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Calcium Niobate $Ca(NbO_3)_2$—A New Laser Host Crystal

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Large single crystals of calcium niobate $Ca(NbO_3)_2$, grown by the Čzochralski technique, are transparent and can be doped with rare earth or transition metal ions. Laser action has been observed in calcium niobate doped with trivalent neodymium, holmium, praseodymium, erbium, and thulium.

INTRODUCTION

Laser action has already been observed in single crystals of Al_2O_3 doped with Cr^{3+} and in CaF_2, SrF_2, BaF_2, LaF_3, $CaWO_4$, and $SrMO_4$ host crystals doped with different rare earths.[1]

A recent study of the calcium oxide–niobium pentoxide phase diagram[2] showed the existence of two congruently melting compounds, $Ca(NbO_3)_2$ which melts at 1560°C and $CaNb_2O_7$ which melts at 1575°C. It was hoped that these congruently melting compounds could be grown as large single crystals, and would show optical qualities of a good host lattice for laser activity.

CRYSTAL GROWTH AND RESULTS

For starting materials reagent grade calcium carbonate and Kawecki Chemical Company's optical grade niobium pentoxide were used. Melts were contained in iridium crucibles and heated by a 10-kW rf generator operating at 450 kc/sec. The $Ca(NbO_3)_2$ and $Ca_2Nb_2O_7$ crystals were pulled in air by the Čzochralski technique. Crystal pulling speeds up to 1 in./h yielded good $Ca(NbO_3)_2$ crystals, although lower pulling speeds were helpful in improving crystal perfection. Single crystals of $Ca(NbO_3)_2$ 5 in. in length by 1 in. in diameter have been grown.

$Ca(NbO_3)_2$ is a colorless material when pure, has a specific gravity of 4.80 g/cc, and a hardness of about 5.5 on the Mohs' scale. The index of refraction of the material varies from 2.07 to 2.20 and the material shows a positive optical character.[3] At room temperature, the calcium niobate, $Ca(NbO_3)_2$, prepared in this work was transparent in the range 0.3 to 5.5 μ. X-ray determinations to compare the crystals grown in this work to the available x-ray powder data for niobates[3] show that $Ca(NbO_3)_2$ has orthorhombic crystal symmetry and its space group is D_{2h}^{14}. These x-ray determinations also show the pulled calcium niobate to be essentially the same as the naturally occurring mineral fersmite.[4]

LASER EXPERIMENTS

Experiments on stimulated emission of radiation were performed with the calcium niobate $Ca(NbO_3)_2$ host doped with Nd^{3+}, Ho^{3+}, Pr^{3+}, Er^{3+}, and Tm^{3+}. These rare earths have also shown stimulated emission of radiation in other hosts, in particular in $CaWO_4$.[5–9] Charge compensation was accomplished by the addition of Na^+ in the Nd^{3+}-doped samples, and by partially substituting Ti^{4+} for Nb^{5+} in the holmium, praseodymium, erbium, and thulium doped crystals.

The crystals were made into rods 3.0 cm long by 0.3 cm in diameter. The two end faces were polished into spherical surfaces of 3.4 cm radius of curvature; one of

[1] For a complete list of laser materials see A. Yariv and J. P. Gordon, Proc. IEEE **51**, 4 (1963).
[2] M. Ibrahin, N. F. Bright, and J. F. Rowland, J. Am. Chem. Soc. **45**, 329 (1962).
[3] J. F. Rowland, N. F. Bright, and A. Jongejan, *7th Proceedings of the Conference on Industrial Applied X-Ray Analysis, Denver, 1958* (University of Denver, Denver, Colorado, 1958).
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[6] A. Yariv, S. P. S. Porto, and K. Nassau, J. Appl. Phys. **33**, 2519 (1962).
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[8] L. F. Johnson, G. D. Boyd, and K. Nassau, Proc. IRE **50**, 86 (1962).
[9] Z. J. Kiss and R. C. Duncan, Proc. IRE **50**, 1531 (1962).

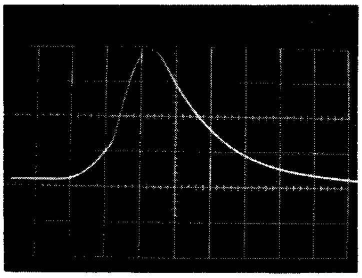

FIG. 1. Light output of a $Ca(NbO_3)_2$:Nd^{3+} crystal at 1.060 μ, just above threshold observed with a PbS cell. The time scale is 100 μsec/div.

the ends was silvered so as to give no light transmission in the visible and the other end had a 2% transmission.

The fluorescence experiments as well as the stimulated emission of radiation and lifetime measurements were conducted at 77°K. For observations involving both Pr^{3+} and Nd^{3+} a 7102 RCA photomultiplier with a silicon filter was used. To detect Ho^{3+}, Tm^{3+}, and Er^{3+} emissions fast PbS and PbSe detectors with germanium windows were used.

The fluorescence of Nd^{3+} in $Ca(NbO_3)_2$ differs from the doped tungstate material in following respects: (a) the line is narrower by a factor of three; (b) there are fewer prominent lines, indicating probably a reduction in the number of important compensation mechanisms for the Nd^{3+} ion.

The excitation source for the stimulated emission experiments was a FT 524 Xe flash lamp surrounding the crystal; oscillation thresholds are then given as the electrical energy input to the lamp necessary to obtain stimulated emission of radiation. The measurement of the laser wavelength was made by focusing the laser beam into a model 210 Perkin–Elmer grating spectrometer with appropriate filters to avoid superposition of grating orders.

Calcium niobate $Ca(NbO_3)_2$ doped with 0.5% Nd^{3+} by weight in the melt and compensated with the stoichiometric amounts of either Na^+ or Ti^{4+} showed stimulated emission of radiation at 1.060 μ (9432 cm^{-1}) corresponding to the transition $^4F_{3/2}-^4I_{9/2}$. Thresholds as low as 2.0 J were observed compared with 1 J for $CaWO_4$:Nd in the same experimental arrangement. Figure 1 shows a typical laser emission of $Ca(NbO_3)_2$:Nd^{3+} at 1.060 μ just above threshold observed with a PbS cell. The Ho^{3+}-doped crystal, (0.5% by weight, compensated with the stoichiometric amount of Ti^{4+}), showed laser action at 2.047 μ (4884 cm^{-1}); the oscillation threshold was 90 J. Figure 2 shows a typical oscillation output of a Ho^{3+}-doped crystal when the electrical input to the lamp was 93 J. Of particular interest here is the regularity of the light spikes and the long delay between them (the time scale is 100 μsec/div).

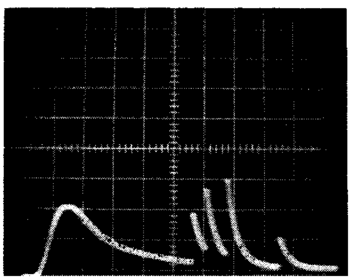

FIG. 2. Oscillation output of a $Ca(NbO_3)_2$: Ho^{3+} crystal at 2.047 μ; the lamp input energy was 93 J and the time scale is 100 μsec/div.

The threshold of oscillation for the Pr^{3+}, Ti^{4+} compensated: $Ca(NbO_3)_2$ crystals was 20–25 J at 77°K and the wavelength of the stimulated radiation was 1.04 μ. Laser action on the Ti^{4+}-charge-compensated, Tm^{3+} and Er^{3+} doped crystals occurred, respectively, at 1.91 and 1.61 μ and the thresholds for the onsetting of the oscillations were 125 and 800 J, respectively. Figure 3 shows the familiar pattern of laser oscillations for a Tm^{3+} doped crystal with the energy input to the lamps of 160 J. It is believed that the threshold values for laser action in Nd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Pr^{3+} doped crystals can be further lowered by optimizing doping concentrations and by improving crystal quality.

FIG. 3. Laser action of a $Ca(NbO_3)_2$:Tm^{3+} crystal at 1.91 μ, at 77°K, and observed with a PbSe detector. The lamp input energy was 160 J.

Lifetimes of the upper states of the laser transitions for Nd^{3+} and Ho^{3+} were measured using the analog method described by Yariv *et al.*[8]

The results obtained for the lifetimes of the laser transitions of Nd^{3+} and Ho^{3+} in the niobate host are

$$\tau_{Nd^{3+}} = 0.12 \pm 0.01 \text{ msec}$$

$$\tau_{Ho^{3+}} = 2.2 \pm 0.1 \text{ msec.}$$

Among the transition ions added to the melt in the crystal growth and incorporated in the final crystals were Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, and Fe^{3+}. Fluorescent studies of these crystals are in progress.

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