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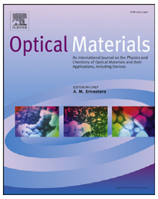

Growth, improved thermal stability and spectral properties of Yb^{3+}-ions doped high temperature phase α-$Ba_3Gd(BO_3)_3$ crystals co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions

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ABSTRACT

To investigate the cause of the thermal instability of Yb^{3+}-ions doped $Ba_3Gd(BO_3)_3$ crystal grown from Czochralski technique, the low temperature phase β-$Ba_3Gd(BO_3)_3$ powder was synthesized at the temperature of 800 °C. To inhibit the phase transition of high temperature phase Yb:α-$Ba_3Gd(BO_3)_3$ during the crystal growth process, co-doping ions Sr^{2+}, Ca^{2+} and La^{3+} ions were introduced in Yb:α-$Ba_3Gd(BO_3)_3$ crystal. The melting point increased and the thermal stability of Yb:α-$Ba_3Gd(BO_3)_3$ crystal was improved by co-doping ions. The absorption peaks of co-doped crystals centered at 976 nm with FWHM of 11, 11 and 12 nm and the absorption cross sections were 3.40×10^{-21} cm^2, 4.00×10^{-21} cm^2 and 2.66×10^{-21} cm^2, respectively. The emission cross sections at 1040 nm were 2.19×10^{-21} cm^2, 2.53×10^{-21} cm^2 and 1.93×10^{-21} cm^2, respectively. The fluorescence times of co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions were shorter than that of Yb:α-$Ba_3Gd(BO_3)_3$ crystal. So Yb:α-$Ba_3Gd(BO_3)_3$ crystals co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions will be more suitable for LD-pumping laser.

1. Introduction

Research on novel garnet, tungstate, silicate and borate laser materials doped by Yb^{3+} ions has been gaining more importance since the rapid development of the diode laser recently [1–5]. As well known, Yb^{3+} ion has only two manifolds, i.e. the ground $^2F_{7/2}$ state and the excited $^2F_{5/2}$ state and it has some advantages in comparison with the Nd^{3+} ions as laser active ion, such as no excited-state absorption reducing effective laser cross-section, no concentration quenching even at high concentration, no up-conversion, and 3 or 4 times longer emission lifetime. Yb^{3+} ion exhibits a strong and broad absorption band centered at about 970 nm and can easily be pumped by InGaAs diode lasers. The small Stokes shift reduces the thermal loading of the material during laser operation and increases the laser efficiency. Therefore, Yb^{3+}-doped crystals attract research interest as promising active media for 1 μm all-solid-state laser pumped by InGaAs diode lasers. Recently, Yb^{3+}-doped $Sr_3Y(BO_3)_3$ crystal has been developed as femtosecond and tunable laser_ [6–9]. $Ba_3Gd(BO_3)_3$ compound crystallizes in space group $R3$, which is isostructural with $Sr_3Y(BO_3)_3$ [10,11]. The growth and spectral properties of Yb^{3+} or Ce^{3+} ions doped $Ba_3Gd(BO_3)_3$ crystals as novel laser or scintillation crystals have also been investigated in recent years [12,13]. Compared with $Y_3Al_5O_{12}$ [14] $KY(WO_4)_2$ and $KGd(WO_4)_2$ [15] crystals, the $Ba_3Gd(BO_3)_3$ crystal can provide two rare earth host sites, which can be occupied by Yb^{3+} ions and may result in broader absorption peak. The melting point $Ba_3Gd(BO_3)_3$ crystal is about 1263.9 °C, which is very suitable to grow single crystal using Czochralski technique. But the as-grown Yb:$Ba_3Gd(BO_3)_3$ crystal cracked seriously during the annealing process, which was harmful to the optical quality of single crystal. Besides the crack of the single crystal, the surface of the as-grown crystals turned into white powder at room temperature. This phenomena can be explained that there may exist a low temperature phase of $Ba_3Gd(BO_3)_3$ compound. The phase transition induced the existence of the white powder and crack of Yb:α-$Ba_3Gd(BO_3)_3$ crystal (hereafter we call the high temperature phase: α-$Ba_3Gd(BO_3)_3$) during the temperature cooling process of the crystal growth. But the synthesis and

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structure of the low temperature phase β-$Ba_3Gd(BO_3)_3$ compound (hereafter we call the low temperature phase: β-$Ba_3Gd(BO_3)_3$) hasn't been reported till now. In this work, the synthesis and cell parameters of β-$Ba_3Gd(BO_3)_3$ will be reported. Furthermore, to improve the thermal stability of as-grown Yb:α-$Ba_3Gd(BO_3)_3$ crystal, Sr^{2+}, Ca^{2+} and La^{3+} ions were introduced to co-dope with Yb^{3+} ions in α-$Ba_3Gd(BO_3)_3$ crystal. The characterization on melting point, cell parameters and spectral properties of Yb:α-$Ba_3Gd(BO_3)_3$ crystals co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions will also be reported.

2. Experimental

The powder of $Ba_3Gd(BO_3)_3$ compound were synthesized by solid-state reaction at 800 °C, 1000 °C and 1200 °C according the stoichiometry using $BaCO_3$ (A.R.), H_3BO_3 (A.R.), and Gd_2O_3 (99.99%) as starting materials, respectively. The raw materials for crystal growth were synthesized at 1000 °C using $BaCO_3$ (A.R.), $SrCO_3$ (A.R.), $CaCO_3$ (A.R.), H_3BO_3 (A.R.), Gd_2O_3 (99.99%), Yb_2O_3 (99.99%) and La_2O_3 (99.99%) as starting materials. The synthesized raw materials with the nominal formulas of 10.at%Yb:10.at%Sr:α-$Ba_3Gd(BO_3)_3$, 10.at%Yb:30.at%Ca:α-$Ba_3Gd(BO_3)_3$ and 10.at% Yb:5.at %La:α-$Ba_3Gd(BO_3)_3$ were melted in a Pt crucible for crystal growth and the growth atmosphere was nitrogen. The co-doped crystals were grown using Czochralski technique which was heated by induction-heating in a PERI-50 crystal growth furnace with the temperature controlled by a Eurotherm 818. A crystal slice with the dimensions of $4 \times 4 \times 10$ mm^3 cut from Yb:$Sr_3Gd(BO_3)_3$ crystal was used as seed crystal [16]. During the crystal growth process, the pulling rates were about 0.5–1 mm/h and the rotation speeds were 5–20 rpm, respectively. The temperature maintained near the melting point before the seed growth and then decreased with the rate of 1 ^{o}c/h during the Equal diameter growth process. After crystal growth, the as-grown crystals were pulled out from the melt and cooled down to room temperature with the temperature cooling rate of 10–50 °C/h.

To identify $Ba_3Gd(BO_3)_3$ compound synthesized at different temperature and the as-grown Yb:α-$Ba_3Gd(BO_3)_3$ crystals co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions, the x-ray powder diffraction analysis was performed using D/max-rA diffractometer and employing CuKα ($\lambda = 1.54051$ Å) at room temperature.

The actual concentration of Yb^{3+}, Sr^{2+}, Ca^{2+} and La^{3+} ions in the as-grown crystals were determined by x-ray fluorescence (XRF) spectrometer analysis experiments. The Differential Scanning Calorimetry (DSC) analysis were performed up to 1350 °C at a heating rate of 10 °C/min in N_2 atmosphere using a NETZSCH-449C Thermal Analyzer to determine the endothermic peaks of Yb:α-$Ba_3Gd(BO_3)_3$ crystals co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions.

The samples with the thickness of 2 mm were cut from the as-grown Yb:α-$Ba_3Gd(BO_3)_3$ crystals co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions. Then the samples was polished and applied for spectral measurements. The room temperature absorption spectra were recorded at UV-VIS-NIR Recording Spectrophotometer with a spectral resolution of 0.5 nm. The fluorescence spectra were measured at room temperature using a Jobin Yvon/SPEX fluorometer. The room temperature fluorescence time was detected which was excited by Xe lamp for$\lambda_{exc} = 976$ nm using the time-correlated single-photon counting (TCSPC) method.

3. Results and discussion

3.1. Synthesis of novel polymorph of $Ba_3Gd(BO_3)_3$ compound

Yb:α-$Ba_3Gd(BO_3)_3$ crystal with the dimensions of 25 mm in diameter and 30 mm in length was grown by Czochralski technique [12]. However, the as-grown Yb:α-$Ba_3Gd(BO_3)_3$ crystal cracked during the temperature cooling process and much white powder covered the whole crystal, but the inner part was still transparent.

Fig. 1 (a) shows a polished sample of Yb:α-$Ba_3Gd(BO_3)_3$ crystal grown from the melt containing 10 at.%Yb^{3+} ions nominal concentrations and it was very transparent. But after it was kept under air atmosphere for about six months at room temperature, white powder appeared at the surface of the polished crystals gradually, the crystal surface became opaque, and some new cracks appeared too, which was shown in Fig. 1 (b). The XRD patterns of different samples of Yb:α-$Ba_3Gd(BO_3)_3$ crystal suggested that there happened slight phase transition in Yb:α-$Ba_3Gd(BO_3)_3$ crystal although no endothermic peak of phase transition was observed in the DSC curve and the process of phase transition might take place after a long time placement at room temperature [12]. But the phase transition temperature of Yb:α-$Ba_3Gd(BO_3)_3$ crystal could not be determined from the DSC curve, which is usually used to analysis the thermal stability properties of chemical substance. Furthermore, the characterization of the low temperature phase of $Ba_3Gd(BO_3)_3$ compound has never been reported. To characterize the novel polymorph, $Ba_3Gd(BO_3)_3$ compound were synthesized at the temperature of 800 °C, 1000 °C and 1200 °C, respectively. The x-ray powder diffraction patterns of $Ba_3Gd(BO_3)_3$ compound synthesized at different temperature are shown in Fig. 2. From Fig. 2, the XRD pattern of the powder synthesized at 800 °C was obviously different from which were synthesized at 1000 °C or 1200 °C. The powder synthesized at 1000 °C was re-sintered at 800 °C and its XRD pattern was the same as the powder synthesized at 800 °C. So the powder synthesized at 1000 °C or 1200 °C was the high temperature phase of $Ba_3Gd(BO_3)_3$ compound. The powder synthesized at 800 °C was a novel polymorph of $Ba_3Gd(BO_3)_3$ compound and it was the low temperature phase β-$Ba_3Gd(BO_3)_3$, and the phase transition of $Ba_3Gd(BO_3)_3$ compound took place between 800 °C and 1000 °C.

3.2. Cell parameters of the low temperature phase β-$Ba_3Gd(BO_3)_3$

$Ba_3Y(BO_3)_3$ compound exists two polymorphs, in which the high temperature phase (α-$Ba_3Y(BO_3)_3$) belongs to space group $R\bar{3}$ and the low temperature phase (β-$Ba_3Y(BO_3)_3$) belongs to space group $P6_3cm$ [11,17]. $Ba_3Gd(BO_3)_3$ and $Ba_3Y(BO_3)_3$ have the similar structure characterization, so the low temperature phase β-$Ba_3Gd(BO_3)_3$ should also belong to space group $P6_3cm$. And the cell parameters were determined to be: a = 9.45(6) Å, c = 17.45(7) Å from the XRD pattern. The hkl index calculated from the XRD pattern of β-$Ba_3Gd(BO_3)_3$ synthesized at 800 °C are listed in Table 1.

3.3. Crystal growth and characterization of Yb:α-$Ba_3Gd(BO_3)_3$ crystals co-doped by Sr^{2+}, Ca^{2+} and La^{3+} ions crystals

The structure of the series double borate $A_3Ln(BO_3)_3$ (A = Ba or Sr, and Ln = La − Lu, Y) are relation to the metal ions radii, which occupy the alkali earth A^{2+} and rare earth Ln^{3+} sites [6]. The crystals with Yb:α-$Ba_3Y(BO_3)_3$, Yb:α-$Ba_3Gd(BO_3)_3$, Yb:$Sr_3Gd(BO_3)_3$ and Yb:$Sr_3Y(BO_3)_3$ formulas grown by Czochrakski method belong to the same space group $R\bar{3}$. But the thermal stabilities of the as-grown crystals of these four kinds of double borate were very different. Most part of as-grown Yb:α-$Ba_3Y(BO_3)_3$ crystal turned into white block and cracked seriously during the temperature cooling process [12]. And DSC curve clearly showed that phase transition took place at 1145.3 °C. For Yb:α-$Ba_3Gd(BO_3)_3$ crystal, the phase transition took place gradually and it would obviously observed after a longer time placement under air atmosphere at room temperature. Whereas Yb:$Sr_3Gd(BO_3)_3$ and Yb:$Sr_3Y(BO_3)_3$ crystals remained transparent during the annealing process and no phase transition happened at room temperature. So the smaller ion