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Crystal structure and lattice dynamics of $Sr_3Y(BO_3)_3$

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ABSTRACT

X-ray, Raman and infrared (IR) studies of the $Sr_3Y(BO_3)_3$ (BOYS) single crystal grown by the Czochralski technique are presented. The crystal structure is trigonal, space group $R\bar{3}$ (no. 148), and comprises six formula units in the unit cell with the hexagonal axes $a = 12.527(2)$ and $c = 9.280(2)$ Å. The assignment of the observed vibrational modes is proposed on the basis of lattice dynamics calculations. The unusual large bandwidth of the internal modes and the enhancement of the principal mean square thermal displacements for BO_3 and Y(1) indicate that some type of disorder is present in the studied crystal.

1. Introduction

Yb-doped materials, both crystals and glasses, are of great interest due to their potential applications in diode-pumped solid-state lasers. The simple electronic structure of Yb^{3+} ion eliminates unwanted effects such as excited-state absorption or upconversion. Moreover, small quantum defect limits the losses of the pumping power and the broad emission band allows the generation of femtosecond pulses. Therefore, Yb-doped materials can be used in high-power continuous wave lasers for material processing, as well as in femtosecond sources and tunable lasers in the near infrared (IR) [1]. One of the promising materials for Yb doping is the $Sr_3Y(BO_3)_3$ (BOYS) crystal [2–7]. It was shown, for instance, that Yb-doped BOYS crystal is a good candidate for femtosecond lasers fabrication: BOYS:Yb (20 at%) crystal was used in the construction of mode locked laser emitting 69 fs pulses at the central wavelength of 1062 nm [2].

Synthesis of strontium rare-earth borates described by the formula $Sr_3Ln(BO_3)_3$ (Ln = Y, Pr–Lu) was reported by Khamaganova et al. [5]. BOYS:Yb single crystals were grown using the Czochralski technique [6]. The crystal structure of BOYS was not resolved but it was reported that it is isostructural with $Sr_3Sc(BO_3)_3$ borate, which crystallizes in the $R\bar{3}$ structure [6,8]. The former studies revealed that phonon relaxations play an important role in the emission properties of this borate doped with Er^{3+} and Yb^{3+} [4]. Moreover, some bands observed in the emission and absorption spectra could be attributed to vibronic features [9,10]. However, phonon properties of this material are not known. Therefore, it is of interest to perform studies of the phonon properties of BOYS in order to understand spectroscopic features of the rare-earth ions in this matrix.

In this paper, results of X-ray diffraction, polarized Raman and IR studies as well as lattice dynamics (LD) calculations of the BOYS single crystal are reported. The experimental data along with the LD calculations give very accurate assignment of the observed modes and information on longitudinal optical (LO)–transverse optical (TO) splitting for this crystal.

2. Experimental

Single crystals of BOYS were grown using the Czochralski method. The thermal system consisted of a 53 mm outer diameter, 50-mm-high and 1.5-mm-thick iridium crucible, in passive iridium afterheater placed around the crucible top on the grog, and alumina heat shields around the afterheater. A charge material was prepared on the base of high purity (4.5 N) oxides and carbonate: Y_2O_3, B_2O_3, Yb_2O_3 and $SrCO_3$. After mixing, the charge material was heated at 1150 °C for 6 h in a resistivity furnace to obtain the BOYS compound. The growing atmosphere was pure nitrogen. The following conditions of the growth processes were applied: growth rate 0.6–1.2 mm h^{-1}; rotation rate 5–20 rpm; cooling after growth—at least 24 h. Firstly, single crystals were obtained by spontaneous nucleation on the

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Table 1
Crystal data and structure refinement parameters for BOYS

Formula weight	386.38
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Trigonal, $R\bar{3}$
Unit-cell dimensions (Å)	
a	12.5270(18)
c	9.2800(19)
γ (deg)	120
Volume (Å^3)	1261.2(4)
Z, calculated density (mg m^{-3})	6,4.173
Absorption coefficient (mm^{-1})	25.792
F (000)	1440
Crystal size (mm)	0.22 × 0.18 × 0.14
Γ Range for data collection	3.25–47.69
Limiting indices	$-21\leqslant h\leqslant 26$; $-16\leqslant k\leqslant 25$; $-12\leqslant l\leqslant 19$
Reflections collected/unique	9676/2517 [$R_{int} = 0.082$]
Completeness to $\Gamma = 47.31$	94.44%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2517/0/51
Goodness-of-fit on F^2	1.009
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0485$, w$R_2 = 0.0865$
Extinction coefficient	0.0092
Largest diff. peak and hole (e Å^{-3})	2.310 and −3.112

platinum wire. Then seeds cut off the crystals were used. The obtained single crystals up to 15 mm in diameter and 35–50 mm in length were free of macroscopic defects and inclusions of other phases. All the single-crystal boules were annealed in oxidizing atmosphere at 950 °C for 3 h, and then slowly cooled down to room temperature.

The single-crystal sample of dimensions given in Table 1 was selected for X-ray diffraction data collection with a four-circle diffractometer KM-4/CCD (Oxford Diffraction). The instrument was operated in κ geometry and used Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The 1150 images were taken in nine runs with different angular settings and applying the ω-scan mode ($\Delta\omega = 1^\circ$ for each image, the exposure time was 25 s). Diffraction data were integrated for intensities and corrected for Lorentz-polarization effects using the *CrysAlis* program package [11]. The structure was solved by Patterson and electron density syntheses. The calculations were performed with the SHELX-97 program system [12].

Polycrystalline IR spectra were measured from the grounded crystals with a Biorad 575C FT-IR spectrometer in KBr suspension for the 1200–400 cm^{-1} region and in Nujol suspension for the 500–30 cm^{-1} region. Polarized IR spectra of a single crystal were measured in the $E||x$ and $E||z$ geometries at near normal incidence of 10° using a specular reflectance accessory. FT-Raman spectra were measured for an oriented single crystal using the BRUKER 110/S spectrometer with the YAG:Nd^{3+} excitation. Both IR and Raman spectra were recorded with a spectral resolution of 2 cm^{-1}.

3. Results

3.1. Structure determination

The BOYS compound is trigonal, space group $R\bar{3}$ (no. 148), and comprises six formula units in the unit cell with the hexagonal axes $a = 12.527(2)$ and $c = 9.280(2)$ Å. The crystal data, experimental details, and the structure refinement parameters are given in Table 1.

The structural motif consists of the strontium–oxygen polyhedron, two symmetrically distinct YO_6 octahedra, and the BO_3 triangle (Figs. 1 and 2). The atomic positional parameters are given in Table 2. The compound is isomorphous with $Sr_3Sc(BO_3)_3$ [8],

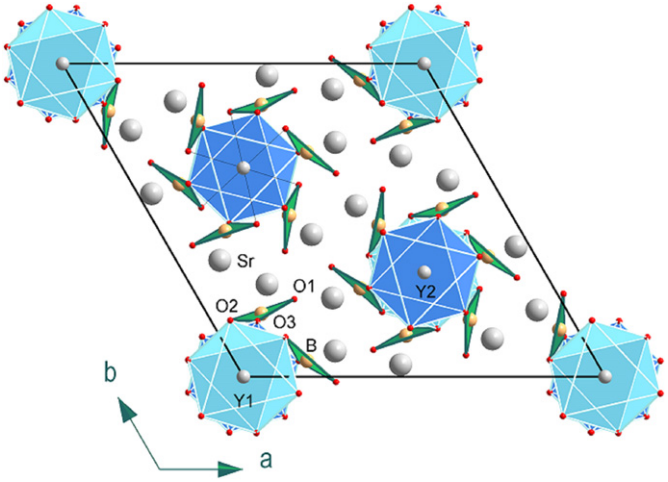

Fig. 1. View of the crystal structure of BOYS along the *c*-axis.

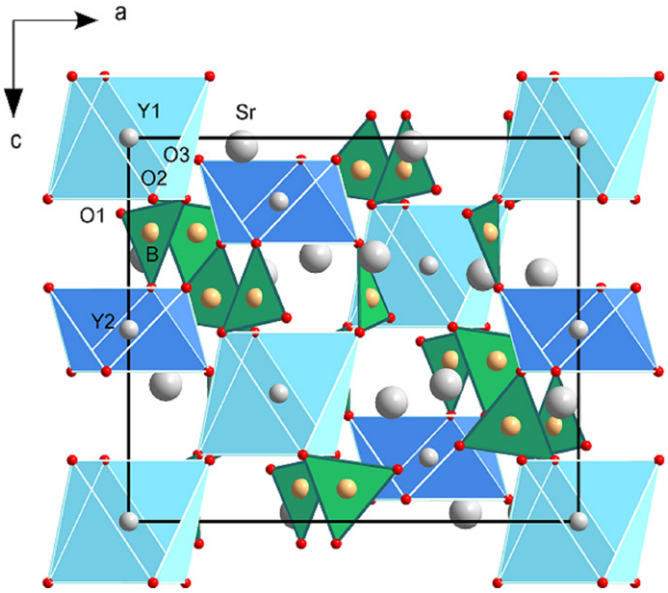

Fig. 2. View of the crystal structure of BOYS along the *b*-axis.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for BOYS

	X	Y	z	U_{eq}
Y(1)	0	0	0	19(1)
Y(2)	0	0	5000	51(1)
Sr(1)	1205(1)	3718(1)	233(1)	29(1)
B	1520(4)	2018(4)	2485(5)	20(1)
O(1)	539(4)	1808(4)	1619(6)	68(1)
O(2)	2658(4)	2487(3)	1982(5)	65(1)
O(3)	1284(5)	1784(4)	3911(4)	72(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

but differs in details resulting from different covalent radii, R, of the Y and Sc-atoms. In the octahedral coordination, $R_{Sc} = 1.610$ and $R_Y = 1.780$ Å [13]. While in the Sc derivative, the Sr-atom exhibits nine-fold coordination, in the present structure the Sr-atom is an eight-fold coordinate (Table 3). The Y-atoms occupy two symmetrically independent Wyckoff positions 3*a*: (0,0,0) and