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X-ray diffraction and FTIR spectroscopy of heat treated $R_2O_3:3Ga_2O_3:4B_2O_3$ systems

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Abstract

In the $R_2O_3:3Ga_2O_3:4B_2O_3$ systems ($R = La, Nd, Sm, Gd, Ho, Y, Er$ and Yb), X-ray diffraction and infrared absorption spectroscopy were used to study the solid-state reactions in the 575–1050°C temperature range. In some samples ($R = Sm, Gd, Ho, Er$ and Y) huntite ($RGa_3(BO_3)_4$) phases accompanied by RBO_3 and $GaBO_3$ intermediate phases were identified. However, in the systems of $R_2O_3:3Ga_2O_3:4B_2O_3$ for $R = La^{3+}, Nd^{3+}$ and Yb^{3+} , instead of the expected huntite phases, La-, Nd-metaborate or $YbGa(BO_3)_2$ dolomite type phases were formed. Detailed XRD of the rare-earth gallium borates are presented for the first time. Based on the above results, some chemical reactions were assumed for the processes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Borates with the structure of huntite have a unique combination of non-linear optical properties and are promising laser materials [1]. The mostly studied huntite type crystal is the yttrium aluminium borate ($YAl_3(BO_3)_4$ or YAB) which belongs to the double borates having trigonal structure with space group R32. The properties of YAB can be improved by activation with various rare-earths (R) and Al substitution by Ga^{3+} -, Cr^{3+} - and Sc^{3+} -ions [1]. Compounds in polycrystalline form can be usually prepared quicker and

easier by classical solid-state reactions without the risk of contamination of flux ions [1,2]. The knowledge of the produced phases can be useful at the growth of single crystals.

Polycrystalline R-gallium double borates ($R = Y, Sm, Eu, Gd, Tb$ and Dy) were reported in Ref. [3]. The formation of dolomite type R-chromium borates were described in Ref. [4], however, none of the dolomite type R-gallium borates have been observed so far.

The goal of this work is to reveal the effect of the R-ion size on the composition and structure of rare-earth gallium borates. Therefore we have studied $R_2O_3:3Ga_2O_3:4B_2O_3$ systems ($R = La, Nd, Sm, Gd, Ho, Y, Er$ and Yb) by solid-state reactions considering especially the formation of huntite type borates. These results will contribute

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to the determination of the optimal conditions for crystal growth.

2. Experimental procedure

R_2O_3 , Ga_2O_3 and B_2O_3 oxide powders were used as reactants and mixed together in the desired ratios ($R_2O_3:3Ga_2O_3:4B_2O_3$) in acetone in order to prepare homogeneous polycrystalline samples. 5 wt% of excess boron oxide was added to the mixture to compensate the possible volatilization during sintering. Pellets were formed after drying the material, then sintered in Pt crucible in air atmosphere and ground. The process of pressing, sintering and grinding was repeated several times at successively higher temperatures (575–1050°C) as described in Ref. [5].

X-ray powder diffraction (XRD) measurements were carried out for phase and crystal structure identification with Philips PW1780 and FPM HZG-4 type diffractometers using CuK_α radiation

and Ni filter. IR spectra were recorded with a Jasco FT/IR 300E spectrophotometer using pellets prepared with KBr of spectral purity.

3. Results and discussion

In stoichiometric $R_2O_3:3Ga_2O_3:4B_2O_3$ ($R = Sm, Gd, Ho, Er, Yb$ and Y) samples X-ray diffraction measurements indicated the following phase formation between 700°C and 975°C: vaterite type RBO_3 (JCPDS files for Yb-, Er-, Ho-, Gd- and Y-borates: 19-1427, 13-486, 13-478, 13-483 and 16-277, respectively), gallium borate ($GaBO_3$) (JCPDS file: 26-668), huntite type R-gallium double borates ($RGa_3(BO_3)_4$) and dolomite type ytterbium–gallium borate ($YbGa(BO_3)_2$). In samples heated at 1050°C for 5 h the presence of small intensity of RBO_3 and $\beta-Ga_2O_3$ (JCPDS file: 11-370) was observed. XRD parameters of huntite- and dolomite type borates are summarized in Table 1.

Table 1

Observed lattice distances, relative intensities, and hexagonal unit cell parameters (with standard deviations) for huntite type gallium borates of Sm, Gd, Ho, Y, and Er and dolomite type gallium borate of Yb

Huntite type hkl	$SmGa_3(BO_3)_4$		$GdGa_3(BO_3)_4$		$HoGa_3(BO_3)_4$		$YGa_3(BO_3)_4$		$ErGa_3(BO_3)_4$		Dolomite type hkl	$YbGa(BO_3)_2$	
	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)		d (Å)	I (%)
101	5.534	19	5.500	11	5.517	7	5.500	2	5.467	11	003	5.121	6
110	4.728	23	4.716	20	4.716	21	4.716	25	4.704	19	101	3.948	17
021	3.587	84	3.587	73	3.587	93	3.580	95	3.559	84	012	3.601	90
012	3.398	9	3.398	5	3.392	4	3.392	2	3.361	5	104	2.816	100
211	2.864	24	2.855	27	2.855	20	2.851	24	2.838	19	006	2.540	23
202	2.765	100	2.753	100	2.744	100	2.744	100	2.736	100	015	2.449	7
220	2.368	30	2.360	27	2.360	28	2.357	29	2.351	27	110	2.360	32
113	2.210	11	2.199	8	2.199	5	2.194	5	2.189	15	113	2.144	14
131	2.179	14	2.169	8	2.169	5	2.164	4	2.164	8	021	2.030	5
401	1.979	17	1.971	20	1.971	16	1.970	13	1.967	16	202	1.978	29
312	1.943	30	1.936	27	1.936	23	1.933	33	1.932	22	024	1.808	16
321	1.823	13	1.819	8	1.819	15	1.816	8	1.816	11	116	1.737	44
410	1.796	13	1.787	11	1.787	9	1.783	8	1.781	11	211	1.541	5
223	1.718	27	1.708	21	1.710	18	1.708	20	1.705	21	122	1.518	17
024	1.701	27	1.697	15	1.694	14	1.691	15	1.688	17	1010	1.449	23
330	1.576	7	1.574	6	1.571	8	1.571	8	1.569	7	214	1.436	4
											208	1.401	2
											125	1.381	7
											300	1.365	5
a (Å)(s.d.)	9.472(5)		9.442(3)		9.439(3)		9.428(2)		9.418(3)			4.726(3)	
c (Å)(s.d.)	7.482(8)		7.452(5)		7.447(5)		7.433(3)		7.414(5)			15.43(2)	

Samples of $R_2O_3:3Ga_2O_3:4B_2O_3$ systems ($R=La$ and Nd) sintered at 575–680°C showed formation of intermediate aragonite type lanthan ($JCPDS$ file: 12-762) and neodymium borates (RBO_3). The intensity of La- and Nd-metaborate phases ($JCPDS$ files: 23-1140 and 23-1260, respectively) increased up to 850°C. After sintering at 1050°C decomposition started: small intensity of RBO_3 and β - Ga_2O_3 were detected. Huntites were not identified at any stage.

The IR spectra of the untreated $R_2O_3:3Ga_2O_3:4B_2O_3$ ($R=La, Y$ and Yb) starting mixtures consist of sharp and broad absorption bands in the ranges 1600–1100 and 900–400 cm^{-1} . In these spectra the bands of the H_3BO_3 and initial oxides can be recognized (curve 1 in Figs. 1–3) similarly to [6].

In order to identify the expected phases by IR the intermediate phases found by XRD were synthesized by solid-state reactions and checked by XRD.

The IR spectra of $La_2O_3:3Ga_2O_3:4B_2O_3$ mixture after different heat treatments are shown in Fig. 1. (The spectra of $Nd_2O_3:3Ga_2O_3:4B_2O_3$ were very similar.) After sintering at 575°C and 680°C the formation of the intermediate phases of aragonite type $LaBO_3$ and $GaBO_3$ were observed in the regions 1500–1100, 900 and 800–430 cm^{-1} . Additionally some new bands between 1500–1350, 1300–1100, 1100–820, 820–580 and 580–430 cm^{-1}

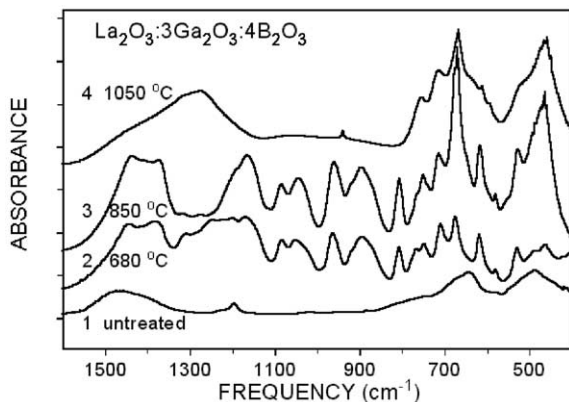


Fig. 1. IR spectra of $La_2O_3:3Ga_2O_3:4B_2O_3$ pellets untreated (curve 1), sintered at 680°C (curve 2), 850°C (curve 3) and 1050°C (curve 4).

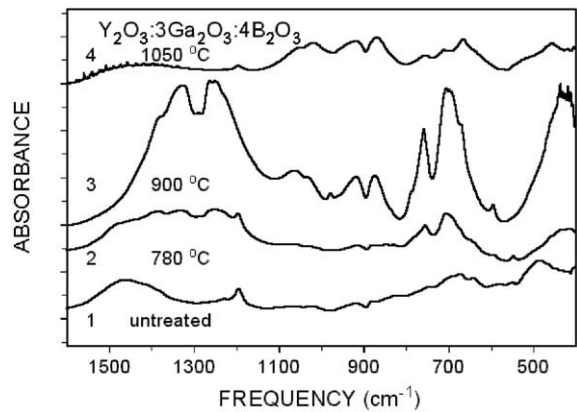


Fig. 2. IR spectra of $Y_2O_3:3Ga_2O_3:4B_2O_3$ pellets untreated (curve 1), sintered at 780°C (curve 2), 900°C (curve 3) and 1050°C (curve 4).

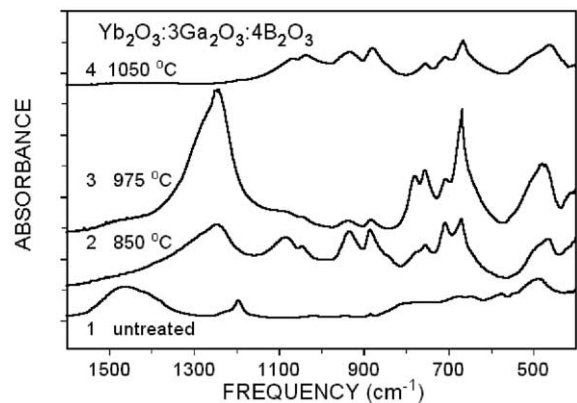
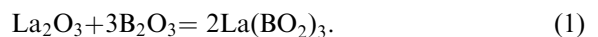


Fig. 3. IR spectra of $Yb_2O_3:3Ga_2O_3:4B_2O_3$ pellets untreated (curve 1), sintered at 850°C (curve 2), 975°C (curve 3) and 1050°C (curve 4).

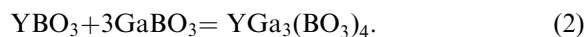
appeared after sintering at 680°C (Fig. 1, curve 2) corresponding to vibrations of mixed BO_4 and BO_3 units in La-metaborate ($La(BO_2)_3$) [7], according to the following reaction:



These bands became dominant after sintering at 850°C (Fig. 1, curve 3). None of the double borates were observed.

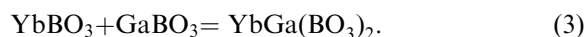
IR and XRD results of the phases formed during the sintering processes in $Y_2O_3:3Ga_2O_3:4B_2O_3$ fit and they were also similar for

$R_2O_3:3Ga_2O_3:4B_2O_3$ ($R = Sm, Gd, Ho$ and Er). The solid-state reaction began between $700^\circ C$ and $780^\circ C$ and the bands of intermediate YBO_3 [5] and $GaBO_3$ phase appeared between 1100 – 800 and 800 – 420 cm^{-1} (Fig. 2, curve 2). Some small and broad bands between 1400 – 1200 , 980 , 800 – 600 and 600 – 400 cm^{-1} corresponding to yttrium–gallium double borate ($YGa_3(BO_3)_4$) appeared after heating at $780^\circ C$ and they became dominant at $900^\circ C$ (Fig. 2, curves 2 and 3) with the corresponding reaction:



The basic IR absorption bands of $RGa_3(BO_3)_4$ ($R = Sm, Gd, Ho$ and Er) corresponding mainly to vibrations of BO_3 -triangle groups are similar to those of $YGa_3(BO_3)_4$ [1].

The solid-state reactions for the $Yb_2O_3:3Ga_2O_3:4B_2O_3$ system began between $700^\circ C$ and $800^\circ C$. The bands of intermediate $YbBO_3$ phase appeared in the regions 1200 – 800 cm^{-1} . Some small and broad bands at 1250 , between 800 – 600 and 600 – 420 cm^{-1} corresponding to dolomite type $YbGa(BO_3)_2$ appeared already after sintering at $800^\circ C$, however, they became more pronounced at $850^\circ C$. The IR bands referring to $YbBO_3$ phase also increased (Fig. 3, curves 2). Upon heating the $Yb_2O_3:3Ga_2O_3:4B_2O_3$ sample to $975^\circ C$ the $YbGa(BO_3)_2$ phase became dominant and its spectrum began to exhibit vibrational spectrum of borate with three separate regions of bands corresponding mainly to vibrations of BO_3 -triangle groups with bands in the regions 1350 – 1200 , 800 – 600 and 600 – 420 cm^{-1} (Fig. 3, curve 3). The corresponding reaction is



The relative absorbance was measured as a function of sintering temperature at relatively sharp bands for both the dolomite type $YbGa(BO_3)_2$ and the huntite type $YGa_3(BO_3)_4$ at 1246 cm^{-1} . The maximum intensities were found at about $975^\circ C$ and $900^\circ C$, respectively.

Sintering the $R_2O_3:3Ga_2O_3:4B_2O_3$ ($R = La, Y$ and Yb) mixtures at $1050^\circ C$ led to the decomposition of the dominant phases and forming of $LaBO_3$ (1400 – 1100 and 900 cm^{-1}), YBO_3 and $YbBO_3$ (1100 – 800 cm^{-1}) and Ga_2O_3 (660 –

460 cm^{-1}) phases shown in curves 4 in Figs. 1–3. One has to mention that mixtures contained usually some Ga_2O_3 (which may be the unreacted oxide or the product of the decomposition of $GaBO_3$), simple borates according to the XRD analysis and IR measurements and unidentified phases. Similar instabilities of R - Ga -borates were observed in Ref. [2].

The borates of the largest size R -ions (La and Nd) contain both BO_3 and BO_4 groups [7] and are identified as La - and Nd -metaborate structures. With decreasing cation size from Sm to Er we observed huntite type borate formation consisting only of BO_3 units. The formation of the dolomite type structure for Yb -gallium borate is due to the even smaller radius of Yb , which is almost at the end of lanthanides.

4. Conclusions

The dominant metaborate ($R(BO_2)_3$ for $R = La$ and Nd), huntite ($RGa_3(BO_3)_4$ for $R = Sm, Gd, Ho, Y$ and Er), the new dolomite ($YbGa(BO_3)_2$ for $R = Yb$), the intermediate RBO_3 and $GaBO_3$ phases were identified in $R_2O_3:3Ga_2O_3:4B_2O_3$ systems, which were sintered between $575^\circ C$ and $1050^\circ C$. Detailed XRD and IR data were given for these compounds. We attribute the various compositions and structures of the formed phases to the different sizes of rare-earth ions. The optimal temperature of formation of the dolomite type $YbGa(BO_3)_2$ and huntite type $YGa_3(BO_3)_4$ was found to be at about $975^\circ C$ and $900^\circ C$, respectively.

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References

- [1] N.I. Leonyuk, *Progr. Crystal Growth Charact.* 31 (1995) 233.
- [2] V.I. Chani, K. Shimamura, K. Inone, T. Fukuda, K. Sugiyama, *J. Crystal Growth* 132 (1993).
- [3] G. Blasse, A. Brill, *J. Inorg. Nucl. Chem.* 29 (1966) 266.
- [4] J. Vicat, S. Aléonard, *Bull. Soc. Fr. Mineral Cristallogr.* 91 (1968) 293.
- [5] E. Beregi, A. Watterich, L. Kovács, J. Madarász, *Vib. Spectrosc.* 22 (2000) 169.
- [6] N.T. McDevitt, W.L. Baun, *Spectrochim. Acta* 20 (1964) 799.
- [7] Y.S. Ysker, W. Hoffmann, *Naturwissenschaften* 57 (1970) 129.