probability of chemical reaction between the vanadate melt and the ceramic thermal insulator. The application of Ir stand prevents against such process.

Rectangular shape dies with sizes up to 10*10 mm were checked during our experiments. All crystals were grown using undoped YVO_4 seed along the c-axis. Pulling rates were 2~3 and 1.5 mm/h for the growth of undoped and Nd-doped crystals respectively. Nd-doped crystals were grown from the melt with addition of 1,2,3,5 at% of Nd^{3+} ions. Few vanadate crystals were grown with addition of CaO to the initial charge. We hypothesized that addition of divalent ions to the melt could suppress the formation of phases like YVO_3 or $Y_8V_2O_{17}$. The influence of divalent ions

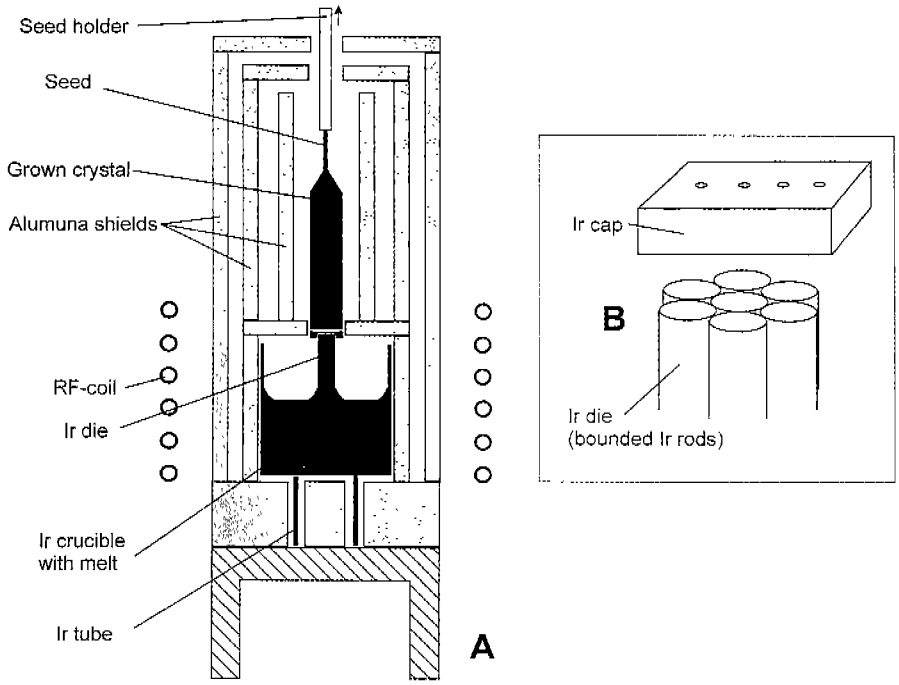

Fig. 1. Schematic diagram of experimental set-up (A) and configuration of the die top.

on the optical properties of EFG-grown YVO_4 crystals was described earlier [7].

3. Results and Discussion

As-grown crystals were transparent, slightly yellow in color for undoped, and green-yellowish for Nd-doped boules. The length of the largest single EFG crystal was 85 mm (Fig. 2). The parts of polished undoped and 3 at% Nd-doped YVO_4 crystals are shown on Fig. 3. The growth interface has been found to be distinctly concave in the case of flat die top. It was found that concave die top was favorable to produce crystal with flat or slightly convex interface with higher growth stability.

The segregation coefficient on Nd^{3+} ions measured by the EPMA method was in the range of 0.43~0.53 according to the Nd concentration in the starting charge. Also, a slight axial inhomogenity was observed. We believe that it can be explained by the crystal diameter oscillation with almost constant amplitude of 0.3 mm on the surface of all grown crystals.

The generation of low-angle boundaries mainly in the narrow peripheral area of the crystal is a main quality problem of EFG grown vanadate crystals. The evident way to avoid it by maintaining of relatively high meniscus height is rather limited due to inevitable lose meniscus anchoring and shape [8]. In contradistinction with the circular shape, the rectangular crystals were much more stable to the meniscus

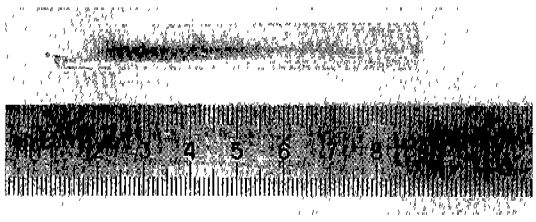

Fig. 2. As-grown undoped YVO_4 crystal (square section, 10 mm per side).

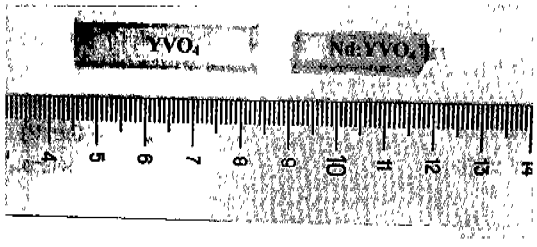

Fig. 3. Polished parts of undoped and Nd-doped YVO_4 crystals.

height increasing without lose of shape. It gave a possibility to avoid the formation of defective area and to improve the quality of crystals.

4. Growth of Few YVO_4 Items Simultaneously

Our experimental set-up made of iridium is shown in Fig. 4. The cap with rectangular lumps was manufactured of Ir plate of 2 mm in thickness.

Capillary channels of 0.5 mm in diameter were situated in the central part of each lump. The composite dies with 2 and 3 mm square lumps were manufactured for the simultaneous growth of 2 and 3 YVO_4 crystals.

The hot zone structure was similar to the single EFG growth of vanadates. However, the requirements of the hot zone symmetry for the multiple growth were higher due to necessity to keep the same temperature conditions for every growing item.

A shoulder part of Cz-grown YVO_4 undoped crystal along c-axis was used as a seed for all multiple growth experiments. Twin Nd-doped (2 at%) YVO_4 single crystals were grown with 2*2 mm square section each up to 100 mm in length with pulling rate 3 mm/h (Fig. 5A). All crystals were transparent, crack-free, without visible inclusions along the body.

Yb-doped (10 at%) YVO_4 crystals were grown using Ir cap with 3 lumps of 3*3 mm squire section. Respectively, three single crystal items were produced simultaneously (Fig. 5B). Pulling rate was 2 mm/h. As-grown crystals were slightly yellow in color, without inclusions. Purposely, at the final stage of growth crystal items were connected together by the solidified melt with the aim to prevent their separation from the seed during post growth cooling. For this aim pulling was stopped and the power was slowly decreased until the space between the lumps was filled by the solidified melt. Finally, power was slightly increased again and bound items were separated from the cap.

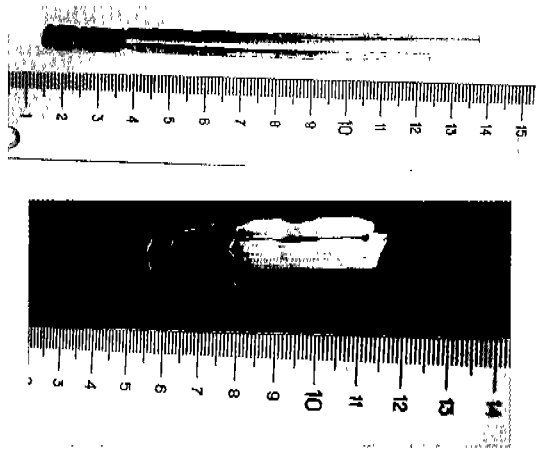

Fig. 5. 2 and 3 simultaneously grown YVO_4 crystals. A-Nd-doped (3 at%), B-Yb-doped (10 at%).

5. Conclusion

The transparent macro-defect-free single crystals of

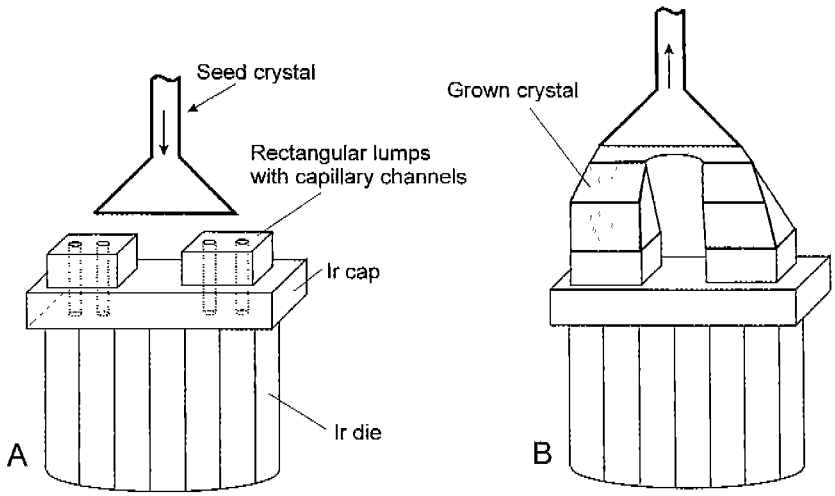

Fig. 4. Schematic diagram of the arrangement for the multiple growth of few vanadate items (A before seed touch, B-at the beginning of the straight growth).

undoped and Nd-doped YVO_4 up to 85 mm in length were grown by the EFG technique. It was estimated that the rectangular die shape is preferable to attain high quality growth. The possibility of simultaneous production of few orthovanadate crystals was confirmed for Nd- and Yb-doped crystals. Multiple crystals up to 110 mm in length were grown successfully. The segregation coefficient on Nd^{3+} ions was determined as 0.43~0.53 according to the Nd concentration in the starting charge.

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