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Anomalies in pure and doped GdCa₄O(BO₃)₃ crystals grown by CZ method

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The X-ray topography results correlated with chemical etching of as grown pure and doped GCOB single crystals show various crystal lattice defects related to anomalies observed in optical measurements. Straight and curved dislocations, spherical inclusions were observed. The etch pits were found mainly at the outer part of the crystal along [010] direction with maximum content of 1.8×10^4 cm². The broad and strong bands of UV absorption edge spectra and the inhomogeneous broadening of emission lines are presented and are explained by the defect structure.

Key words: doped-GCOB crystal, defects, optical properties.

Introduction

Single crystals of calcium oxyborates with the general formula $\text{Re}^{3+}\text{Ca}_4O(\text{BO}_3)_3$, where Re are rare earth elements and yttrium, have been reported as an excellent candidate for application in nonlinear optics [1]. One of the most investigated crystal pure and doped crystals is $\text{GdCa}_4O(\text{BO}_3)_3$ (abbreviated as GCOB). Optical linear and non-linear properties of gadolinium calcium oxyborate GCOB were investigated in [2-4]. Non-linear optical parameters such as the efficiency of second harmonic generation depend on the quality of the grown crystal. Crystal lattice defects introduce into the crystal lattice strains, which change the refractive indices.

To explain the reason of unexpected low efficiency of the second harmonic generation some investigations of optical and structure properties were performed.

Crystal structure

Iliukhin and Dzhurinskii [5] obtained some crystals by the flux method with $\text{Re}^{3+} = \text{Gd}$, Tb, Lu ions and measured the crystal structure of GCOB by X-ray diffraction methods, which was found to be related to the structure of fluoroborate and fluoroapatite. The unit cell parameters are a = 0.8095(7), b = 1.6018(6), c =0.3558(8) nm and $\beta = 101.260^{\circ}$ [5]. The space group is monoclinic noncentrosymetric Cm. The Gd³⁺ ions are located in the crystallographic mirror plane. The environment of Gd³⁺ is a distorted octahedron with C_s site symmetry. There are two types of Ca²⁺ ion occupy distorted octahedral sites, Ca(1) and Ca(2). The Gd³⁺ and Ca(1) ions occupy eight-coordinated sites with C_s symmetry. Ca(2) ions occupy eight-coordinated sites with C_3 symmetry. All octahedra share corners with BO₃ triangles to form a three-dimensional network. There are two kinds of boron site, B(1) and B(2), with threefold coordination. Three planar borate units lie approximately parallel to the (001) plane. Four oxygen ions are shared with the BO₃ groups. The existence of a probable disorder between calcium and gadolinium atoms in the two octahedral positions is expected [5].

Crystal growth

Crystals were grown by the Czochralski method. The GCOB compound was prepared by solid state reaction, with the stoichiometric composition of Gd_2O_3 and $CaCO_3$ of 4 nines purity and B_2O_3 of 5 nines purity. B_2O_3 was prepared in the special way of III-V technology and contained no higher than 70 ppm water. The mixture was heated to 950°C, cooled and ground, and then heated again at 1150°C, for 20 h.

The synthesised charge was melted in an iridium crucible and a seed of orientation (010) was used. The growth processes were computer-monitored by a weightand-diameter system. A nitrogen atmosphere was provided during growth. The typical growth rate was about 1 mm/h and crystal was rotated at 20-35 rpm. The crystals obtained in this way are colourless, with a good optical quality. The grown crystals had a non uniform outer part of their crystal surface. The size of crystals obtained without macroscopic defects and without cracks was 25 mm in diameter and 50 mm in length, using a crucible 50 mm in diameter An as grown crystal is shown in Fig. 1.

Optical properties

Absorption of GCOB is in the ultraviolet region.

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Absorption spectra



Fig. 1. Single crystal of GCOB.



Fig. 2. UV absorption edge spectrum of GCOB:Nd:Yb crystal at 300 K and absorption spectrum of Gd ³⁺ and Nd³⁺ ions in the GCOB:Nd:Yb crystal (upper part) [6].

Absorption spectra of the crystals doped Nd^{3+} and Yb^{3+} are considered to show discrepancy in the GCOB crystals.UV absorption edge spectrum recorded for the GCOB : Nd^{3+} : Yb^{3+} crystal at 300 K is shown in Fig. 2. The broad and strong bands appear at about 240 nm and 210 nm. They may assigned to either charge-transfer or 4f to 5f transitions. The origin of the bands may be connected with point defects of the host.

Emission spectra

Eu³⁺ ions were introduced in to a GCBO crystal to investigate the possible substitution of Re ions in the oxyborate lattice. The emission spectra with different excitations recorded at 5 K are shown in Fig. 3. The results present the ${}^{5}D_{o} \bullet {}^{7}F_{o}$ emission spectra of Eu³⁺ in GCOB crystals recorded upon selective excitation into the ${}^{5}D_{2}$ multiplet. The emissions obtained for each excitation wavelength are quite different and three well-resolved lines are observed (Fig. 3). The ${}^{7}F_{o} \bullet {}^{5}D_{o}$ levels are non-degenerate and the optical spectra associated with transitions between them should contain as many lines as the number of non-equivalent sites in the



Fig. 3. Multiside-structure Eu^{3+} in GCOB single crystal. The ${}^{5}D_{0} \bullet {}^{7}F_{0}$ emission spectra of Eu^{3+} in the GCOB crystal, at 5 K with different excitations in the ${}^{5}D_{2}$ region.

structure. The emissions obtained for each excitation wavelength are quite different. It should be noted that the low temperature absorption spectrum corresponding to the ${}^{7}F_{0} \bullet {}^{5}D_{2}$ transition does not furnish information on the presence of different Eu³⁺ ions in C_s symmetry [7]. It indicates that the majority of europium ions reside in equivalent sites and their contribution to the absorption spectrum is dominant. Different kinetics for the observed sites related to emission lines were found. The decay time constants of the emission lines 17 290, 17 308 and 17 330 nm, recorded at 5 K were found to be 2.9 ms for the first two lines and 2.3 for the third. The presence of three Eu³⁺ sites indicates that, although Eu^{3+} are expected to replace Gd^{3+} , substitution of Ca(1) and Ca(2) cation sites is possible. It should be noted that Mougel *et al.* observed three sites for Yb^{3+} [8] and more than two sites for Nd^{3+} [9] in GCOB.

Defects

X-ray topography

A topograph is a map of diffracted beam intensity as a function of position in a crystal. The Bragg – reflected beam intensity differs for deformed and ideal crystal lattices – and diffraction contrast arises. X-ray topographs were taken using $AgK\alpha_1$ or $MoK\alpha_1$ radiation from a laboratory X-ray source. Topographs were recorded on nuclear plates with emulsion L4 of thickness 50 µm.

The samples investigated by X-ray topography were cut perpendicular to the [010] growth axis (sample A), or parallel to it with crystallographic directions **b** and **c** lying in the sample plane (sample B and C) [10]. The samples were polished mechanically and chemically to the thickness of about 150 µm-200 µm. Some typical defects such as straight dislocations, bundles of dislocations and spherical inclusions in sample A are shown in Fig. 4.

Dislocations

Chemical etching was performed on planes of parallelepipeds cut along the three monoclinic crystal axes. The etching agent was a water solution of HCl (1-4%). The etching process was performed at room temperature over several minutes, depending on the sample.

The optical pictures of etch pits were observed on (010) and (100) planes of the parallelepiped. The etch pits, attributed to dislocations were detected on all planes of the parallelepiped, however, they were observed very easily on (010) and (100) planes, and less so on (001) plane [11]. An optical microscope picture of an etched crystal surface of (100) orientation is shown in Fig. 5. The density of the etch pits along the sample



Fig. 4. Optical microscope picture of etched of crystal surface Crystal plane (100) 4% HCl, T=293K t=4 minutes.





Fig. 5. X-ray transmission topographs of sample A, (440) reflection, AgK α_1 radiation.

diameter is not uniform, - it is low in the sample centre and higher at the sample edge. The densities of etch pits was 1.8×10^4 cm⁻².

The pictures were related to the outer part of crystal, the central part was dislocation free. No etch pits were observed on (001) planes. This is probably because this is a rough type of surface.

In some samples stacking faults along the crystal growth direction were also observed [10].

Conclusion

Optical and structural investigations confirm the presence of structural anomalies in GCBO single crystals. The origin of the broad and strong bands of UV absorption edge spectra recorded for the GCOB : Nd : Yb crystal at 300 K may be connected with point defects of the host. Site-selective excitation into the ⁵D₂ region shows the existence of three Eu³⁺ crystal-field sites.

The decay times of the observed lines are different and this confirms the existence of three sites.

The existence of three Eu³⁺ sites indicates that, although Eu³⁺ are first expected to replace Gd³⁺, the substitution of other cationic sites is possible. This confirms the previous results obtained for Yb and Nd ions.

In addition, the inhomogeneous broadening of emission lines indicates a crystal-field perturbation and structural disorder of the matrix.

The crystals investigated were partially defective showing etch pits and stacking faults along the crystal growth direction, [010]. The etch pits were revealed mainly at the outer part of the crystal along [010] direction and the maximum content was 1.8×10^4 cm².

X-ray topography shows on samples cut perpendicular to **b** (the growth direction) straight dislocations, curved dislocations, spherical inclusions and on samples cut parallel to **b** (the growth direction) straight dislocations and bundles of dislocations.

Crystals are easy to grow, colorless, of good optical quality, of high hardness, non hydroscopic and easy to polish. However, crystal growth conditions related to the defect structure should be controlled.

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