

GROWTH AND HOMOGENEITY OF Cr³⁺ DOPED GdAlO₃ SINGLE CRYSTALS

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ABSTRACT

We describe systematic High-Temperature Solution crystal growth experiments on Cr³⁺ doped GdAlO₃, where the flux and or solute stoichiometry was changed for process optimization to obtain homogeneous and inclusion free larger crystals. Transparent single crystals up to 3.8 cm³ have been grown by slow cooling technique from PbO/PbF₂ flux containing other oxides as additives. Stable growth conditions were also noted.

MATERIALS INDEX: rare-earths, aluminates, oxides, chromium, gadolinium,

Introduction

The rare earth aluminates are of considerable interest on account of their optical and magnetic properties (1,2,3) and technological applications. The perovskite structures are strong candidates for solid state lasers as the host material for Cr³⁺ and Nd³⁺ in cubic and centrosymmetric sites, a condition necessary for obtaining long fluorescence lifetimes (4). The factor that restricts the technological application of the GdAlO₃:Cr³⁺ solid solutions in those systems was been the inhomogeneity and the difficulties in obtaining large and high perfection single crystals. In this paper, we describe systematic GdAlO₃:Cr³⁺ crystal growth using High-Temperature Solution and Czochralski methods.

Experimental

The Cr³⁺ doped GdAlO₃ single crystals were grown by Czochralski and flux methods. However we could only obtain high quality single crystals from the flux method due the development

of cracks in all the single crystals grown in the Czochralski method. These macroscopic defects are attributed to a structural phase transition during the annealing process at temperatures near 1800°C (5).

The high quality and homogeneous Cr^{+3} doped GdAlO_3 single crystals were grown by usual flux experiments carried out in sealed platinum crucibles as described previously (6). The accelerated crucible rotation technique (7) was also used in some experiments for to homogenize the liquid phase and to control the natural convection. The experimental and theoretical temperature programs, based on maximum stable growth rate criteria (8), carried out in most of our crystal growth experiments, are shown in the figure 1. The nucleation control method was the same described before (9).

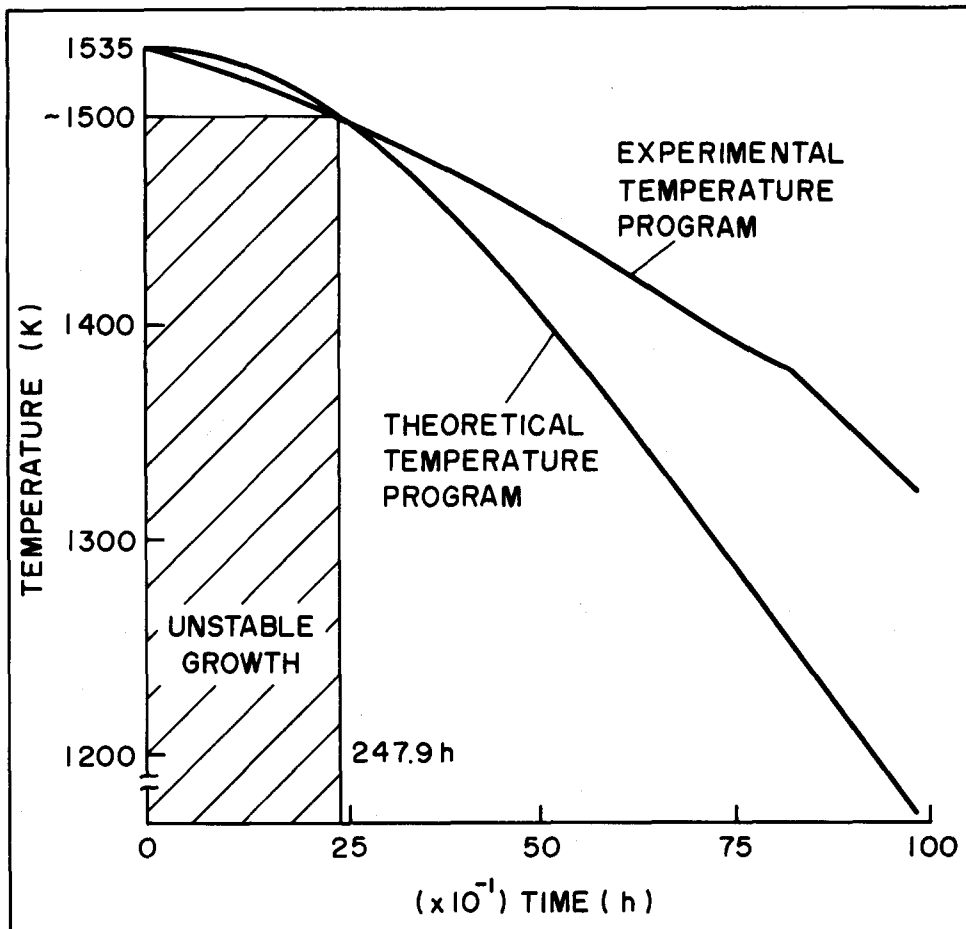


FIG. 1

The experimental and theoretical temperature programs, based on the maximum stable growth rate criteria after (8)

TABLE I
High-Temperature Solution Growth Experiments

Exp.	Charge (mol%)	Cr ³⁺ concentration (mol%)	Stoichiometric deviation* Gd ₂ O ₃ (mol%)	Crystals size and remarks
1 (ACRT)	Gd ₂ O ₃ 8.7 Al ₂ O ₃ 7.5 Cr ₂ O ₃ 0.1 PbO 42.5 PbF ₂ 36.1 B ₂ O ₃ 4.6 PbO ₂ 0.5	1.7	16	23x21x8 mm ³ clear (see text) 7x7x5 mm ³ clear
2	Gd ₂ O ₃ 8.6 Al ₂ O ₃ 7.4 Cr ₂ O ₃ 0.4 PbO 42.5 PbF ₂ 36.1 B ₂ O ₃ 4.5 PbO ₂ 0.5	5.0	16	12x8x7 mm ³ 9x8x6 mm ³ clear
3	Gd ₂ O ₃ 8.0 Al ₂ O ₃ 6.4 Cr ₂ O ₃ 0.6 PbO 43.2 PbF ₂ 36.7 B ₂ O ₃ 4.6 PbO ₂ 0.5	9.1	27	7x10x2 mm ³ 5x4x3 mm ³ clear
4	Gd ₂ O ₃ 11.9 Al ₂ O ₃ 10.2 Cr ₂ O ₃ 1.0 PbO 37.2 PbF ₂ 31.8 B ₂ O ₃ 7.5 PbO ₂ 0.4	10.1	16	15x10x5 mm ³ intergrown crystals with inclusions
5	Gd ₂ O ₃ 12.1 Al ₂ O ₃ 10.5 Cr ₂ O ₃ 1.1 PbO 38.3 PbF ₂ 32.7 B ₂ O ₃ 3.8 V ₂ O ₅ 1.5	10.1	16	10x6x2 mm ³ intergrown clear crystals
6	Gd ₂ O ₃ 11.8 Al ₂ O ₃ 10.2 Cr ₂ O ₃ 1.0 PbO 37.2 PbF ₂ 31.7 B ₂ O ₃ 7.5 V ₂ O ₅ 0.6	10.1	16	8x5x3 mm ³ clear
7	Gd ₂ O ₃ 7.4 Al ₂ O ₃ 10.7 Cr ₂ O ₃ 0.8 PbO 38.1 PbF ₂ 34.7 B ₂ O ₃ 7.0 V ₂ O ₅ 1.3	7.5	-31	hopper growth

* -deviation between the ratio Gd/Al = 1 (see text)

From the maximum stable growth rate criteria we can distinguish, for experiment 1, two growth conditions: a) unstable growth, b) stable growth. In this experiment the transition to stability conditions occurred near 1500 K and 2,9 mm crystal size.

To optimize the crystal growth experiments, several flux compositions were tried. These starting materials and the results of the main experiments are shown in the Table I. All flux compositions were based on intrinsic properties related previously by several authors (10). The major solvent constituents have a low eutectic temperature (490 C; 66 mol% of PbF_2), high solubility for the crystal constituents and suitable viscosity at growth temperature that can contribute to mass transport. The additive compounds (B_2O_3 , PbO_2 and V_2O_5) are important as oxidizing agents and to control the nucleation rates, probably by increasing the width of the metastable regions.

From the solvent system PbO-PbF_2 we could obtain the best results in the preparation of the Cr^{+3} doped GdAlO_3 when we added B_2O_3 and PbO_2 as additives. In this experiment, large area, clear, and inclusions free single crystal were grown. The inclusions are present only near the nucleation region as estimated by the maximum stable growth rate conditions. All changes in the solvent composition, however, can modify strongly the effective segregation coefficient (9).

Results

In all the experiments (except in run 7) an excess of Gd_2O_3 was added (non-stoichiometric composition) to avoid a decrease in the Gd^{+3} concentration in the solution which might GdOF formation during the crystallization process. Stoichiometric deviations in most of the experiments, was 16%. Increasing the deviation to 27% an increase in the nucleation rate, without change in the crystals quality was noted.

Working with a stoichiometric deviation in the Al_2O_3 direction (run 7), we only could grow poor quality single crystals (hopper growth).

The best results in the preparation of the chromium doped GdAlO_3 were obtained in runs 1, 2 and 3 where the solvent composition was keep constant at 42.5% PbO ; 36.1% PbF_2 ; 0.5% PbO_2 and 4.6% B_2O_3 (molar ratio). These experimental results allowed us to verify the hydrodynamic control, the stoichiometric deviation, and the doping concentration influences on the growth process. The best combination of these parameters was done in experiment 1, that associated with a suitable temperature program (except in the nucleation region) provide large and nearly homogeneous, free inclusions single crystals.

The solvent composition effects can be evaluated in the experiment 4. This solvent composition has a slight modification in the PbO and PbF_2 relation, whereas the B_2O_3 quantity was drastically increased. Under these conditions we could obtain less favorable results.

In the experiments 5, 6 and 7 the PbO_2 additive was replaced by V_2O_5 in the solvent composition. When the stoichiometric deviation, the doping concentration, and the major solvent constituents were kept constants, as in runs 5 and 6, we

could verify that the single crystal quality was improved when the V₂O₅ and B₂O₃ concentration was increased. The bad result in experiment 7 we can attribute to an excess of Al₂O₃ since other parameters were intermediate between experiments with better results.

The Cr⁺³ doping concentration and the Pb solvent incorporation was determined by electron microprobe technique in several samples. (Figure 2).

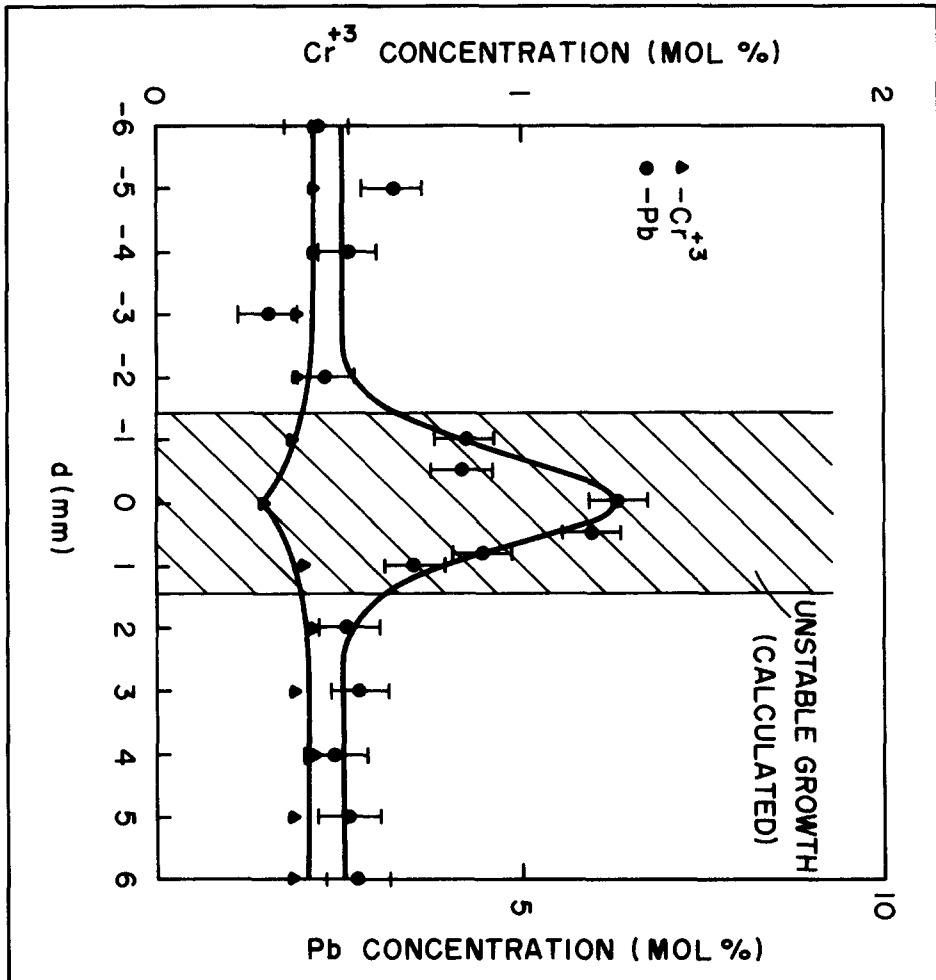


FIG. 2

Cr⁺³ concentration and Pb incorporation profiles in the larger crystal grown in experiment 1. The distance (d) was measured from the nucleation point.

The profile for the Cr⁺³ concentration does not obey accurately the Burton, Prim and Slichter equation (11) for a $K_{eff} = 0.38$ (9). The Cr⁺³ distribution is nearly constant in all

crystal, whereas the Pb incorporation has a maximum in the nucleation point due, probably, to instable growth as estimated from the calculated temperature program.

Conclusions

We can grow, using a suitable solvent composition and temperature program, large and nearly homogeneous Cr^{+3} doped GdAlO_3 single crystals. Pb solvent impurity contamination was also observed in most of the crystals, mainly in the nucleation regions where unstable growth was predicted. In the region of high Pb impurity incorporation, a low Cr^{+3} doping concentration was noted. This relationship was observed in all crystals.

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