Synthesis and Structure of ACa$_9$(VO$_4$)$_7$ Compounds, A = Bi or a Rare Earth

J. S. O. Evans,[1] J. Huang,[2] and A. W. Sleight[3]

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Phases of the type ACa$_9$(VO$_4$)$_7$ have been prepared where A can be a trivalent rare earth cation or Bi^{3+}. The structure of BiCa$_9$(VO$_4$)$_7$ was determined from single crystal X-ray diffraction data. The space group is $R3$ with $a = 10.8511(2)$ and $c = 38.0505(9)$ at 120 K and $Z = 6$. The structure is related to that of Ca$_3$(VO$_4$)$_2$, but a site partially occupied by Ca in Ca$_3$(VO$_4$)$_2$ is completely vacant in BiCa$_9$(VO$_4$)$_7$. All the ACa$_9$(VO$_4$)$_7$ phases prepared showed a significant second harmonic signal. For the rare-earth compounds, the magnitude of the signal was comparable to that of KH$_2$PO$_4$; a value three times higher was found for BiCa$_9$(VO$_4$)$_7$. © 2001 Academic Press

Key Words: vanadate; polar structure; nonlinear optical material.

INTRODUCTION

Investigations of the Ca/Bi/V/O system in air have revealed six compounds: BiCaVO$_5$, BiCa$_2$VO$_6$, BiCa$_4$V$_3$O$_{12}$, Bi$_3$Ca$_9$V$_{11}$O$_{41}$, BiCa$_9$V$_7$O$_{28}$, and Bi$_2$CaV$_2$O$_9$ (1–6). A significant second harmonic signal found in BiCa$_9$V$_7$O$_{28}$ suggests possible applications associated with its nonlinear optical properties (6). Large single crystals of BiCa$_9$V$_7$O$_{28}$ have recently been grown (7), and detailed studies of the properties are underway. Here we report the synthesis, structure, and preliminary characterization of BiCa$_9$V$_7$O$_{28}$ and related materials.

EXPERIMENTAL

Reactants were Bi$_2$O$_3$ (Aldrich, 99.9%), CaO (Baker, reagent), and V$_2$O$_5$ (Johnson Mathey, 99.9%). Appropriate

[1] Present address: Department of Chemistry, University of Durham, Durham DH1 3LE, UK.

[2] Present address: Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.

[3] To whom correspondence should be addressed at Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331-4003. Fax: (541) 737-2062. E-mail: arthur.sleight@orst.edu.

quantities were ground together under hexane in an agate mortar. This mixture was heated in alumina crucibles at 700°C for 6 h, cooled to room temperature, reground, and heated at 900°C for 10 h. An analogous procedure was used to prepare rare-earth compounds using Y$_2$O$_3$, La$_2$O$_3$, Nd$_2$O$_3$, Dy$_2$O$_3$, Er$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, Ho$_2$O$_3$, Lu$_2$O$_3$, Pr$_6$O$_{11}$, Sm$_2$O$_3$, Tb$_4$O$_7$, Yb$_2$O$_3$, and Sc$_2$O$_3$. Crystals of BiCa$_9$V$_7$O$_{28}$ were obtained by melting at 1240°C followed by slow cooling.

The second harmonic signal was evaluated on powders using a Nd^{3+}:YAG laser ($\lambda = 1064$ nm). Particle sizes were controlled by a set of sieves so that all comparisons are with crystallites of similar size. The reference was KH$_2$PO$_4$, and the accuracy of the measurement was confirmed by comparing the signals from KH$_2$PO$_4$ and NH$_4$H$_2$PO$_4$.

A single crystal of approximate dimensions $0.36 \times 0.24 \times 0.24$ mm^3 was mounted on a glass fiber for single crystal X-ray data collection. X-ray diffraction data were collected at 120 K on a Bruker SMART three-circle diffractometer with graphite monochromatized Mo$K\alpha$ radiation and a CCD area detector. Unit cell dimensions were refined using the centroid values of 995 reflections. Data were integrated using the SAINT program (8) and corrected for absorption using the sadabs routine (9). Further details about the crystal and data collection are given in Table 1. Data also recorded at room temperature on a Rigaku AFC6R diffractometer, giving essentially identical results, are not discussed in detail here.

STRUCTURE DETERMINATION

Preliminary calculations confirmed that the structure of BiCa$_9$(VO$_4$)$_7$ is closely related to that of Ca$_3$(VO$_4$)$_2$ ($R3c$; $a = 10.809$, $c = 38.028$ Å) and Ca$_3$(AsO$_4$)$_2$, which are in turn related to the mineral whitlockite (10–13). However, since 20 reflections with $I > 3(\sigma I)$ were observed that violate the extinction conditions of $R3c$, refinement was performed in $R3$. This point is discussed in more detail below.

Vanadium positions derived from the structure of Ca$_3$(VO$_4$)$_2$ were introduced and oxygen and calcium/

TABLE 1
Crystallographic Details for $BiCa_9(VO_4)_7$

Empirical formula	$BiCa_9V_7O_{28}$
Molecular weight/amu	1374.274
F_{000}	2733
Space group	$R3$ (hexagonal setting)
a (Å)	10.8511(2)
c (Å)	38.0505(9)
V (Å^3)	3880.1(2)
Z	6
Calculated density (g/cm^{-3})	3.529
μ (mm^{-1})	11.09
Temperature (K)	120
Crystal dimensions (mm^3)	$0.36 \times 0.24 \times 0.24$
Diffractometer	Siemens Smart
Radiation	Mo$K\alpha$ ($\lambda = 0.71069$ Å)
Data collected	$-14 \leq h, k \leq 14 - 49 \leq l \leq 49$
No. of unique data	3953
No. of data $F_o^2 > 3(\sigma F_o^2)$	3375
R_{INT} (%)	4.8
No. parameters	302
Weighting scheme	Three-parameter weighting scheme
R_F (%)	4.09
wR_F (%)	4.23
Max $\Delta\rho$ (electrons Å^{-3})	4.3

bismuth positions found by subsequent cycles of least-squares refinement and difference Fourier synthesis. It became apparent during early stages of refinement that the Ca/Bi ions were disordered over the same crystallographic sites. Several approaches were used to model this disorder. For the model judged to be chemically most sensible, total occupancies of Bi and Ca atoms in the unit cell were restrained to give an overall charge balanced formula of $BiCa_9(VO_4)_7$. For final cycles of refinement, atomic positions, Ca/Bi site occupancies, and anisotropic temperature factors (equated for Ca/Bi atoms disordered on the same site, $A1/11$ and $A2/21$ split sites refined isotropically) were allowed to refine freely giving a final agreement factor of $R_F = 4.09\%$. Maximum and minimum residual peaks were -2.1 to 4.3 electrons/Å^3 (the maximum being located some 2.2 Å from V1/V2 on the three-fold axis). All calculations were performed within the Oxford CRYSTALS suite of programs (14).

SECOND HARMONIC SIGNAL

All the $ACa_9(VO_4)_7$ compounds evaluated ($A =$ Bi, La, Nd, Er, Eu, Gd, Ho, Lu, Pr, Sm, Tb, Yb, Y, and Sc) showed a definite second harmonic signal. In most cases, the magnitude of this signal was comparable to that of KH_2PO_4. However, a magnitude three times higher was observed when A was Bi. A second harmonic signal can be expected for compounds with structures in either the $R3$ or $R3c$ space group. However for $Ca_3(VO_4)_2$ in space group $R3c$, we observed a second harmonic signal only about 30% that of KH_2PO_4.

DISCUSSION OF THE STRUCTURE

The structure of $BiCa_9(VO_4)_7$ is shown in Fig. 1. Atomic positions and fractional occupancies are reported in Table 2, and metal–oxygen bond distances in Table 3. The structure is closely related to those of $Ca_3(VO_4)_2$ and $Ca_3(AsO_4)_2$ ($R3c$), which have been described in some detail by Calvo and Gopal (10, 11), and can in turn be related to the more highly symmetrical $Ba_3(VO_4)_2$ (15). The formal relationship between $Ca_3(VO_4)_2$ and $BiCa_9(VO_4)_7$ can be understood by considering the full unit cell contents of $Ca_3(VO_4)_2$, i.e., $Ca_{63}(VO_4)_{42}$. This stoichiometry can only be achieved in space group $R3c$ by having one of the two $6a$ sites for Ca 50% occupied (3 Ca ions on general $18b$ sites, one fully occupied on $6a$, and one 50% occupied on $6a$). Charge balance can, however, also be achieved by the formal replacement of 9 Ca^{2+} ions by 6 Bi^{3+} ions, giving an overall formula of $Bi_6Ca_{54}(VO_4)_{42}$ (or $BiCa_9(VO_4)_7$). This removes the need for partial occupancy of the $6a$ site.

Structural refinement on such a premise proceeded smoothly in space group $R3$, giving rise to vanadium and oxygen positions very similar to those of $Ca_3(VO_4)_2$. No evidence for significant occupation of the $6a$ site partially occupied in $Ca_3(VO_4)_2$ was obtained. Refinement of a Ca atom at this site led to an occupancy of 0.05(1). The Ca/Bi atoms appeared to be disordered over the remaining eight cation sites (hereafter referred to as A cation sites). In addition, A1 and A2 atoms (corresponding to Ca(IB) of Ref. 11) appeared to be disordered over two positions separated by ~ 0.4 Å. Bond valence calculations on both the coordinates obtained in this study, and those reported for $Ca_3(VO_4)_2$ and $Ca_3(AsO_4)_2$, reveal a valence of 1.6 for a single, unsplit Ca at this site (8). This suggests that these A sites are considerably underbonded, and it is therefore perhaps unsurprising that this results in some positional disorder.

In an attempt to model the Ca/Bi occupancy of the different A sites, various approaches were investigated. During initial stages of refinement the distribution of A site atoms was simulated using solely Ca atoms. Restrained refinement in which the total Ca occupancy was fixed to give the same total electron count as $Ca_{54}Bi_6$ (1578 electrons per unit cell) resulted in an R_F of 3.82%. When the total Ca occupancy was allowed to refine freely (resulting in 1454 electrons per unit cell), a slight reduction in R_F to 3.63% was achieved. As such there is perhaps some suggestion of partial occupancy of the A site.

To achieve a more chemically reasonable model, a refinement strategy was adopted whereby the total occupancy of Ca and Bi ions in the cell was restrained to give the charge balanced formula of $Ca_{54}Bi_6$ and individual site occupancies were restrained such that each A site was fully occupied. To avoid correlation problems it also proved necessary to introduce the additional restraint that the Ca1/Ca11 and Bi1/Bi11 split-site occupancy ratios were
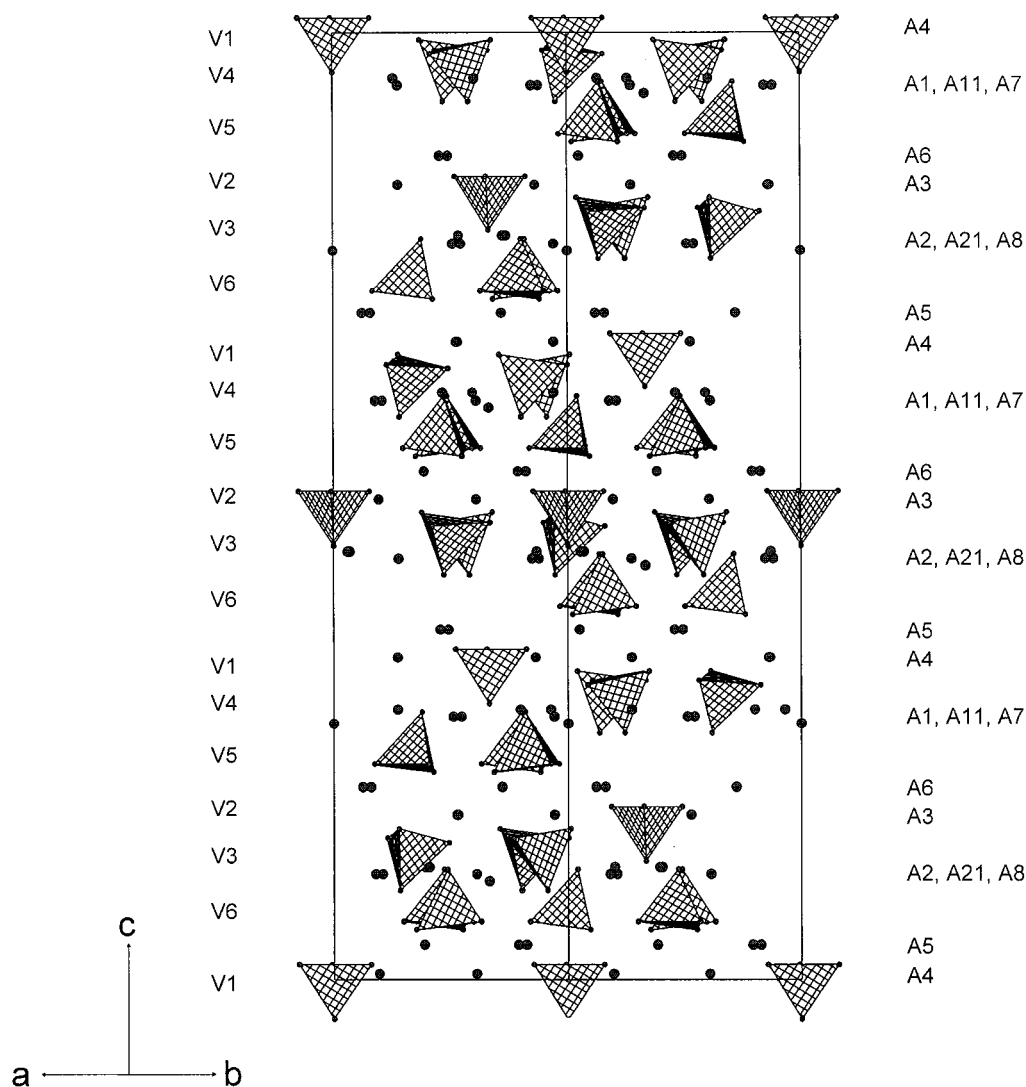
FIG. 1. Crystal structure of BiCa$_9$ (VO$_4$)$_7$ with VO$_4$ groups as hatched tetrahedra and A sites as small shaded circles. Labels refer to the individual V/A sites found at each z coordinate (see Table 1).

equal (also Ca2/Ca21 = Bi2/Bi21). Using this protocol, refinement was performed with both isotropic and anisotropic thermal parameters, resulting in R factors of 5.12 and 4.09% respectively. When the total occupancy restraints were relaxed, the R factor decreased slightly (3.8%), and a reduction in the total A site occupancy was apparent. A site occupancies derived from two different anisotropic refinement strategies are shown in Table 3; both models show similar relative scattering power from the eight different A cation sites.

These refinement strategies suggest some partial occupancy of the A site cations. However, since there is both occupational (Ca/Bi/vacancy) and positional ($A1/A11$ and $A2/A21$) disorder possible in the structure, and refined occupancies may be significantly correlated to both temperature factors and positions, we have chosen to report the refine-

ment based upon the chemically most plausible model of full Ca/Bi occupancy. There is, however, some further support from electron microprobe analysis of partial occupancy, a single crystal from the same batch as that used for single crystal studies showing an empirical formula of Bi$_{0.84}$Ca$_{8.9}$ V$_7$O$_{28}$. We note also that refinement of a data set recorded at room temperature on a Rigaku AFC6R diffractometer at room temperature gave a number of refined A site electrons identical to that of the low temperature data, suggesting that temperature factors are not strongly correlated with site occupancies.

Examination of the final atomic coordinates obtained from the restrained Bi/Ca refinement revealed only minor distortions (± 0.015 Å) from the ideal $R3c$ symmetry. In fact the only significant deviations lie in the Bi/Ca ratios of the split $A1/A11$ and $A2/A21$ sites. Refinement was therefore

TABLE 2
Atomic Positions

Atom	x/a	y/b	z/c	U(iso)	Occ	Valence	Atom	x/a	y/b	z/c	U(iso)	Occ	Valence
V(1)	0.0000	0.0000	0.00367(6)	0.0058		5.08	V(2)	0.0000	0.0000	0.50363(7)	0.0064		5.08
V(3)	− 0.17437(13)	− 0.31367(13)	0.13661(5)	0.0070		5.10	V(4)	0.31386(14)	0.17447(13)	0.63664(5)	0.0077		5.13
V(5)	− 0.31857(12)	− 0.18227(13)	− 0.09452(5)	0.0050		5.27	V(6)	0.18234(13)	0.31888(12)	0.40549(5)	0.0053		5.27
Ca(1)	− 0.1228(3)	− 0.2760(3)	− 0.05517(13)	0.019(1)	0.54(2)	1.68	Ca(2)	0.2762(4)	0.1226(3)	0.44466(13)	0.0181(11)	0.53(2)	1.69
Ca(11)	− 0.1316(4)	− 0.2607(6)	− 0.0472(2)	0.0215(16)	0.35(2)	—	Ca(21)	0.2609(6)	0.1312(4)	0.4526(2)	0.0212(15)	0.37(2)	—
Ca(3)	− 0.13812(13)	0.13774(12)	− 0.15974(5)	0.0147	0.918(12)	2.04	Ca(4)	− 0.13769(12)	0.13808(13)	0.34021(5)	0.0145	0.918(12)	2.03
Ca(5)	− 0.21038(11)	− 0.38508(11)	0.03694(5)	0.0135	0.878(12)	2.02	Ca(6)	0.38510(11)	0.21028(11)	0.53691(5)	0.0139	0.877(12)	2.03
Ca(7)	0.3333	0.6667	− 0.06258(8)	0.0225	0.938(13)	2.52	Ca(8)	− 0.6667	− 0.3333	0.43731(8)	0.0232	0.934(13)	2.55
O(11)	− 0.1469(5)	− 0.1569(5)	0.01582(16)	0.0159		1.92	O(21)	0.1568(5)	0.1470(5)	0.51592(17)	0.0163		1.75
O(12)	0.0000	0.0000	− 0.0414(3)	0.0286		1.91	O(22)	0.0000	0.0000	0.4586(3)	0.0235		1.75
O(31)	− 0.2427(6)	− 0.4917(6)	0.1450(2)	0.0243		2.15	O(41)	0.4914(6)	0.2428(6)	0.6448(2)	0.0236		2.09
O(32)	− 0.2913(5)	− 0.2778(5)	0.15974(12)	0.0069		1.87	O(42)	0.2780(5)	0.2918(5)	0.65972(13)	0.0086		1.84
O(33)	0.0010(6)	− 0.2291(7)	0.14914(16)	0.0199		2.18	O(43)	0.2288(7)	− 0.0005(5)	0.64914(16)	0.0190		1.83
O(34)	− 0.1974(7)	− 0.2833(9)	0.09451(17)	0.0357		2.09	O(44)	0.2834(9)	0.1968(7)	0.59445(17)	0.0362		1.89
O(51)	− 0.2386(7)	− 0.0202(6)	− 0.11453(18)	0.0263		2.00	O(61)	0.0203(6)	0.2380(7)	0.38563(18)	0.0262		2.06
O(52)	− 0.2615(6)	− 0.2965(6)	− 0.10569(13)	0.0149		2.17	O(62)	0.2959(6)	0.2613(6)	0.39426(14)	0.0143		1.96
O(53)	− 0.4942(6)	− 0.2599(6)	− 0.10588(17)	0.0152		2.17	O(63)	0.2605(5)	0.4952(5)	0.39436(16)	0.0144		1.95
O(54)	− 0.2899(6)	− 0.1520(6)	-0.05073(16)	0.0160		2.07	O(64)	0.1524(6)	0.2901(6)	0.44935(16)	0.0170		2.00

Note. Atoms in the same horizontal line are approximately related by a *c*-glide. *A* sites are modeled as containing a disordered mixture of Ca/Bi, with occupancies restrained such that occ(Ca) + occ(Bi) = 1. Bond valence sums (15, 16) are calculated on the basis of *A* sites being occupied solely by Ca and split sites *A*11/*A*21 being unoccupied.

TABLE 3
Summary of Bi/Ca Site Occupancies

Model	Site	1	11	2	21	3	4	5	6	7	8	No. Atoms	Σe^-	R_F	$\Delta\rho$ (e Å^{-3})
Ca only	Ca	0.77	0.44	0.73	0.47	1.19	1.19	1.35	1.35	1.06	—	—	1454	3.63	−1.3/+3.8
Anisotropic	Ca	0.54(2)	0.35(2)	0.53(2)	0.37(2)	0.921	0.92(1)	0.88(1)	0.88(1)	0.94(1)	0.93(1)	54.05	1576	4.09	−2.1/4.3
Restrained	Bi	0.065(4)	0.042(3)	0.062(3)	0.043(3)	0.081(4)	0.08(1(4)	0.123(3)	0.124(4)	0.062(5)	0.066(5)	5.97			

also performed in $R3c$, and similar agreement factors were obtained ($R_F = 4.17\%$ versus 4.09%), However, since 20 reflections with $I > 3(\sigma I)$ violating space group $R3c$ were observed during data collection, the lower symmetry space group was retained. In the numbering scheme of Table 2, pairs of atoms with an odd/even first digit to their serial number are related to each other by the c-glide, e.g., V1/V2, A11/A21, O54/O64.

The structure (Fig. 1) contains fairly regular VO$_4$ tetrahedra (bond lengths, 1.68–1.74 Å, average = 1.710 Å; min/max deviation from tetrahedral angles, 101.8/118.4°). All the VO$_4$ tetrahedra have a local approximately threefold axis approximately parallel to the crystallographic c axis. The polar nature of the structure can then be appreciated from Fig. 1. The V3 and V4 tetrahedra are compensated by the V5 and V6 tetrahedra, whereas the V1 and V2 tetrahedra all "point" in the same direction with respect to the polar axis. The tetrahedra are arranged so as to give rise to six-, eight-, and nine-coordinate Ca/Bi ions. The positionally disordered $A1/A11$ and $A2/A21$ are both nine coordinate, though with >90% of their bond valence sum being contributed by the first seven neighbors. The average A–O bond distance is 2.61 Å, and the bond valence sum (16, 17) for a cation at this site is 1.7. $A3$ and $A4$ are formally eight coordinate with an average A–O distance of 2.52 Å (bond valence, 2.0). The $A5$ and $A6$ cations are eight coordinate (average A–O, 2.52 Å; bond valence, 2.0). The $A7$ and $A8$ cations on the threefold axis have a distorted octahedral coordination, with relatively short A–O bonds (average, 6×2.28 Å; valence = 2.6). A Ca atom at this site is thus considerably overbonded. The A cation environments are shown in Fig. 2.
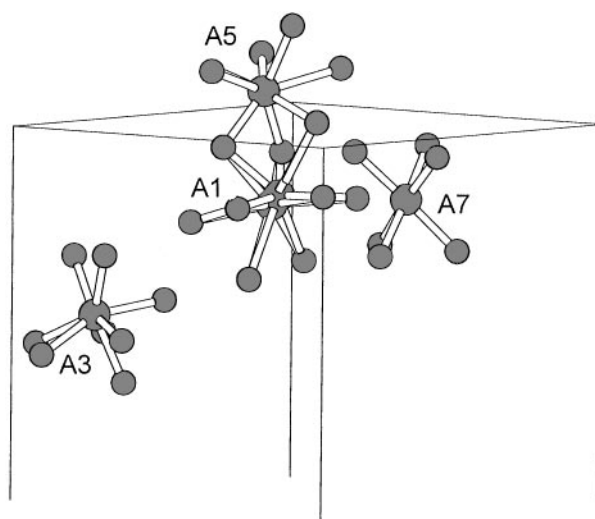

FIG. 2. Local coordination environments of sites $A1$, $A3$, $A5$, and $A7$. All A–O distances up to 3.1 Å are shown as bonds.

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