Ce,Er,Yb:$YCa_4O(BO_3)_3$ 단결정성장과 결정구조분석
Growth and crystallographic data of Ce,Er,Yb:$YCa_4O(BO_3)_3$ crystals

V.L. Panyutin, Y.M. Yu, A.Yu. Ageev*, G.M. Kuzmicheva**, V.I. Chizhikov*, S.S. Choi
Korea Photonics Technology Institute, Gwangju, Korea
*Kuban State University, Krasnodar, Russia
**Lomonosov Moscow State Academy of Fine Chemical Technology, Moscwo, Russia
ymyu@kopti.re.kr

Abstract

Undoped $YCa_4O(BO_3)_3$ (sp. gr. Cm) single crystals as well as singly or co-doped with Yb, Er and Ce were grown using Czochralski technique. With the aid of x-ray analysis, crystallographic data of Ce,Er,Yb:$YCa_4O(BO_3)_3$ crystals were found.

Introduction

Recently a lot of attention was paid to the crystals of calcium-based rare-earth borates of $LnCa_4O(BO_3)_3$ composition. Lasing properties of the crystals and their nonlinear characteristics are comparable to those of such well-known active and active-nonlinear media as Nd, Yb or Er,Yb doped $YAl_3(BO_3)_4$, $LaSc_3(BO_3)_4$ and (Ce, Gd)$Sc_3(BO_3)_4$ [1, 2]. They are resistant to 1 μm laser radiation of nanosecond pulsewidth at powers up to 1 GW/cm^2, have effective nonlinear susceptibility of about 10^{-12} m/V, allow doping with active ions in high concentrations and, most important, they are highly adaptable to streamlined growth.

In laser materials, doped with Er and Yb, the key role in defining efficiency of laser action at 1.5 μm plays a ratio of probability value of excitation energy reverse transition Er($^4I_{11/2}\rightarrow{}^4I_{15/2}$)$\rightarrow$ Yb($^2F_{7/2}\rightarrow{}^2F_{5/2}$) to probability value of multiphonon nonradiative relaxation Er($^4I_{11/2}\rightarrow{}^4I_{13/2}$). Of great importance are also such effects as cumulative interactions, nonlinear quenching and so on. In phosphate glasses doping with cerium ions results in more than three-fold decrease in $^4I_{11/2}$ level lifeteme, due to the effect of phonon relaxation, which takes place in Ce-Er according to $^4I_{11/2}$(Er), $^2F_{5/2}$(Ce)$\rightarrow{}^4I_{13/2}$(Er), $^2F_{7/2}$(Ce) scheme [3].

So, in this sense, our works focused on growth of $YCa_4O(BO_3)_3$ crystals, codoped with Ce, Er and Yb. This can be a possible way to substantially reducing threshold pump power density. Purpose of the present work is to grow and to conduct x-ray studies of $YCa_4O(BO_3)_3$ single crystals (sp. gr. Cm) codoped with Ce, Er, Yb.

Experimental technique and results

(Yb; Yb,Er; Yb,Er,Ce): $YCa_4O(BO_3)_3$ crystals were grown by Czochralski method from (Yb; Yb,Er; Yb,Er,Ce): $YCa_{4.2}O_{1.2}(BO_3)_3$ melt in an iridium crucibles 50 mm in diameter, making use of a pre-oriented seed. Pulling rate was 1.5-2.0 mm/h and the seed was rotated at 810 rpm. Diameter of the grown crystals was 18 mm, length was 40-50 mm.

X-ray powder diffraction studies were carried out by DRON-2.0 (CuKα radiation, flat graphite monochromator, 2-75° 2θ angular interval, 1° per minute counter rate, 60 mm/hr chart strip speed) and HZG-4A (CuKα radiation) diffractometers. Qualitative phase analysis of the samples was done using an automated database ICDD PDF-2. Presence of impurity phases was not detected within the limits of sensitivity of x-ray phase analysis (< 2% wt.) in all of the samples, except for the lower part of Er,Yb:YCa4O(BO3)3 crystal (table I, sample No. 4), where Y_2O_3 solid solution was found. Single crystalline experiment was carried out at room temperature, making use of CAD-4 [4] diffractometer (CuK radiation, graphite monochromator, ω-scanning, scanning interval 1.1 + 0.345 tg θ°, scanning rate 1-7 deg./min). Cell parameters were refined by 24 reflections in an angular interval 21.0° < θ < 21.5°. Accuracy of crystalline structure of the compounds was improved with a full-matrix least-squares technique in an anisotropic approximation for all atoms with the aid of a software complex SHELXL-97 [5], taking into account atomic dispersion curves for neutral atoms. Unit cell parameters of the investigated crystals, refined with the aid of least-squares technique are listed in table I. Analysis of diffractional reflections of single crystalline experiment on sample No. 1 has revealed presence of additional reflections with I > 2.57 σ(I), which are not conditioned by the spatial group Cm, but could be indexed with a doubled a-parameter, what confirms data in [6]. We would also like to point out, that the discovered superstructure was not observed in doped $YCa_4O(BO_3)_3$ crystals.

References

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Table I. Crystallographyc data of studied samples

No	Melt compositions of single crystals grown by Czochralski method	Cell parameters (A)			
		a	b	c	β (°)
1	$YCa_4O(BO_3)_3$	8.073(3)	16.013(1)	3.5287(4)	101.17(2)
2	$(Y_{0.97}Yb_{0.03})Ca_4O(BO_3)_3$	8.071(3)	16.014(1)	3.5265(4)	101.16(1)
3	$(Y_{0.85}Yb_{0.15})Ca_4O(BO_3)_3$	8.066(5)	16.008(2)	3.5248(7)	101.15(3)
4	$(Y_{0.73}Yb_{0.25}Er_{0.02})Ca_4O(BO_3)_3$ (up)	8.069(4)	16.009(2)	3.5251(5)	101.16(2)
4	$(Y_{0.73}Yb_{0.25}Er_{0.02})Ca_4O(BO_3)_3$ (down)	8.06(1)	15.984(5)	3.517(1)	101.15(6)