

## Crystal Structure of $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$

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The structure of a single crystal, grown by a slow cooling a melt of  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  composition, was analyzed. The crystals belong to the rhombohedral space group R3c and the dimensions of the unit cells are  $a = 10.848(1)$  Å,  $c = 38.048(6)$  Å,  $V = 3877.6(8)$  Å<sup>3</sup> for the pale yellow crystal, and  $a = 10.857(1)$  Å,  $c = 38.063(6)$  Å,  $V = 3885.6(8)$  Å<sup>3</sup> for the yellow crystal, respectively. Unit cell dimensions of the crystal were larger than those of the host crystal,  $\text{Ca}_3(\text{VO}_4)_2$ , owing to the Bi that replaced Ca in the unit cell. Ca in the unit cell formed six, eight and nine coordinated polyhedra with O atoms and Bi replacing Ca entered the eight or nine coordinated Ca sites with different crystallographic environments in the unit cell. All the V in the unit cell formed four coordinated tetrahedra with O atoms, however V-O bond lengths in the tetrahedra were different from one another.

**Keywords :** Nonlinear optical crystal, Crystal structure, Unidirectional crystal growth.

### Introduction

Rhombohedral crystals,  $\text{Ca}_3(\text{VO}_4)_2[(\text{Ca}_{1.5}\text{VO}_4)]$ , that belong to the noncentrosymmetric space group R3c, have been investigated in order to use it as a host crystal for lasers.<sup>1-4</sup> Recently, it has become apparent that crystals made by replacing a part of Ca in  $\text{Ca}_3(\text{VO}_4)_2$  by Bi,  $\text{Ca}_{1.5-1.5x}\text{Bi}_x\text{VO}_4$ , can be used as nonlinear optical (NLO) crystals. The crystal,  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$ , formed when  $x = 0.14$  in  $\text{Ca}_{1.5-1.5x}\text{Bi}_x\text{VO}_4$  system, is assumed to have three times larger NLO effect than that of  $\text{KH}_2\text{PO}_4$  (KDP).<sup>5</sup> The authors carried out experiments to evaluate the fundamental crystallographic and thermochemical data for the  $\text{Ca}_{1.5-1.5x}\text{Bi}_x\text{VO}_4$  solid solution system.<sup>6</sup> We found the value corresponding to the maximum Bi substitution to be 0.14 and in their range  $x = 0.0\sim 0.14$  a single phase with the  $\text{Ca}_3(\text{VO}_4)_2$  structure could be identified. It also became apparent that the composition of the single phasic  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  ( $x = 0.14$ ) was incongruent melting one, so that no definite melting point could be observed, but its solidus temperature was detected to be 1182 °C. The single crystal of the solid solution in this system was grown by the slow cooling method of the melt made from the starting material of  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  composition. The relationships between growth conditions and crystal compositions, and the basic optical properties of the grown crystal were investigated.<sup>7-8</sup>

In this study, the crystal structure was analyzed by the X-ray diffraction method using the above single crystal and the determined structure was compared with that of the host crystal,  $\text{Ca}_3(\text{VO}_4)_2$ .

### Experimental Section

**Crystal growth.** The starting material of the  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  composition was made by mixing  $\text{CaCO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  (Aldrich, 99.9%) powders in alumina mortar in the mole ratio 1.29 : 0.07 : 0.5. This mixture was placed in a 50 cm Pt crucible, calcined at 650 °C for 10 hours, and then sintered at

1100 °C for 72 hours in a muffle furnace. The sintered materials in the Pt crucible were melted by heating at 1400 °C in a temperature-gradient furnace for crystal growth. The melts formed in the crucible were slowly cooled from 1400 °C to 300 °C at a constant rate, and the resulting unidirectional solidification caused the growth of large single crystals in the Pt crucible. The optimum cooling rate of the melt was 2 °C/hr and the detail conditions for crystal growth were described in our earlier paper.<sup>7</sup>

**Structure analysis.** Powder XRD (Shimadzu, XRD-6000) analysis was carried out to identify the phases of the grown crystals. A grown crystal with the approximate dimensions of  $0.35 \times 0.62 \times 0.72$  mm<sup>3</sup> was selected and mounted on a glass fiber with epoxy for structure determination. All measurements were made with graphite-monochromated Mo  $K_\alpha$  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  $2.42^\circ \leq \theta \leq 24.95^\circ$ . 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  $\omega$  scan technique to a maximum  $2\theta = 50^\circ$ . Of the 2173 reflections collected, independent reflections were 772. R3c was chosen as the space group. The structure was solved by direct methods using SHELXS-86<sup>9</sup> and refined using SHELXS-93.<sup>10</sup> The function minimized during the refinement was  $\Sigma \omega (|F_o| - |F_c|)$ .

### Results and Discussion

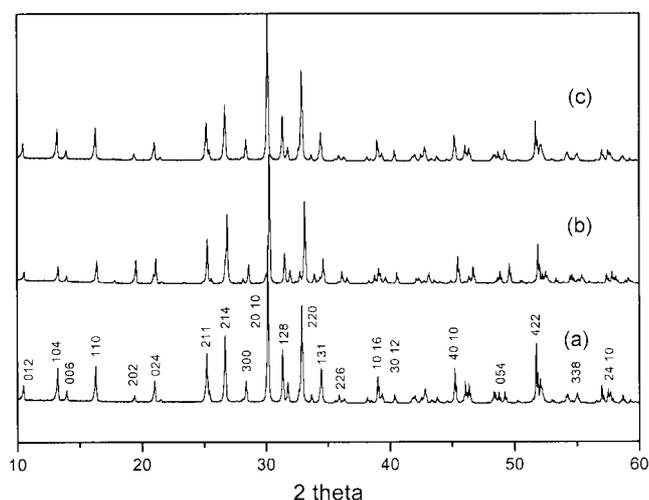
Differently colored crystals were formed in the Pt crucible as a result of slowly cooling the melt of the starting material. The pale yellow crystals in the lower part of the crucible and the yellow crystals in the upper part can be seen in Figure 1.

The result of the powder XRD analysis for the grown crystals are shown in Figure 2.

The XRD pattern of the pale yellow crystal (Figure 2(a)) and that of the yellow one (Figure 2(b)) did not differ from



**Figure 1.** Photographs of the crystals grown at the cooling rate of 2 °C/hr.



**Figure 2.** (a) XRD pattern of  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  composition sintered for 72 hr at 1100 °C. (b) XRD pattern of pale yellow crystals grown at a rate of 2 °C/hr. (c) XRD pattern of the yellow crystals grown at a rate of 2 °C/hr.

each other. This means that the phases of both crystals are essentially identical regardless of their colors. However, the dimensions of the unit cells of these crystals are not the same. The crystallographic data for analysis of the crystal structures using single crystal X-ray diffractometer are given in Table 1.

It can be seen from Table 1 that these crystals belong to the rhombohedral space group R3c and the dimensions of the unit cells are  $a = 10.848(1)$  Å,  $c = 38.048(6)$  Å,  $V = 3877.6(8)$  Å<sup>3</sup> for the pale yellow crystal, and  $a = 10.857(1)$  Å,  $c = 38.063(6)$  Å,  $V = 3885.6(8)$  Å<sup>3</sup> for the yellow crystal, respectively. The unit cell dimensions of the grown crystals are larger than those of  $\text{Ca}_3(\text{VO}_4)_2$  which were determined by Rowland *et al.* ( $a = 10.809(1)$  Å,  $c = 38.028(1)$  Å) or Gopal *et al.*<sup>11</sup> ( $a = 10.806(1)$  Å,  $c = 38.020(1)$  Å). Gopal *et al.* used a  $\text{Ca}_3(\text{VO}_4)_2$  single crystal with dimensions of  $0.04 \times 0.06 \times 0.07$  mm<sup>3</sup> for the structure analysis. The unit cell dimensions of a solid solution, formed when a part of Ca in  $\text{Ca}_3(\text{VO}_4)_2$  is replaced by Bi, are subject to change. The

**Table 1.** Crystallographic Data for  $\text{Ca}_{1.5-1.5x}\text{Bi}_x\text{VO}_4$  ( $x = 0.14$ ) Crystals

	I	II
empirical formula (mole ratio)	Bi 0.18 Ca 3.16 O 9.33 V 2.33	Bi 0.21 Ca 3.12 O 9.33 V 2.33
space group	R3c	R3c
fw	431.54	437.92
$a(=b)$ Å	10.848(1)	10.857(1)
$c$ , Å	38.048(6)	38.063(6)
$V$ , Å <sup>3</sup>	3877.6(8)	3885.6(8)
Z	18	18
F(000)	3710	3753
wavelength, Å	0.71069	0.71069
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	7.995	8.723
density (calcd.), Mg/m <sup>3</sup>	3.326	3.369
goodness-of-fit on F <sup>2</sup>	1.132	1.122
R <sub>1</sub>	0.0713	0.0539
wR <sub>2</sub>	0.1581	0.1283

\*Remark: I; pale yellow crystal. II; yellow crystal.

ionic radius of eight coordinated  $\text{Bi}^{3+}$ , 1.31 Å, is larger by 0.05 Å than that of  $\text{Ca}^{2+}$ , 1.26 Å. Thus, the increase of unit cell dimensions is expected and the above unit cell data supports this expectation. Table 1 shows that the yellow crystal has a larger unit cell than that of the pale yellow one. This is because the Bi content is greater in the yellow crystal than in the pale yellow one. Also, the difference of Bi content is shown in empirical formulae evaluated from the X-ray data for both the crystals, as given in Table 1.

Crystal growth theory explains that the yellow crystal is formed in a later stage of crystal formation and in this stage the Bi content is greater than in the earlier stage when the pale yellow crystal is formed. The crystal structures of yellow and pale yellow crystals are not different fundamentally except unit cell dimensions, so we will describe only one structure of the yellow crystal (crystal II). The coordinates and equivalent isotropic displacement of atoms in the yellow crystal are given in Table 2.

It can be seen from Table 2 that there are four types of Ca atoms with different crystallographic environments in the unit cell. The Bi atoms that replace Ca in the unit cell enter the site of Ca1, Ca2 and Ca3, and never enter the site of Ca4. Coordination of the four types of Ca atoms in the unit cell and Ca-O bond lengths are given in Table 3. The linkage structures of the Ca-O polyhedra evaluated from the data in Table 3 are shown in Figure 3.

As shown in Figure 3, Ca1 forms eight coordinated polyhedron with O atoms and this  $\text{Ca1O}_8$  polyhedron is bound to two O3 atoms sharing the corners with another two  $\text{Ca1O}_8$  polyhedra. The lengths of two Ca1-O3 bonds in Figure 3 are not the same and these read to 2.455(10) Å and 2.486(9) Å, respectively in Table 3. Ca2 also forms eight coordinated polyhedron with O atoms in a similar manner as Ca1 and  $\text{Ca2O}_8$  polyhedron is bound to two O6 atoms sharing the corners with another two  $\text{Ca2O}_8$  polyhedra. In the  $\text{Ca2O}_8$  polyhedron, the Ca2-O<sub>8</sub> bond length 3.100(12) Å, as given in Table 3, is much larger than those of the other

**Table 2.** Atomic Coordinates ( $\times 10^{-4}$ ) and Equivalent Isotropic Displacement ( $\text{\AA}^2 \times 10^{-3}$ ). U(eq) is Defined as One Third of Trace of the Orthogonalized  $U_{ij}$  Tensor

	X	Y	Z	U(eq)
Ca(1)	523(2)	5096(2)	636(1)	13(1)
Bi(1)	523(2)	5096(2)	636(1)	13(1)
Ca(2)	-1387(2)	7242(2)	341(1)	13(1)
Bi(2)	-1387(2)	7242(2)	341(1)	13(1)
Ca(3)	-624(3)	4778(2)	-257(1)	33(1)
Bi(3)	-624(3)	4778(2)	-257(1)	33(1)
Ca(4)	3333	6667	1311(1)	14(1)
V(1)	1382(2)	8188(2)	991(1)	7(1)
O(1)	1402(10)	8466(11)	1426(3)	22(2)
O(2)	2196(12)	9804(11)	795(3)	34(1)
O(3)	2356(8)	7401(8)	872(3)	15(2)
O(4)	-328(9)	7076(10)	872(2)	23(1)
V(2)	1592(2)	8068(2)	-29(2)	11(1)
O(5)	1363(13)	7571(17)	-457(3)	48(3)
O(6)	894(10)	9145(9)	63(3)	28(2)
O(7)	441(8)	6534(8)	196(2)	14(2)
O(8)	3321(9)	8968(9)	102(2)	20(2)
V(3)	-3333	3333	303(1)	9(1)
O(9)	-1774(9)	3431(10)	427(2)	25(2)
O(10)	-3333	3333	-138(5)	28(4)

Ca2-O bond lengths. Ca3, in distinction from Ca1 and Ca2, forms nine coordinated polyhedron with O atoms and the three polyhedra are linked to one another sharing the edge connecting O1 and O10. The polyhedra linked through the edge are, according to Pauling's principle, unstable compared with the polyhedra linked by the corner like  $\text{Ca1O}_8$  and  $\text{Ca2O}_8$ . The instability of the  $\text{Ca3O}_9$  polyhedron seems to make the value of equivalent isotropic displacement of Ca3 relatively large among the four kinds of Ca, i.e., Ca1, Ca2, Ca3 and Ca4 as shown in Table 2. Ca4 forms six coordinated polyhedron with O atoms and is not replaced by Bi atoms.

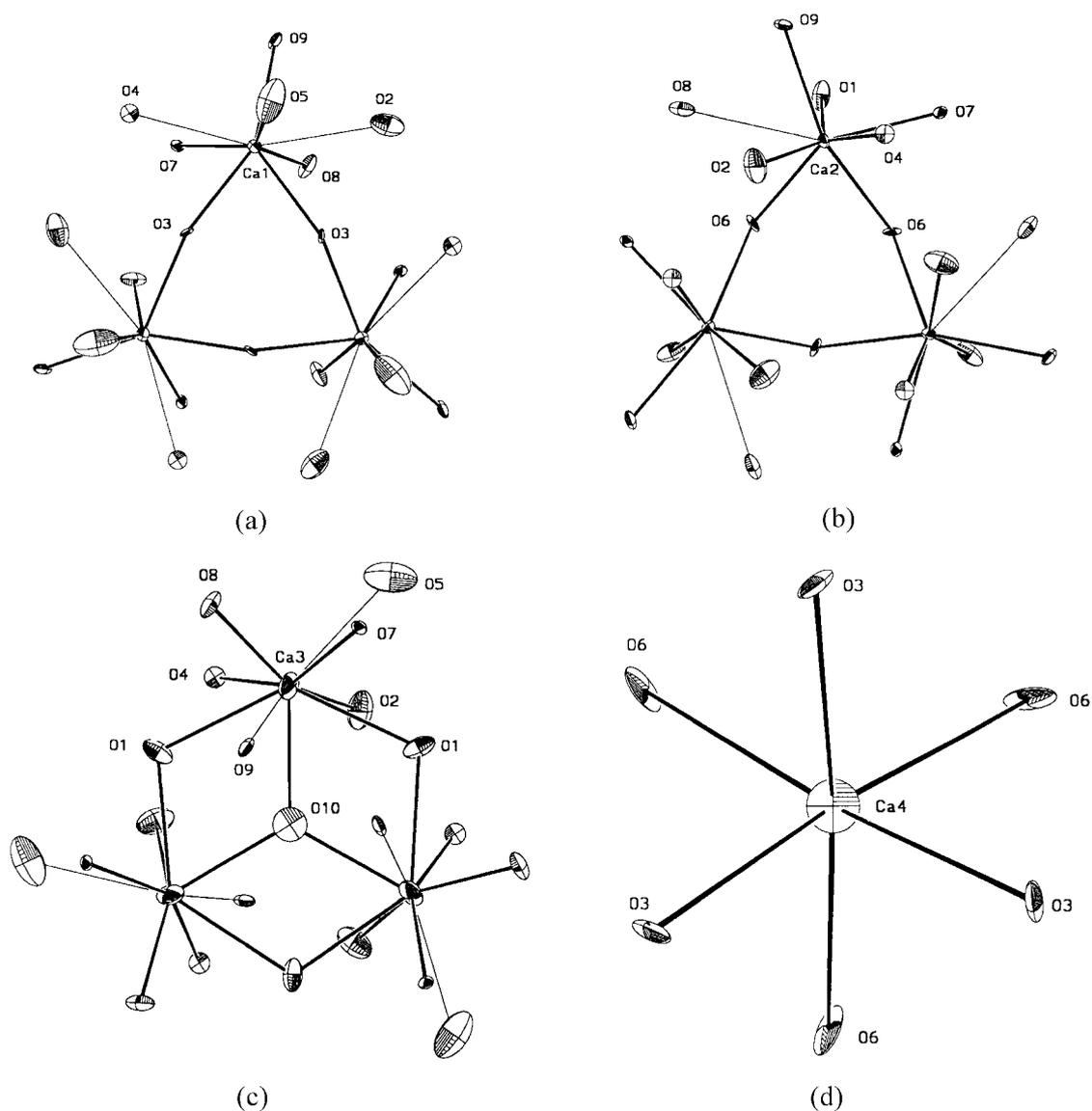
R. Gopal *et al.*<sup>11</sup> reported that there were five types of Ca atoms with different crystallographic environments in the  $\text{Ca}_3(\text{VO}_4)_2$  unit cell. Among them, three kinds of Ca, i.e., Ca1, Ca2 and Ca3 form eight coordinated polyhedra with O atoms in the unit cell. Ca4, one of the other type Ca, forms

six coordinated polyhedron with O atoms and occupies the full sites of Ca4. The last type, Ca5, also forms six coordinated polyhedron, however, one half of Ca5 is absent in their sites to create vacancies in the unit cell. All of the Ca atoms being in the  $\text{Ca}_3(\text{VO}_4)_2$  unit cell ( $Z=21$ ) are expressed as  $\text{Ca}_{18}\text{Ca}_{218}\text{Ca}_{318}\text{Ca}_{46}\text{Ca}_{533}(\text{VO}_4)_{42}$ , here stands for vacancy, and this formula can be abbreviated to  $\text{Ca}_{10.50.5}(\text{VO}_4)_7$  ( $Z=6$ ). When a part of Ca in this unit cell is replaced by Bi, Bi atoms enter the Ca sites that are energetically favorable. Ca sites coordinated with eight O atoms are of greater advantage to be replaced by Bi compared to those coordinated with six O atoms because  $\text{Bi}^{3+}$  is larger than  $\text{Ca}^{2+}$  as described above. Therefore, in  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  the replacement of a part of Ca by Bi occur only in Ca1, Ca2 and Ca3 sites. In the unit cell structure of  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$ , we explained the four types of Ca, i.e., Ca1, Ca2, Ca3 and Ca4, based on the results of Table1, Table 2 and Figure 3. It can be seen that the types of Ca in this unit cell differ from those in the host crystal  $\text{Ca}_3(\text{VO}_4)_2$ ; five types of Ca1, Ca2, Ca3, Ca4 and Ca5 are present in  $\text{Ca}_3(\text{VO}_4)_2$ .

The above difference of Ca types comes from the balancing the excess charges of  $\text{Bi}^{3+}$  replacing  $\text{Ca}^{2+}$  ions in the  $\text{Ca}_3(\text{VO}_4)_2$  unit cell. When a part of  $\text{Ca}^{2+}$  is replaced by  $\text{Bi}^{3+}$ , vacancies are created in  $\text{Ca}^{2+}$  sites for balancing the excess charges. This process can be expressed as a general formula,  $\text{Ca}_{10.5-1.5y}\text{Bi}_{y0.5+0.5y}(\text{VO}_4)_7$  and in the case of  $y=1$ , this formula becomes  $\text{Ca}_9\text{Bi}(\text{VO}_4)_7$ . According to the formula, the replacement of one  $\text{Ca}^{2+}$  by  $\text{Bi}^{3+}$  results in one half vacancy in the Ca site for the charge balancing. The creation of Ca vacancy could occur most likely at the site of six coordinated Ca5 that was energetically unstable because a half of the sites are vacant. It has been known that half populated sites of Ca5 in  $\text{Ca}_3(\text{VO}_4)_2$  unit cell do not affect the stability of the crystal even if the sites become completely vacant.<sup>11</sup> The effect of the completely vacant site for the crystal stability was investigated in several crystal systems including  $\text{Ca}_3(\text{VO}_4)_2$ , for example,  $\text{Na}_3\text{VO}_4\text{-Ca}_3(\text{VO}_4)_2\text{-EuVO}_4$  system.<sup>12</sup> In this study, the y value indicating the content of Bi that replaces Ca in  $\text{Ca}_{10.5-1.5y}\text{Bi}_{y0.5+0.5y}(\text{VO}_4)_7$  is about 1 (exactly 0.98), so the half populated Ca5 sites become completely vacant, creating six vacancies in the unit cell. Consequently, there were four types of Ca in the unit cell of

**Table 3.** Four Types of Ca Atoms in the Unit Cell (bond lengths)

Ca <sub>1</sub>		Ca <sub>2</sub>		Ca <sub>3</sub>		Ca <sub>4</sub>	
bond	length	bond	length	bond	length	bond	length
-O2	2.840(11)	-O1	2.395(11)	-O1	2.635(10)	-O3	2.323(10)
-O3	2.460(8)	-O2	2.283(10)	-O1	2.691(10)	-O3	2.323(10)
-O3	2.501(8)	-O4	2.378(9)	-O2	2.725(11)	-O3	2.323(10)
-O4	2.876(9)	-O6	2.483(9)	-O4	2.448(9)	-O6	2.229(11)
-O5	2.405(12)	-O6	2.531(11)	-O5	2.810(2)	-O6	2.229(11)
-O7	2.321(7)	-O7	2.522(8)	-O7	2.395(8)	-O6	2.229(11)
-O8	2.352(8)	-O8	3.098(9)	-O8	2.477(9)		
-O9	2.368(8)	-O9	2.490(9)	-O9	2.940(10)		
				-O10	2.589(4)		



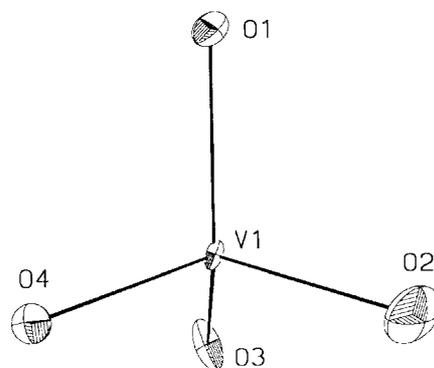
**Figure 3.** Labeled diagrams of  $\text{CaO}_n$  polyhedron in the unit cell. (a)  $\text{Ca}(1)\text{O}_8$ , (b)  $\text{Ca}(2)\text{O}_8$ , (c)  $\text{Ca}(3)\text{O}_9$ , (d)  $\text{Ca}(4)\text{O}_6$

**Table 4.** Three Types of V Atoms in the Unit Cell

$\text{V}_1$		$\text{V}_2$		$\text{V}_3$	
bond	length	bond	length	bond	length
-O(2)	1.680(14)	-O(5)	1.690(12)	-O(9)	1.690(10)
-O(1)	1.688(10)	-O(8)	1.714(11)	-O(9)	1.690(10)
-O(4)	1.693(11)	-O(7)	1.721(10)	-O(9)	1.690(10)
-O(3)	1.714(10)	-O(6)	1.727(14)	-O(10)	1.740(2)

$\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  as described above. It can be concluded from the above results that structure of  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  is essentially same as that of host crystal  $\text{Ca}_3(\text{VO}_4)_2$ .

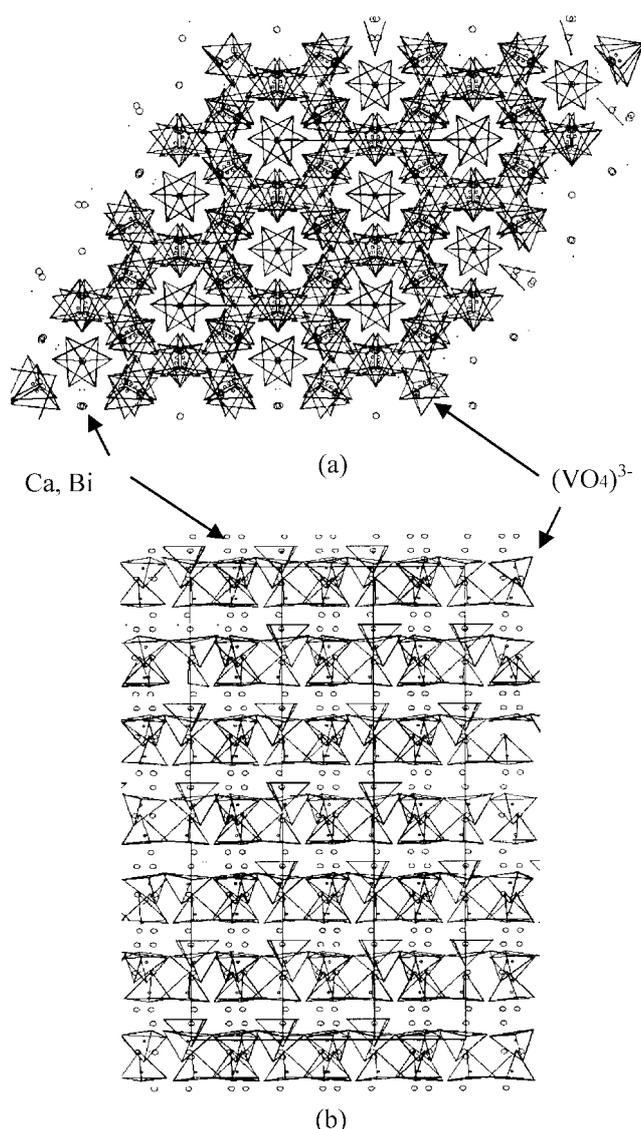
There are three types of V with different crystallographic environments. All the V forms four coordinated tetrahedra with O atoms; nevertheless, the V-O bond lengths are not the same. The coordination and bond lengths of the three kinds of V are given in Table 4 and the  $\text{VO}_4$  tetrahedra described



**Figure 4.** Labeled diagram of  $(\text{VO}_4)^{3-}$  tetrahedron in the unit cell.

on the basis of the data in Table 4, are shown in Figure 4.

The  $\text{V1O}_4$  groups form distorted tetrahedra with different V1-O bond lengths as shown in Table 4 and Figure 4.  $\text{V2O}_4$



**Figure 5.** ORTEP diagrams of the unit cell on the  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  crystal. (a) unit cell looking down the  $c$ -axis. (b) unit cell looking down the  $a$ -axis.

groups form distorted tetrahedral as well, but V2-O bond lengths in  $\text{V}_2\text{O}_4$  tetrahedra are all longer than those of V1-O in the  $\text{V}_1\text{O}_4$  tetrahedra.  $\text{V}_3\text{O}_4$  groups form regular tetrahedra which have the same bond lengths of V3-O. The bond lengths are identically 1.690(10). However, there is one more type of regular tetrahedra which have the bond lengths of V3-O, 1.73(2) Å.

R. Gopal *et al.*<sup>11</sup> also reported the three types of V with different crystallographic environments in their structure analysis of  $\text{Ca}_3(\text{VO}_4)_2$ . All of the V atoms form four coordinated tetrahedra with O atoms in the  $\text{Ca}_3(\text{VO}_4)_2$  as in

$\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  unit cell explained above, though the V-O bond lengths in two unit cells are somewhat different.

The whole unit cells evaluated from the data of interatomic distances and bond angles of  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  are shown in Figure 5.

## Conclusion

Single crystals were grown from the starting material of  $\text{Ca}_{1.29}\text{Bi}_{0.14}\text{VO}_4$  composition by a slow cooling method of melt. The structure was analyzed by means of the X-ray diffraction method using the single crystal and the following results were obtained.

1) The grown crystal belonged to the rhombohedral space group  $R\bar{3}c$  and the unit cell dimensions were larger than those of the host crystal,  $\text{Ca}_3(\text{VO}_4)_2$ . The increase of unit cell dimensions in the grown crystal is due to a Bi with a larger ionic radius than Ca replaces a part of Ca in the host crystal,  $\text{Ca}_3(\text{VO}_4)_2$ .

2) The yellow crystal formed in later stages of crystal growth had larger unit cell dimensions than the pale yellow one formed in an earlier stage. This is because the Bi content is greater in yellow crystal than in pale yellow one.

3) In the unit cell, there existed four types of Ca atoms with different crystallographic environments and the Ca atom formed six, eight and nine coordinated polyhedra with O atoms, respectively.

4) There were three types of V with different crystallographic environments. All the V formed four coordinated tetrahedra with O atom; nevertheless, the V-O bond lengths were not the same.

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