

Growth, structure and SHG properties of Li, Mo-containing huntite-borates $\text{YbAl}_3(\text{BO}_3)_4$

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Li, Mo을 포함하는 huntite-borate 결정 $\text{YbAl}_3(\text{BO}_3)_4$ 의 성장, 구조 및 SHG 특성

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Abstract Li^+ and Mo^{6+} containing huntite borates $\text{YbAl}_3(\text{BO}_3)_4$ were grown by spontaneous crystallization. All crystal show only the huntite-borate phase detected by X-ray powder diffraction analysis. On the basis of the data of the composition analysis, the occupation mechanism of each cation in the huntite structure has been discussed. Li^+ and Mo^{6+} containing $\text{YbAl}_3(\text{BO}_3)_4$ shows a six times higher intensity of the green light SHG detected by the powder technique than $\text{YAl}_3(\text{BO}_3)_4$.

요약 Li^+ 과 Mo^{6+} 를 포함하는 huntite borates $\text{YbAl}_3(\text{BO}_3)_4$ 는 자발적인 결정화 방법에 의해 성장하였으며, 이들 결정은 X선회절 분석방법에 의해 huntite-borate 구조를 갖고 있음을 알 수 있었다. 또한 구조 및 조성분석을 실시함에 따라 이들 양이온이 huntite 구조 내에서 어떤 위치를 점유할 수 있는지에 대해 검토하였으며, 성장 huntite borate 결정의 분말을 사용한 SHG 효과의 관찰에 의해 녹색광의 SHG 강도는 Li^+ 과 Mo^{6+} 를 포함한 $\text{YbAl}_3(\text{BO}_3)_4$ 가 $\text{YAl}_3(\text{BO}_3)_4$ 보다 6배 이상 높음을 알 수 있었다.

1. Introduction

Crystals of rare-earth huntite-borates $RMe_3(BO_3)_4$ (R: rare earth elements, Me: Al^{3+} or Ga^{3+}) are well known for use in nonlinear optical devices and lasers [1,2]. Recently we reported the results of our study on such crystals with different compositions [3,4]. It has been shown that the most equilibrium composition of the huntite structure is $YbAl_3(BO_3)_4$ within the investigated composition region. Further, we have investigated the crystal growth conditions for this compound doped with Li^+ , Si^{4+} , Ge^{4+} and transition metal cations such as Ti^{4+} , V^{5+} , Cr^{3+} and Mn^{4+} [5]. Also, we have discussed the growth of Mo^{6+} -substituted huntite-borates and the possibility of congruent melting [6].

However, few literatures have precisely reported not only the substitution behaviour of each cation in the huntite structure, but also the effect of second harmonic generation (SHG) in these crystals. In this paper some new aspects of the $YbAl_3(BO_3)_4$ huntite-borate structure doped with Li^+ and Mo^{6+} will be studied. Some problems of the cation distribution between the sublattices

of this huntite structure will be discussed in detail. Additionally, the SHG effect observed by the powder technique will be reported.

2. Experimental

$YbAl_3(BO_3)_4$ crystals were grown by spontaneous crystallization technique which is described in Refs. [3] and [5] in detail, and is briefly explained here. A furnace with resistance heater made of SiC was used. A balanced starting mixture of oxides Yb_2O_3 , Al_2O_3 , B_2O_3 , Bi_2O_3 , Li_2O and MoO_3 was kept in a covered platinum crucible located in the furnace. The mixture of oxides was heated during 10 hours to temperature of $1370^\circ C$, and held there for a time period 8 hours and then cooled quickly to $1260^\circ C$ in time 0.5 hours. Thereafter the melt was cooled slowly in time 150 hours to $500^\circ C$ for crystal growth. The spontaneously grown crystals were removed from the melts using a solution of hot water and HNO_3 using ultrasonic vibration. After the cleaning of crystals, we separated them by the use of a mesh.

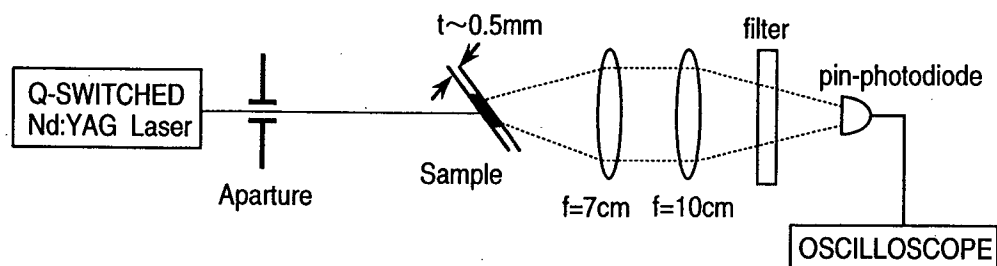


Fig. 1. Scheme of the SHG measurement system by the powder technique.

The crystal composition was determined by the electron probe micro-analysis (EPMA). Two crystals with smaller and larger sizes were studied simultaneously.

The crystal structure was investigated using X-ray powder diffraction analysis (Cu K_α , 1.5418 Å).

The SHG effect of the huntite-borate crystals was adapted for the powder technique [7]. The basic configuration of this measuring method is shown in Fig. 1. The crystals were crushed and sieved to the desired particle size of 125-149 μm before the measurement. Selected particles were fixed between two parallel microscope slides. A Q-switched Nd:YAG laser with a frequency of 10 Hz having the peak power of about 100 mJ at pulsewidth of about 10 ns was used as source. The SHG intensity was observed by an oscilloscope using a pin-photodiode.

3. Results and discussion

Table 1

Melt and grown crystal composition (in mol%) of different huntite borates which are provided on two kinds of crystal size

No	11-3			11-5		
	Melt	Crystals		Melt	Crystals	
Size, mm.		< 0.25	> 2.0		< 0.25	> 2.0
Yb_2O_3	12.33	11.76	11.60	12.40	11.76	11.53
Al_2O_3	36.41	39.57	39.89	37.21	40.28	41.18
B_2O_3	49.39	48.22	47.53	48.84	47.56	46.26
Bi_2O_3	0.50	0.12	0.13	0	0	0
Li_2O	0.76	0.20	0.51	0.52	0.24	0.62
2 MoO_3	0.61	0.13	0.34	1.03	0.16	0.41



Fig. 2. Photograph of $\text{YbAl}_3(\text{BO}_3)_4$ crystals grown by spontaneous crystallization technique.

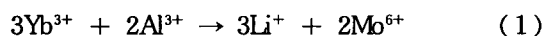
The as-grown $\text{YbAl}_3(\text{BO}_3)_4$ crystals were mostly transparent and white-colored with a prismatic habit and hexagonal rod like shape. Some slightly green colored samples were additionally observed if the concentration of MoO_3 was slightly enriched. Figure 2 shows a typical $\text{YbAl}_3(\text{BO}_3)_4$ crystals with sizes of about $1 \times 1 \times 1 \text{ mm}^3$ by the spontaneous crystallization technique.

Table 1 shows the crystal composition in comparison with the composition of the

starting melt during the two growth runs (11-3 and 11-5). The achieved productivity (the weight ratio of crystal to melt) for the different melts 11-3 and 11-5 were 78 and 62 wt%, respectively.

After solidification, no other distinct layer such as HBO_3 [5] except borate crystals has been observed in each growth run. The flux soaking into the spaces between growing crystals shrinks toward the crucible bottom during the growth process, because of the high thermal expansion coefficients of B_2O_3 and Bi_2O_3 .

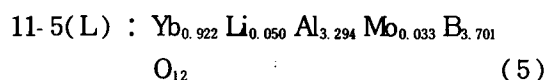
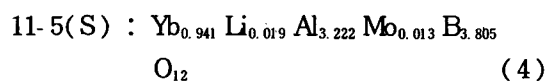
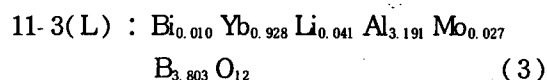
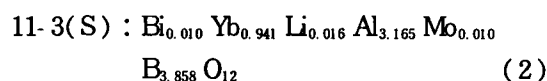
Also, composition analyses, which are provided on two kinds of crystal size (smaller than 0.25 mm and larger than 2 mm), are summarized in Table 1. The concentrations of Yb_2O_3 , Al_2O_3 , Bi_2O_3 and MoO_3 were measured by EPMA. B_2O_3 and Li_2O concentrations in huntite-borates were estimated theoretically because of the impossibility of practical determination. Firstly, the Li_2O content was calculated by the formula $[\text{Li}_2\text{O}]_s = 1.5 \times [2\text{MoO}_3]_s$ where the symbol $[\]_s$ represents the oxide concentration in the solid phase. This relation agrees with the charge balance of a substitution reaction for the Li^+ - Mo^{6+} pairing in huntite structure as following,



Subsequently, the B_2O_3 concentration can be calculated by subtracting of the sum of all other known oxide concentrations from 100 % as reported in Refs. [8] and [9].

Using the chemical formula of rare-earth

huntite-borates $\text{RMe}_3(\text{BO}_3)_4$ and the data of Table 1, the crystal compositions of samples 11-3 and 11-5 are given as following,



where (S) and (L) indicate the smaller and the larger crystals, respectively. Generally, the amount of atoms per formula unit is only authentic for Bi, Li and Mo which is relatively small concentrations in the crystals. In the case of Yb and Al the concentration data are obtained by recalculation assuming the total amount of cations per formula unit equal 8.

Concerning the data of X-ray diffraction analysis the structure uniformity of all prepared crystals was relatively high. The full width at half maximum (FWHM) was about 0.1° and nearly similar for all samples. Therefore we can conclude that all cations in the formulas (2)-(5) are located in a structure with huntite symmetry.

According the compositions in equations (2)-(5), the B^{3+} concentration shows in all investigated crystals in comparison with the ideal huntite formula containing four $[\text{B}^{3+}]_s$ per formula unit. Similar results were obtained for almost gallium huntite-borates in Ref. [8] where the average values

of the cation concentrations were $[\text{Ga}^{3+}]_s = 3.193$ and $[\text{B}^{3+}]_s = 3.443$. For iron huntite-borates a relation of $[\text{Fe}^{3+}]_s = 2.968$ to $[\text{B}^{3+}]_s = 3.827$ was observed [7]. In our crystals we found a relation of $[\text{Al}^{3+}]_s = 3.218$ to $[\text{B}^{3+}]_s = 3.792$. Therefore, the comparison of all above mentioned values yields,

$$[\text{Al}^{3+}]_s > [\text{Ga}^{3+}]_s > [\text{Fe}^{3+}]_s \quad (6)$$

Concerning the coordination number $n=6$ (octahedral positions in the huntite structure) [4], the comparison of the cation radii R_6 gives [10],

$$R_6(\text{Al}^{3+}) < R_6(\text{Ga}^{3+}) < R_6(\text{Fe}^{3+}) \quad (7)$$

Therefore we can assume that some part of Al^{3+} cations occupies the center of oxygen triangles in the huntite structure. In proof of this concept the sum of the $[\text{Me}^{3+}]_s$ and $[\text{B}^{3+}]_s$ concentrations was always 7.000 ± 0.027 in all analyzed crystals. These results agree with the chemical formula of huntite-borates of equations (2)-(5) where $\text{Me} = \text{Al}, \text{Ga}$ or Fe . Of course, the capacity of oxygen triangles is very small for $\text{Al}^{3+}, \text{Ga}^{3+}$ or Fe^{3+} cations. Nevertheless, we assume that the decreasing cation radius from Fe^{3+} to Al^{3+} increases the probability of substitutional position from considering equations (6) and (7). In this case all other cations ($\text{Yb}^{3+}, \text{Li}^+, \text{Mo}^{6+}$ and Bi^{3+}) can be almost located in trigonal prismatic positions. Contradictory to this, Mn^{6+} cation is located by an occupation ability of octahedral positions [5]. Further more detailed

Table 2

Relative intensity of green light SHG for huntite-borate crystals represented as $\text{LnMe}_3(\text{BO}_3)_4$ formula

Lu	Me	Relative intensity
Y	Al	0.4
Ho	Al, Ga	0.9
Er	Al	0.5
Yb	Al	1.1
Yb, Li	Al, Si	2.4
Yb, Li	Al, Ge	2.4
Yb, Li	Al, Mo	2.4
Yb, Li	Al, Ti	0.8
β -BaB ₂ O ₄		3.2

investigations of this relationship are necessary.

The relative intensities of the green light SHG detected at grown crystals are shown in Table 2. It can be seen that the relative intensity of $\text{YbAl}_3(\text{BO}_3)_4$ is of two times higher than of $\text{YAl}_3(\text{BO}_3)_4$. Moreover, mixing crystals of the type $(\text{Yb}, \text{Li})(\text{Al}, \text{M})_3(\text{BO}_3)_4$ with $\text{M} = \text{Si}^{4+}, \text{Ge}^{4+}$ or Mo^{6+} were also able to achieve six times higher SHG intensity. Although the crystals have the smaller relative SHG intensity than in β -BaB₂O₄ crystals (Table 2), the effective nonlinear optical constants of $(\text{Yb}, \text{Li})(\text{Al}, \text{M})_3(\text{BO}_3)_4$ mixing crystals are of order in the range between β -BaB₂O₄ and LiB₃O₅. The Mohs hardness measured for $\text{YAl}_3(\text{BO}_3)_4$ and $\text{YbAl}_3(\text{BO}_3)_4$ was about 8. It seems that these crystals have no effect of deliquescence because they were removed from the crucible and subsequently were cleaned by hot water and HNO₃.

Our results show that $\text{YbAl}_3(\text{BO}_3)_4$ doped with Li^+ and Mo^{6+} seems to be the most favourable composition with high SHG effect and strong hardness without deliquescence effect. Additionally this composition possesses a possibility of congruent melting [6]. Furthermore, it is well-known that the borate crystals have a high degree of intrinsic transparency. These properties are very promising for different practical applications. A more detailed analysis of the optical properties including the absorption spectra will be studied.

4. Summary

$\text{YbAl}_3(\text{BO}_3)_4$ crystals containing Li^+ and Mo^{6+} cations were grown by spontaneous crystallization. It has been shown by the X-ray powder diffraction analysis that all crystals have only the huntite-borate structure. On the basis of the results of composition analysis, it was proposed that the Mo^{6+} cations occupy the center of oxygen triangles.

The detected SHG effect shows a high relative intensity of the green light in these crystals. It seems that $\text{YbAl}_3(\text{BO}_3)_4$ containing Li^+ and Mo^{6+} is an optimal composition for practical applications combining favourable physical and chemical properties (congruent melting point, strong hardness, no effect of deliquescence) with high nonlinear optical efficiency, especially SHG intensity.

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References

- [1] H.Y.-P. Hong and K. Dwight, *Mater. Res. Bull.* 9 (1974) 1661.
- [2] F. Lutz and G. Fuber, *J. Crystal Growth* 52 (1981) 646.
- [3] V.I. Chani, K. Shimamura, K. Inoue, T. Fukuda and K. Sugiyama, *J. Cryst. Growth* 132 (1993) 173.
- [4] K. Shimamura, V.I. Chani, D.H. Yoon and T. Fukuda, *J. Kor. Asso. Crystal Growth* 8. (1998) 521.
- [5] V.I. Chani, K. Shimamura, K. Inoue and T. Fukuda, *Jpn. J. Appl. Phys.* 32 (1993) 4669.
- [6] V.I. Chani, K. Shimamura, K. Inoue and T. Fukuda, *J. Cryst. Growth* 133 (1993) 181.
- [7] S.K. Kurz and T.T. Perry, *J. Appl. Phys.* 39 (1968) 3798.
- [8] L.I. Al. Shinskaya, N.I. Leonyuk, N.V. Pozdnyakova and N.V. Belov, *Soviet Phys.-Cryst.* 23 (1978) 296.
- [9] V.I. Chani, K. Inoue, K. Shimamura, K. Sugiyama and T. Fukuda, *J. Cryst. Growth* 132 (1993) 335.
- [10] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751.