Crystal synthesis and structure in $Ca_{1.43-x}Bi_xVO_4$ system

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1. Introduction

Nonlinear optical(NLO) materials have played an important role in laser science and technology, and the search for new NLO materials, particularly for UV(ultraviolet) and far-IR(infrared) applications, is still very active[1].

As an excellent NLO materials, β-BaB_2O_4(BBO), $KTiOPO_4$(KTP) were reported and studied widely for growing crystals, optical measurement and application to the laser wave length converters [2-8]. However, some special nonlinear optical problems called for crystals with improved properties (high transparency in the UV region, higher nonlinearity, lower hygroscopicity, and so on). The resulting intensive scientific search for new materials has led to the synthesis of a number of new nonlinear crystals with high optical quality.

$Ca_{1.43-x}Bi_xVO_4$, Bi replaced solid solutions of $Ca_3V_2O_8$, are reported as a promising candidate of new NLO crystal with good optical property. It is assumed that there maybe crystal composition having a three times larger NLO effect than that of KDP(KH_2PO_4) in $Ca_{1.43-x}Bi_xVO_4$ system.

We have investigated the fundamental thermochemical and crystallographic data of $Ca_{1.43-x}Bi_xVO_4$ system to determine the optimum conditions for growing good quality crystals. As a first step of our investigation, $Ca_{1.29}Bi_{0.14}VO_4$ composition crystal was grown by simple slow cooling method of the melt and analyzed by use of X-ray diffractometer.

2. Crystal synthesis

$Ca_{1.29}Bi_{0.14}VO_4$ sintered crystals were synthesized in the $Ca_{1.43-x}Bi_xVO_4$ system. 10g batch of reagent grade chemicals of $CaCO_3$, Bi_2O_3 and V_2O_5 were calcined at 800℃ for 5 hours, then reheated at 1100℃ for 10 hours, and the sintered material pulverized into 200 mesh powder. Crystalline phase of the powder was identified by XRD. A part of the powder was subjected to differential thermal analysis(DTA), in order to determine approximate liquidus temperature. The sample was heated up to 1300℃ at a rate of 10℃/min. The peak pattern of the powder was fundamentally same as that of $Ca_3V_2O_8$. DTA analysis showed that the liquidus temperature of $Ca_{1.29}Bi_{0.14}VO_4$ composition was about 1222℃.

$Ca_{1.29}Bi_{0.14}VO_4$ crystal growing was carried out as following procedure. The above powder was put into a 50㎖ Pt-crucible and heated to 1300℃ at a rate of 200℃/hr in a super kanthal furnace which had temperature gradient of 65℃ /㎝ to vertical direction. The melt was cooled to 1000℃ at various cooling rate of 50℃/hr~2℃/hr, then cooled to room temperature at a rate of 100℃/hr. As a result of the above slow cooling of the melt, we obtained two kind of crystals, one was a colorless transparent crystal formed in the lower part of the crucible, and the other pale yellow crystal formed in the upper part of crucible. Phases of crystal obtained were identified by powder X-ray diffraction. The peak pattern of these crystals were same as that of sintered powder, however, showed the peak shift to lower angle (2θ=0.2°) in the case of yellow crystal compared to white crystal. Fig.1 shows the polished $Ca_{1.29}Bi_{0.14}VO_4$ crystals grown at a cooling rate of 2℃/hr.

3. Crystal structure

A colorless transparent crystal with approximate dimensions of 0.35×0.62×0.70mm^3 was selected and mounted on a glass fiber with epoxy for structure determination. All measurements were made with graphite-monochromated Mo Kα radiation on a Enraf-Nonius CAD4 diffractometer. Unit-cell parameters and an orientation matrix for data collection were obtained from a least-squares refinement with 25 automatically-centered reflections in the range 2.42° $\leq \theta \leq$24.95° . Laue symmetry rhombohedral was determined on

the diffractometer. Intensity data were collected over the range of indices $0 \leq h \leq 12$, $-12 \leq k \leq 11$, $0 \leq l \leq 45$ by using the $\omega - 2\theta$ scan technique to a maximum $2\theta = 50°$. Of the 2173 reflections collected, independent reflections were 772 [R(int)=0.1878].

The structure was solved by direct methods using SHELXS-86[9] and refined using SHELXS-93[10]. The function minimized during the refinement was $\Sigma\omega(|F_o| - |F_c|)^2$. Final R factors were R_1=0.0713 and wR_2=0.1581.

Crystallographic data for a colorless transparent crystal are listed in Table 1. Structural analysis of the single crystal showed that the crystal belonged to the noncentrosymmetric rhombohedral space group R3c and unit cell dimensions were a(=b)=10.848(1)Å, c=38.048(6)Å and V=3877.6(8)$Å^3$. Using this procedure, structure for the pale yellow transparent crystal was also investigated. We couldn't find out any remarkable difference between the structures of colorless and pale yellow crystal. Unit cell dimensions of the yellow crystal, however, were a(=b)=10.857(1)Å, c=38.063(6)Å and V=3885.6(8) $Å^3$, which are slightly larger value than that of the colorless crystal. The slight difference of Bi content between the colorless and pale yellow crystals, more Bi content in the yellow crystal, was considered from the crystallographic data. Bi content difference of two kind of crystals was explained by crystal growth theory. Experimental analytic data for the crystal compositions agreed with our consideration for the difference of Bi content. Vandalism atoms are coordinated by four oxygen atoms and these tetrahedra form the fundamental frame work of the crystal(Fig.2). Fig.3 shows ORTEP diagram of unit cell.

Reference

[1] D. H. Auston et al. " Research on Nonlinear Optical Material: an Assesment" Appl. Opt Vol. 26(2) (1987) 211.

[2] T. Kobayashi "Introduction to Nonlinear Optical materials", Nonlinear Optics Vol. 1 (1991) 91.

[3] D. Eimerl, L. Davis, S. Velsko, E.K. Gram, and A. Zalkin, "Optical, mechanical and thermal properties of barium borate," J. Appl. Phys., vol. 62, (1987) 1968.

[4] D. Eimerl, "Electro-Optic, linear, and nonlinear optical properties of KDP and its isomorphs," Ferroelec., vol. 72, (1986) 95.

[5] J. F. Reintjes, Nonlinear Optical Processes In *Encyclopedia of Laser and Optical Technology*, Academic Press Inc, (1991) 331.

[6] E. M. Vogel, M. H. Weber and D. M. Krol "nonlinear optical phenomena in glass", Phys. chem. Glasses Vol. 32(6), (1991) 231.

[7] P. N. Prasad and D. J. Williams, "Measurement technique for third-order nonlinear optical effects" in *Inroduction to nonlinear optical effects in molecule and polymers*, p.199.

[8] S. Sudo " Application of Nonlinear Optical Materials to Optical Communication Devices", Nonlinear Optics Vol. 1 (1990) 213.

[9] G. M. Sheldrick, Acta Crystallogr., A46 (1990) 467.

[10] G. M. Sheldrick, J. Appl Cryst., (1993) in preparation.

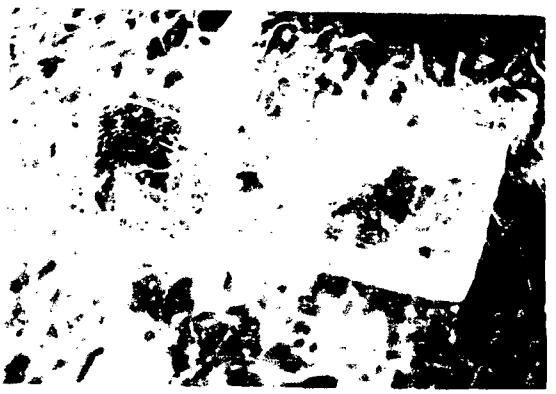


Fig. 1. Photographs of the polished $Ca_{1.29}Bi_{0.14}VO_4$ crystals grown at a rate of 2℃/hr.

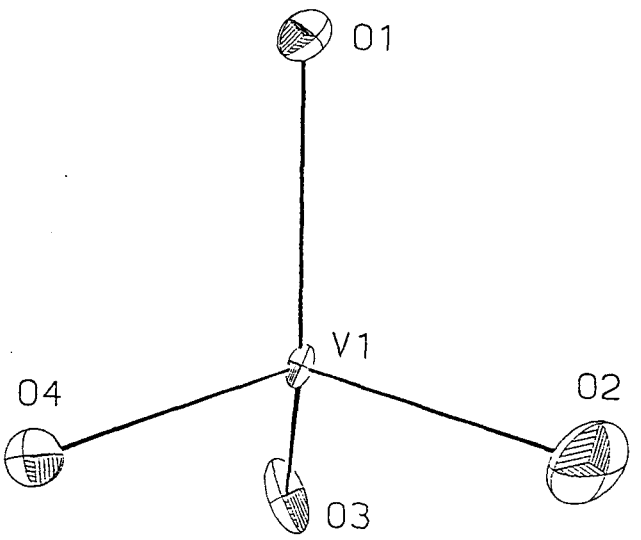
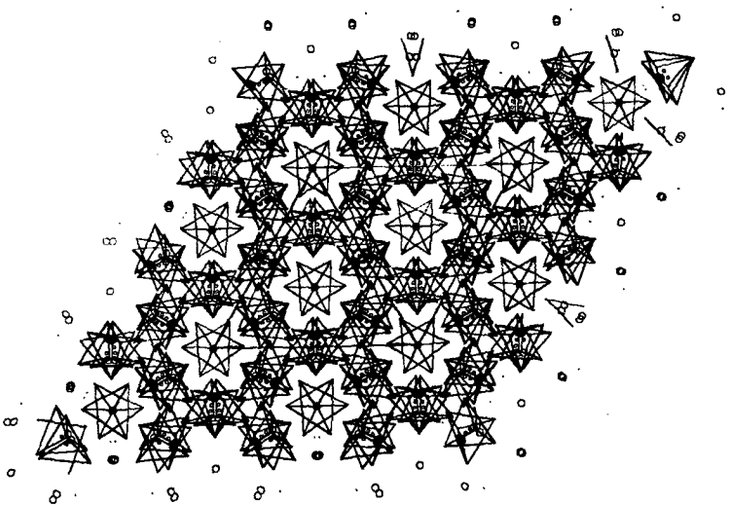
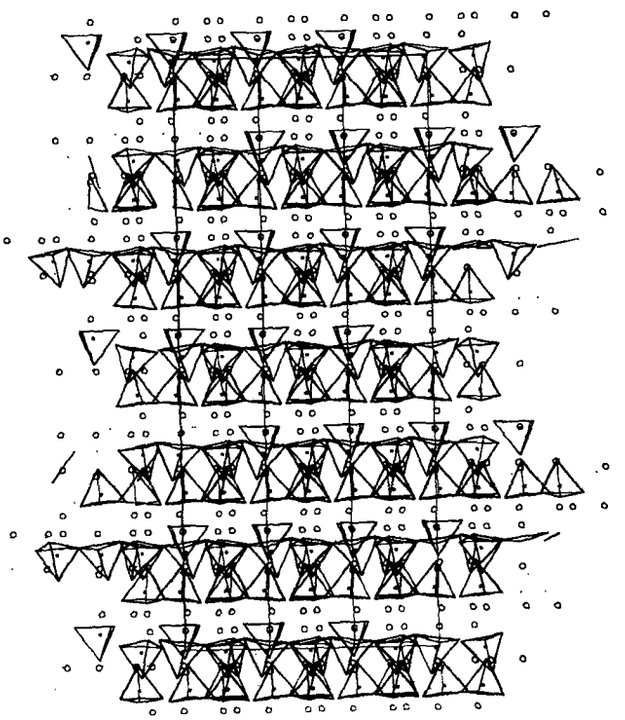


Fig. 2. Labeled diagram of the $(VO_4)^{3-}$ tetrahedron. (Basic unit of crystal frame work)



(a)



(b)

Fig. 3. ORTEP diagram of the unit cell on the $Ca_{1.29}Bi_{0.14}VO_4$ crystal
(a) The rhombohedral unit cell looking down the c-axis.
(b) The rhombohedral unit cell looking down the a-axis.

Table 1. Crystallographic data for a colorless $Ca_{1.29}Bi_{0.14}VO_4$ crystal.

Formular weight	431.54	Absorption coefficient	$7.995mm^{-1}$
Crystal system	Rhombohedral	Independent reflections	772 [R(int)=0.1878]
space group	R3c	Refinement method	Full-matrix least-squares on F^2
a(=b)	10.848(1) Å	Goodness-of-fit on F^2	1.132
c	38.048(6) Å	Final R indices $\{F^3 > 2\sigma(F^2)\}$	R_1=0.0711, wR_2=0.1577
V	3877.6(8) $Å^3$	R indices (all data)	R_1=0.0713, wR_2=0.1581
F(000)	3710	Absolute structure parameter	0.02(5)
Wavelength	0.71069 Å		