

The Double Borates $Ba_3Ln(BO_3)_3$, $Ln = La-Lu, Y$

T. N. Khamaganova, N. M. Kuperman, and Zh. G. Bazarova

The Laboratory of Oxide Systems, the Baikal Institute of Nature Using, Russian Academy of Sciences, Siberian Department, Sakhjanovoj St., 6, Ulan-Ude, 670047, Russia

Received June 1, 1998; in revised form December 29, 1998; accepted January 8, 1999

New compounds of the compositions $Ba_3Ln(BO_3)_3$, $Ln = La-Lu, Y$ were obtained in the ternary systems $BaO-Ln_2O_3-B_2O_3$. Single crystals were grown for $Ba_3Yb(BO_3)_3$. X-ray diffraction analysis showed a hexagonal structure with space group $P6_3cm$ and lattice parameters $a = 9.411(1)$, $c = 17.481(5)$ Å, $Z = 6$. The compounds with $Ln = Dy-Lu, Y$ also crystallize in the space group $P6_3cm$. New temperature data on melting points and unit-cell dimensions were obtained for each compound. The borates with $Ln = La-Tb$ are isostructural and crystallize in the space group $R\bar{3}$. Optical second harmonic generation (SHG) measurements of laser radiation showed that $Ba_3Yb(BO_3)_3$ has type I phase transition. By investigation of the crystals of the double borate $Ba_3Yb(BO_3)_3$ it was established that the compound possesses a pyroelectric effect. © 1999 Academic Press

INTRODUCTION

Complex borates of alkaline earth and rare earth elements are used as luminophors and thermoelectronic cathodes for microgenerators (1, 2).

Recently, we studied the synthesis of complex borates of alkaline earth and rare-earth elements to determine their crystalline structure and properties.

At present, the number of papers on investigation of complex borates $Ba_3Ln(BO_3)_3$, Ln -rare-earth elements, has increased. However, all works are devoted to the study of compounds with $Ln = Dy-Lu, Y$ (3–6). Until now, information on double barium borates with the large lanthanides has been absent.

This work is a continuation of our systematic investigations of double barium borates with rare-earth elements. We report the results of these experiments on the synthesis and properties of the compound, on growing $Ba_3Yb(BO_3)_3$ crystals, and on the determination of their structure.

EXPERIMENTAL

Colorless single-crystals of $Ba_3Yb(BO_3)_3$ were grown under flux conditions using the corresponding chlorine-borate

with composition $Ba_2Yb(BO_3)_2Cl$ at 1200°C. The composition of the compound $Ba_3Yb(BO_3)_3$ was confirmed by determining the crystal structure. The new $Ba_3Ln(BO_3)_3$ compounds were prepared by means of solid-state reactions from the initial oxides of rare-earth elements, barium carbonate, and boric acid. Stoichiometric powder mixtures of $BaCO_3$ (A.R.), H_3BO_3 (A.R.), Ln_2O_3 (rare-earth products 99.9%) were heated in Pt crucibles at 600 to 1000°C for 60 h. Phase identification was carried out by powder X-ray diffraction (Enraf-Nonius Guinier camera FE-552 with CuK_α radiation with germanium as an internal standard).

A single-crystal X-ray diffraction analysis was made for $Ba_3Yb(BO_3)_3$ crystals with the dimensions $0.018 \times 0.18 \times 0.28$ mm. The experimental intensity data were obtained on the Enraf-Nonius CAD-4 automatic diffractometer with a graphite monochromator using MoK_α radiation (ω -2 θ scan). Lattice parameters were specified from 25 high-angle reflections. A total of 4503 independent reflections was measured, 834 of them with $I \geq 3\sigma(I)$ were used to solve the structure. The structure of $Ba_3Yb(BO_3)_3$ was solved by using the ENX-SDP program package (7). The analysis of systematic absences did not allow us to determine a unique space group. The presence of reflexes with the indexes $h\bar{h}hol$, $l \neq 2$ showed the probable space groups $P6_3/mcm$, $P6_3cm$, or $P\bar{6}c2$. We analyzed the results of refinement of some versions of structure models in all probable space groups. At first, the structure determination was carried out in centrosymmetric space group $P6_3/mcm$. The position of five atoms (two atoms were given by Yb atoms and three by Ba atoms) was determined from three-dimensional Patterson map $P(UVW)$. The refinement of the atoms' coordinates gives $R = 46.9$. The unreal Ba-Ba distances were found among the distances of metal-metal. This fact showed that the space groups was incorrect. The model structure was converted to noncentrosymmetric space group $P6_3cm$, in which the refinement of atom coordinates and B_{iso} was made. The refinement of all atoms' coordinates decreased R to 26. The position of another Ba atom was found from Fourier synthesis $\rho(xyz)$.

Successive execution of four cycles of full-matrix least-squares refinement of metal atomic coordinates decreased

TABLE 1
Atomic Parameters for Ba₃Yb(BO₃)₃

Atom	x	y	z	B, Å ²
Yb1	0	0	0	0.18(2)
Yb2	0.667	0.333	-0.0039(1)	0.07(1)
Ba1	0	0	0.2182(2)	0.60(4)
Ba2	0.667	0.333	0.2694(1)	0.33(2)
Ba3	0.3429(2)	0.343	0.12706(7)	0.06(1)
Ba4	0.3227(2)	0.323	0.36928(7)	0.36(1)
B1	0.341(2)	0.341	0.575(2)	0.2(4)
B2	0.345(4)	0.345	0.746(3)	0.5(3)
B3	0.332(5)	0.332	0.922(2)	0.1(3)
O1	0.187(2)	0.187	0.584(1)	0.9(3)
O2	0.328(3)	0.478(2)	0.574(1)	0.9(2)
O3	0.185(1)	0.336(3)	0.746(1)	0.4(2)
O4	0.483(6)	0.483	0.747(2)	0.6(4)
O5	0.338(4)	0.476(3)	0.921(1)	2.6(5)
O6	0.196(8)	0.196	0.932(2)	0.9(5)

Note. Space group $P6_3cm$, $Z = 6$; Lattice parameters $a = 9.411(1)$, $c = 17.481(5)$ Å. $V = 1334.4(1)$ Å³, $\rho_{\text{calc}} = 3.790$ g/cm³.

R to 11.9, which allowed us to construct versatile synthesis $\Delta\rho(xyz)$ and locate 6 oxygen atoms and 3 boron atoms. The model of the structure has been found and the composition of the compound has been identified. The final refinement of positional and thermal parameters of the structure was made with simultaneous refinement of a secondary extinction coefficient $q = 1.18(7) \times 10^{-7}$ to $R = 0.049$ and $R_w = 0.043$. Correction on absorption was not introduced because of the thin plate-shape of the crystal. Atomic parameters and bond distances for Ba₃Yb(BO₃)₃ are listed in Tables 1 and 2, respectively.

TABLE 2
Bond Distances (Å) for Ba₃Yb(BO₃)₃

Yb1-O1	3 × 2.29(2)	Yb2-O2	3 × 2.22(2)
-O6	3 × 2.20(3)	-O5	3 × 2.23(3)
⟨Yb1-O⟩	2.24(3)	⟨Yb2-O⟩	2.23(3)
Ba1-O1	3 × 2.93(2)	Ba2-O3	3 × 2.72(2)
-O3	6 × 2.78(2)	-O4	3 × 2.75(5)
		-O5	3 × 3.21(2)
⟨Ba1-O⟩	2.83(2)	⟨Ba2-O⟩	2.89(3)
Ba3-O1	2 × 2.89(2)	Ba4-O3	2 × 2.72(2)
-O2	4 × 2.84(2)	-O5	2 × 2.92(3)
-O3	2 × 2.74(2)	-O4	2.81(3)
-O4	2.66(3)	-O5'	2 × 2.90(3)
		-O6	2 × 2.86(6)
⟨Ba3-O⟩	2.76(2)	⟨Ba4-O⟩	2.84(3)
B1-O1	1.45(2)	B2-O3	2 × 1.46(4)
-O2	2 × 1.35(3)	-O4	1.29(3)
⟨B1-O⟩	1.40(3)	⟨B2-O⟩	1.38(4)
B3-O5	2 × 1.33(4)		
-O6	1.29(4)		
⟨B3-O⟩	1.31(4)		

Thermal Analysis

DTA scans were carried out using a thermal analyzer THY-2000C (CETARAM) in Pt crucibles in air (Pt-Pt/Rh thermocouple, Al₂O₃ as a standard, the heating rate was 8–10°C/min).

Pyroelectrical Properties

Single crystals of Ba₃Yb(BO₃)₃ were investigated for the presence of a pyroelectrical effect. A plate-shaped crystal of dimensions 2.5 × 3.0 × 0.4 mm³ was selected. A coincidence of geometrical and polar axes are in the range of 8°. The cuprous electrodes were placed on the sides perpendicular to the polar axis of the crystal by the vacuum pulverization method. The pyroelectrical coefficient was measured by the static method (8) in the range 300–380 K.

SHG Measurements

The investigation of optical second harmonic generation of laser radiation (SHG), $\lambda = 1.064$ mkm was carried out on polycrystalline samples and single crystals of Ba₃Yb(BO₃)₃ at the L. J. Karpov Research Physicochemical Institute.

RESULTS AND DISCUSSION

Crystal Structure

The oxygen polyhedra of two independent Yb sites are the distorted trigonal antiprisms (YbO₆). The four crystallographically independent Ba atoms are encircled by 9 oxygen atoms. Ba and O atoms are packed according to the motive of a two-layer densest packing. Projection of Ba₃Yb(BO₃)₃ crystal structure on the (001) plane is shown in Fig. 1. The Ba-Ba distances within the plane are 5.392(2) Å, between atoms of two planes 4.234(2) Å. Yb atoms occupy the vacancies between every second plane, threefold oxygen-coordinated boron atoms are placed parallel to the (001) plane between the metal/oxygen layers. The nearest Yb-Yb distance in the structure is 5.42(1) Å, B-B in the plane are 2.98(1) Å. The O-O distances in the three crystallographic independent boron oxygen triangles vary in the range 2.25(6)–2.46(4) Å, the average B-O distance is 1.36(1) Å.

The structure consists of BaO₉-polyhedra layers, among which YbO₆-polyhedra and BO₃ groups are sprinkled.

X-Ray Powder Diffraction Analysis

On the basis of our X-ray diffraction results we suggest a possible structural change in the series of Ba₃Ln(BO₃)₃ compounds when going from Ho³⁺ to larger Ln³⁺ ions due to the good agreement of the X-ray diffraction patterns of barium borates with Gd, Eu, and Sm, which are clearly

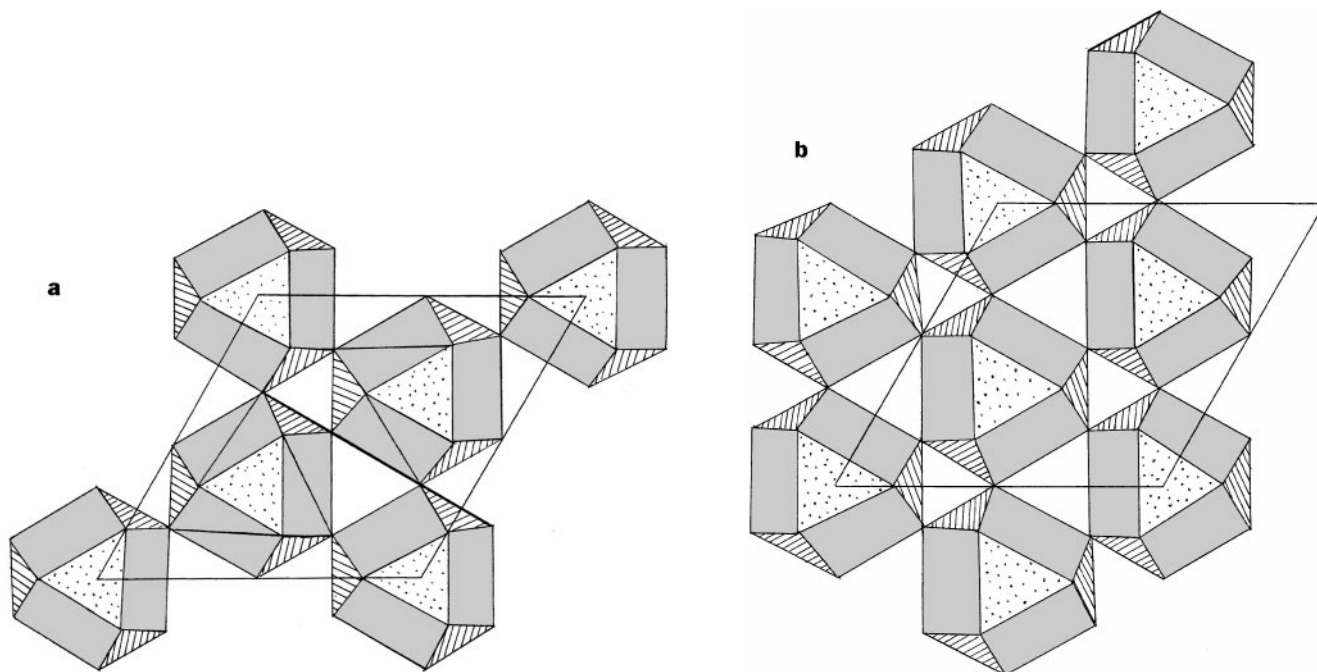


FIG. 1. Projection of the structure $Ba_3Yb(BO_3)_3$ on the (001) plane at the height (a) 0.125 and (b) 0.250.

different from analogous patterns with heavy rare-earth elements.

The structure of $Ba_3Dy(BO_3)_3$ was determined in (3). The compound crystallized in trigonal space group ($R\bar{3}$, $Z = 6$) with lattice parameters $a = 13.041(3)$ and $c = 9.523(2)$ Å and is related to the $Sr_3Sc(BO_3)_3$ type (4, 6, 9).

X-ray diffraction analysis demonstrated that the $Ba_3Ln(BO_3)_3$ powder patterns ($Ln = La-Tb$) were similar to those of trigonal $Ba_3Dy(BO_3)_3$. The single-crystal data of $Ba_3Dy(BO_3)_3$ were used for refinement of the lattice parameters of the isostructural compounds (Table 3).

It should be emphasized that the $Ba_3Dy(BO_3)_3$ specimen, fired according to the same procedure at $900^\circ C$, showed an X-ray pattern similar to those of the $La-Gd$ specimens at $1000^\circ C$. A structure transformation was observed when the temperature was raised above $1000^\circ C$. The X-ray powder pattern showed a great similarity to the X-ray patterns of compounds containing $Ho-Lu$ elements, except for some reflexes of weak intensity. Analysis of the powder X-ray diffraction data of $Ba_3Dy(BO_3)_3$ proved that the compound crystallized in a hexagonal cell and the weak reflexes belong to a rhombohedral cell.

DTA

The dependence of unit-cell volume on the ionic radius of the rare-earth elements is illustrated in Fig. 2. The melting temperatures were determined for samples with $Ln = Ho-Lu, Y$ (Table 4). The melting temperatures in the

range of $Ho-Lu$ increase due to smaller unit cells and increased lattice energy. The atoms of rare-earth elements in the structures of these compounds are arranged between the layers of Ba polyhedra parallel to the (001) plane, thus the distances between the layers are influenced only by the size of the Ln atoms. Therefore, the reduction of the Ln radius from Ho to Lu assists the reduction of layer

TABLE 3
Structural Types and Lattice Parameters for $Ba_3Ln(BO_3)_3$,
 $Ln = La-Lu, Y$

Ln	Structural type	Space group	a , Å	b , Å	V/Z , Å ³
Ln	I-trigonal	$R\bar{3}$			
Pr	I				
Nd	I		13.110(1)	9.602(8)	238.2(1)
Sm	I		13.080(1)	9.579(2)	236.5(1)
Eu	I		13.021(1)	9.549(1)	233.7(1)
Gd	I		13.067(3)	9.552(3)	235.4(3)
Tb	I		13.011(1)	9.539(1)	233.1(1)
Dy	II hexagonal	$P6_3cm$	9.437(2)	17.656(5)	226.9(3)
Ho	II		9.422(2)	17.616(5)	225.7(3)
Y	II		9.418(2)	17.602(5)	225.3(2)
Er	II		9.411(1)	17.543(3)	224.3(1)
Tm	II		9.404(2)	17.510(6)	223.5(5)
Yb•	II		9.411(1)	17.481(5)	222.3(1)
Lu	II		9.385(1)	17.444(4)	221.8(1)

Note. (•) denotes monocrystal data.

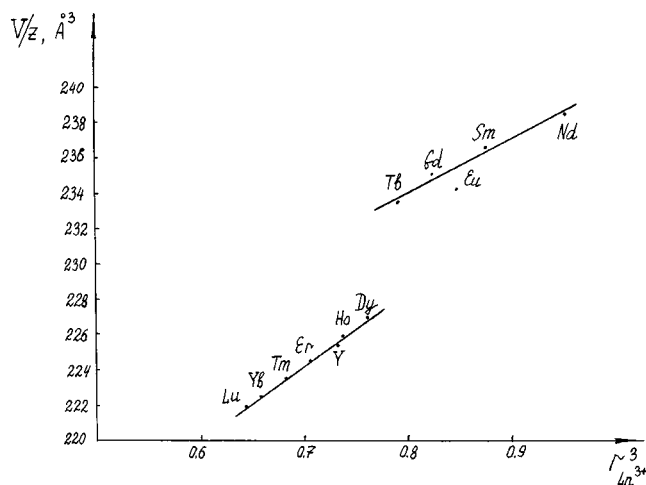


FIG. 2. Dependence of V/Z from $r^3(Ln^{3+})$.

distances. The structure then becomes more compact along the c axis and the melting temperature increases.

Pyroelectrical Properties

The measured value of electroconductivity of the crystal $Ba_3Yb(BO_3)_3$ is found on the level $10^{-12} \text{ Ohm}^{-1} \text{ cm}^{-1}$. The pyroelectrical coefficient, measured in the range 300–380 K is $5 \times 10^{11} \text{ K}^{-1} \text{ cm}^{-2} \text{ K}^{-1}$ and does not depend on the temperature in this range. The result obtained is only an estimate due to the small size of the crystal, which complicates the mechanical processing in preparing the sample for measurements.

SHG Measurements

The investigation proved that the compound $Ba_3Yb(BO_3)_3$ under room temperature revealed a SHG effect ($9I_{2\omega}/2\omega \times SiO_2$ —meaning the intensity of the SHG signal in conventional units in relation to a quartz standard). This fact proves the noncentrosymmetry of the structure. Testing by this method confirmed the correctness of the noncentrosymmetric space group choice during structure determination. The temperature dependence of the SHG signal is shown in Fig. 3. One can see that the intensity of

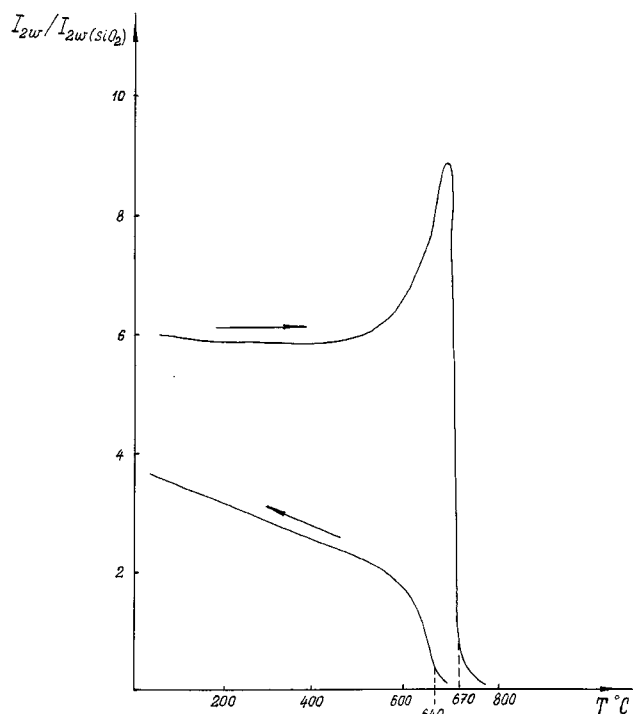


FIG. 3. Temperature dependence of SHG signal for $Ba_3Yb(BO_3)_3$.

the signal in the 640–670°C range decreases practically to zero. When heating the sample, the rapid decrease of the SHG signal practically to zero shows the existence of a type I phase transformation. Measurement of the SHG signal has been carried out when heating the sample up to 700°C and subsequent cooling to room temperature. It was established that when raising the temperature above 670°C the existence of the centrosymmetric phase of $Ba_3Yb(BO_3)_3$ takes place, when lowering the temperature below 640°C the polar phase is detected.

REFERENCES

1. S. Postolov and L. P. Benderskaya, ASII of luminofors and apart pure substances, *Stavropol.* **12**, 84 (1975).
2. G. Blasse, *J. Inorg. Nucl. Chem.* **31**, 1519 (1969).
3. A. B. Iluhin and B. F. Dzhurinsky, *J. Inorg. Chem. (Russia)* **38**, 1625 (1993).
4. P. D. Thompson and D. A. Keszler, *Chem. Mater.* **1**, 292 (1989).
5. T. N. Khamaganova, V. K. Trunov, and L. G. Makarevich, *J. Inorg. Chem. (Russia)* **38**, 1792 (1993).
6. J. R. Cox, D. A. Keszler, and J. Huang, *Chem. Mater.* **6**, 2008 (1994).
7. "SDP Users Manual." Enraf-Nonius, Holland, 1977.
8. N. K. Novic, N. D. Gavrilova, and M. B. Roitberg, *Ellectron. Tech. Mater. (Russia)* **1**, 167 (1969).
9. K. I. Schaffers, P. D. Thompson, T. (III) Alekel, J. R. Cox, and D. A. Keszler, *Chem. Mater.* **6**, 2014 (1994).

TABLE 4
Melting Points for Some $Ba_3Ln(BO_3)_3$ Phases

Ln	Ho	Y	Er	Tm	Yb	Lu
$T, ^\circ C$	1105	1137	1160	1200	1250	1255