

New phase in the $\text{KB}_3\text{O}_5\text{-CsB}_3\text{O}_5$ system : $\text{K}_3\text{CsB}_{12}\text{O}_{20}$

Masayuki Fukuda, Ryuichi Komatsu and Ko Ikeda

Graduate School of Science and Engineering, Yamaguchi University

2-16-1 Tokiwadai, Ube, Yamaguchi, 755-8611, Japan

Fax: 81-0836-85-9631, e-mail: a055fg@yamaguchi-u.ac.jp

With the rapid development of devices for short wavelength light such as solid-state UV laser, borate crystal has been attracted much attention because of its low transmittance in UV region. Many efforts have been made to look for new advanced borate crystal for UV devices such as windows, lens and wavelength conversion devices. We have investigated the phase relation in $\text{KB}_3\text{O}_5\text{-CsB}_3\text{O}_5$ system, and found two new compounds. In the present study, we characterize these new compounds, and their phase relations are discussed.

Key words: phase diagram, KB_3O_5 , CsB_3O_5 , $\text{K}_3\text{CsB}_{12}\text{O}_{20}$, congruent compound

1. Introduction

There have been strong and continuing demands for a low-cost, high-power UV light source for various applications. Under such circumstances, in addition to excimer laser, solid-state UV laser which consists of wavelength-conversion crystals and infra-red solid-state laser (Nd:YAG laser) attracted much attention because of its low-cost, high-reliability and easier maintenances [1]. Thus, qualified nonlinear crystals are indispensable in developing such solid-state laser.

Various borate crystals, $\beta\text{-BaB}_2\text{O}_4$ (BBO) [2], LiB_3O_5 (LBO) [3], $\text{CsLiB}_6\text{O}_{10}$ (CLBO) [4], CsB_3O_5 (CBO) [5] and $\text{Li}_2\text{B}_4\text{O}_7$ (LB4) [6] have been already studied as promising nonlinear crystals for wavelength-conversion in UV region. However, it is also very important to develop new nonlinear UV crystal since properties of this UV laser is dependent heavily on the UV wavelength-conversion crystal.

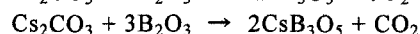
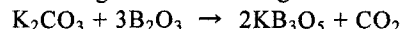
CBO found by Wu et al. [5] is one of superior nonlinear optical (NLO) crystals, and belongs to the space group of $P2_12_12_1$ with unit cell parameters $a=6.213\text{ \AA}$, $b=11.8521\text{ \AA}$ and $c=9.170\text{ \AA}$ [7]. The crystal structure of CBO can be described as a continuous three-dimensional network of spiral chains formed from $(\text{B}_3\text{O}_7)^{5-}$ units. Cs is located in the interstices between each chain [5]. Fourth- (266nm) and fifth-harmonics (213nm) of the Nd:YAG laser can not be generated by using CBO crystal. But, the nonlinear coefficient of this crystal is rather large and the system containing CBO is promising. We have been studied the phase-diagram of some systems including CBO. One of the most promising systems is KBO-CBO. KB_3O_5 (KBO) was reported in 1938, but it may be metastable.

In this paper, we describe the phase relation of the KBO-CBO system to find new nonlinear materials in this system.

2. Experimental procedure

KBO and CBO ceramics were synthesized using

K_2CO_3 , Cs_2CO_3 and B_2O_3 with the purity of 99.9% according to the following reactions:



Synthetic temperatures were at 1063K for KBO and 993K for CBO. After the synthesized KBO and CBO ceramics were mixed in an agate mortar in the molar ratios of $[\text{KBO}:\text{CBO}] = [50:50]$ to $[75:25]$, they were pressed into pellets under about 100MPa and sintered at 973 and 993K.

Crystallization experiments by slow cooling from the melt were also performed using several mixtures to grow new compounds found in this system. Cooling rate was from 2.5 to 10K/hr. However, glass phases are frequently formed by this cooling method from the melt in borate system, and so the ceramic powder with the same composition as melt was often added to the melt during cooling to originate crystal growth.

Sintered mixtures and crystallized products (poly crystals) were examined by X-ray diffraction (XRD). XRD measurements were carried out using a RINT2000 with $\text{Cu K}\alpha_1$ radiation. Obtained crystals from slow cooling were also examined by means of polarizing microscope and EPMA.

3. Results and discussion

3.1 Sintering products

XRD patterns of the synthesized ceramics are shown in Fig.1. This figure shows that KBO and CBO remain in all mixtures. This reason is due to low firing temperature. New XRD peaks were also observed as shown in Fig.1. Although intensities of these new peaks were weak, these became stronger in the range from $[\text{KBO}:\text{CBO}] = [60:40]$ to $[70:30]$. Therefore, it may be considered that the composition of this new phase (new phase A) was in this range.

3.2 Crystallization products

XRD patterns of products by crystallization experiments are shown in Fig.2. Though products obtained from the melt with the composition of

[KBO:CBO] = [60:40] were glass because of fast cooling rate, others included crystals. XRD patterns of new phase A were clearly observed in the range between [KBO:CBO] = [70:30] and [66:33]. Because intensity of XRD of [66:33] was stronger, it may be considered that the composition of new phase A is near [KBO:CBO] = [66:33]. In addition, other new XRD peaks, indicating new phase except for new phase A, was observed only in [75:25] product. This new phase is defined below as new phase B.

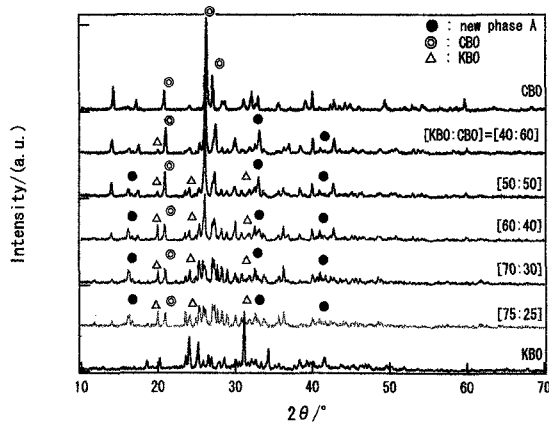


Fig.1 X-ray diffraction patterns of samples sintered at 973K for 10 hours

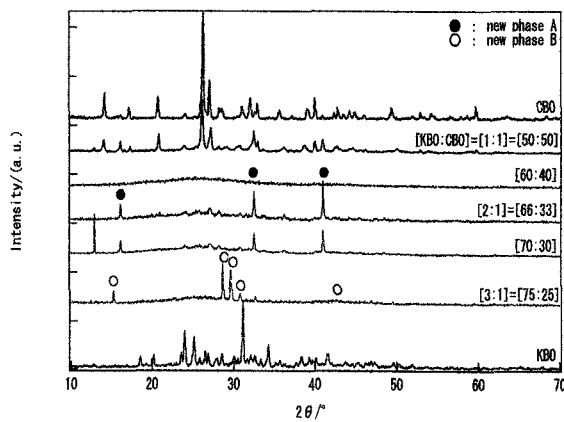


Fig.2 X-ray diffraction patterns of crystallized samples with the range from [KBO:CBO] = [50:50] to [75:25]

3.3 New phase A

Mixture of [KBO:CBO] = [66:33] was fired at 993K to clear phase relation of new phase A. XRD patterns of ceramics fired at 993K and 973K, and crystallized products from the melt are shown in Fig.3. The intensities of XRD peaks of new phase A in ceramics fired at 993K were stronger than those in ceramics fired at 973K. This indicates that reaction at 993K was enough to generate new phase A compared with that at 973K. XRD pattern in crystallized products was coincided with that of ceramics at 993K although XRD pattern in crystallized products slightly includes peaks of CBO. This reason is not clear. But there is possibility of the deviation of chemical composition because each reagent,

especially K_2CO_3 includes water up to 5 wt%.

Morphology changes of crystallized products from the [2:1] melt with cooling rate are summarized in Table 1. Morphology of crystals was affected with cooling rate and powder addition. Spherulites and needle crystals were observed. Spherulite was consisted of many acicular crystals. Spherulites and glass (Category I) was obtained from the melt by normal slow cooling, and glass was hardly observed in Category II. Added powders may act as preferential sites for the nucleus of acicular crystals. This also indicates that this method may be useful to grow crystal from glass-forming borate melt. The size of acicular crystal becomes larger with smaller cooling rate and powder addition, and eventually acicular needle crystals with 3-5 mm length, -1mm width and thin thickness (below 0.1mm) grew as shown in category III.

The structural analysis of new phase A was performed using crystal of category III (-2.5K/hr). Consequently, the crystal system of new phase A was monoclinic system and the unit cell parameter was $a=11.257 \text{ \AA}$, $b=6.596 \text{ \AA}$, $c=11.419 \text{ \AA}$ and $\beta=105.28$ degree.

Photoimage of spherulite in category I by means of polarized microscope is shown in Fig. 4. Each acicular crystal showed rather large birefringence under cross nicol.

As for the phase relation of this phase in the KBO-CBO system, most of crystallized products are consisted of this new phase A, and new phase A ceramics was dominantly formed at 993K. Thus, it may be concluded that this new phase A is a congruent compound.

Table.1 Results of crystallization experiments of [KBO:CBO]=[2:1]

category	Cooling rate [K/hr]	Powder addition [K]	results
I	10.0	—	spherulites and glass
	7.0		spherulites and glass
II	7.0	1005 ± 5	spherulites
III	3.0	1005 ± 5	spherulites and needle crystals
	2.5		spherulites and needle crystals

3.4 New phase B

This phase was obtained only in crystallization experiment. Crystallized products from the [3:1] melt with cooling rate are summarized in Table 2. XRD patterns of ceramics fired at 973K are also shown in Fig.5 together with those of crystallized products. This figure shows that new phase B was obtained only in cooling rate of 7 K/hour without powder addition. New phase A and other phases such as CBO and KBO grew in other cooling rates. This reason and structural analysis of new phase

B will be investigated in future.

Photoimage of new phase B by means of polarized microscope is shown in Fig.6. This phase was elongated platelet and showed clear cleavage. From EPMA analyses, atomic ratio (K/Cs) is 3.00. Thus the chemical formula of this phase is $K_3CsB_{12}O_{20}$.

As for the phase relation of this phase, ceramics of this phase could not be synthesized and the crystal growth of this phase from the melt with [3:1] was affected by cooling rate. Thus it may be considered that this phase is a metastable or an incongruent compound.

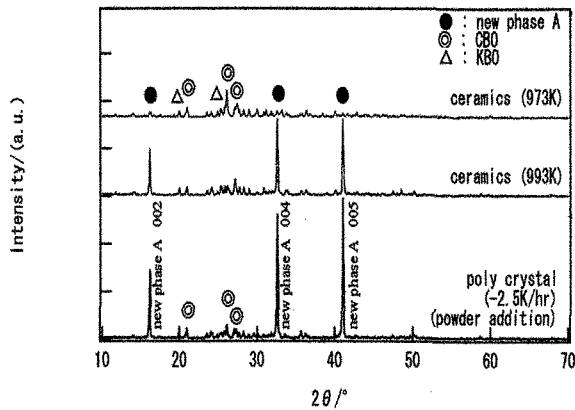


Fig.3 X-ray diffraction patterns of ceramics and polycrystal with [KBO:CBO] = [66:33] = [2:1]

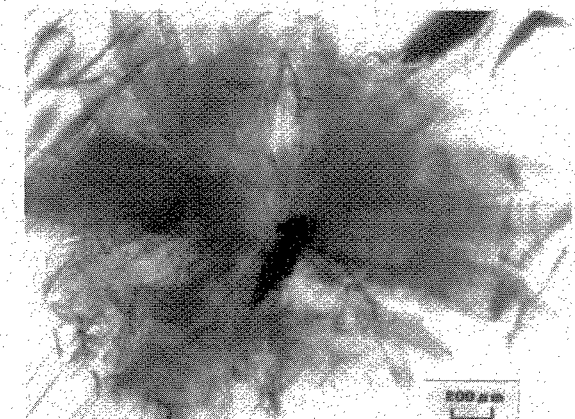


Fig.4 Observation of spherulite by polarizing microscope (open nicol)

Table.2 Results of crystallization experiments of [KBO:CBO] = [3:1]

Category	Cooling rate [K/hr]	Powder addition [K]	results
I	7.0	1000	spherulites and glass
		—	needle crystals and glass
II	5.5	—	spherulites and glass

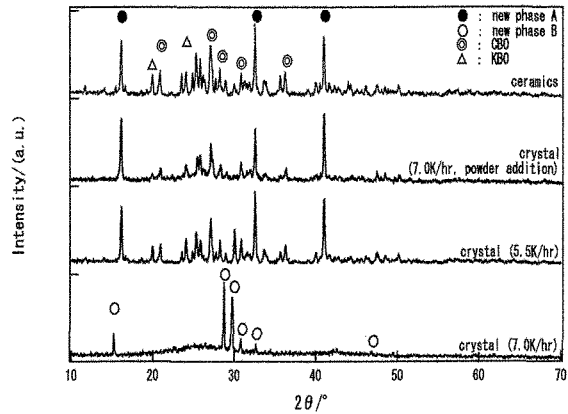


Fig.5 X-ray diffraction patterns of ceramics and polycrystal with [KBO:CBO] = [75:25] = [3:1]

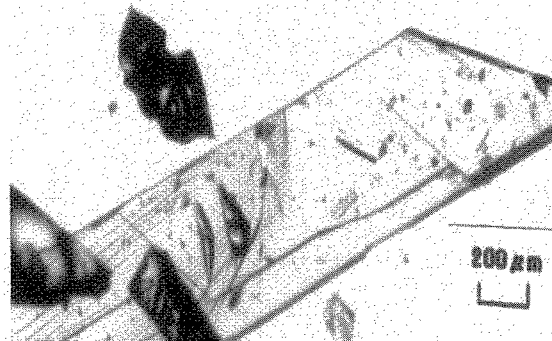


Fig.6 Observation of needle crystal($K_3CsB_{12}O_{20}$) by polarizing microscope (open nicol)

4. Conclusions

Phase relations of the KBO-CBO system were investigated by conventional ceramics method and improved by crystal growth method from the melt to find new advanced materials for optical applications. Consequently, two new phases A and B were found and these phases were new materials. New phase A is probably a congruent compound and its chemical composition is near [KBO:CBO] = [2:1], whereas new phase B is not probably a congruent compound and its composition is $K_3CsB_{12}O_{20}$.

References

- [1] R. Komatsu et al, *The Review of Laser Engineering*, Vol.27, No.8, 541-546 (1999).
- [2] C. T. Chen, B. C. Wu, A. D. Jiang and G. M. You, *Sci. Sin. Ser.B*, **18**, 235 (1985).
- [3] C. T. Chen, Y. Wu, A. Jiang, G. You, R. Li and S. Lin, *J. Opt. Soc. Am.*, **B 6**, 616 (1989).
- [4] Y. Mori, S. Nakajima, A. Taguchi, A. Miyamoto, M. Inagaki, W. Zhou, T. Sasaki and S. Nakai, *Jpn. J. Appl. Phys.*, **36**, 1818 (1995).
- [5] Y. Wu, T. Sasaki, S. Nakai, A. Yokotani, H. Tahg and C. Chen, *Appl. Phys. Lett.*, **62**, 2614-2615 (1993).
- [6] R. W. Whatmore, N. W. Shorrocks, C. O'Hara, F. W. Ainger and I. W. Young., *Electron. Lett.*, **17**, 11 (1981).
- [7] J. Krogh-Moe, *Acta Cryst.*, **B 30**, 1178 (1974).