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Synthesis and structure of $Bi_3Ca_9V_{11}O_{41}$

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The synthesis and single crystal structure determination of the new bismuth calcium oxovanadate $Bi_3Ca_9V_{11}O_{41}$ is reported. $Bi_3Ca_9V_{11}O_{41}$ crystallizes in space group $P\bar{1}$, $a=9.4099(5)$, $b=10.0036(6)$, $c=18.881(1)$ Å, $\alpha=79.891(2)$, $\beta=85.382(2)$, $\gamma=89.057(2)°$, $V=1744.0(3)$ Å^3 and has been refined to $R_F=3.93\%$. The unit cell contains a total of 64 atoms in the asymmetric unit. The structure consists of 3 distinct types of V_nO_m polyhedra ($10\times VO_4$, $2\times V_2O_7$, $2\times V_4O_{14}$ in the unit cell). Bi and Ca atoms are disordered over 12 sites coordinated by 7–10 oxygens in the range 2.0–3.0 Å, with Bi showing a tendency to adopt structurally less symmetric sites.

Introduction

There are five structurally characterized Bi/Ca/V/O quaternary phases reported in the literature: $BiCa_9V_7O_{28}$, $BiCa_4V_3O_{13}$, $BiCa_2VO_6$, $BiCaVO_5$ and $Bi_2CaV_2O_9$.[1–5] Of these $BiCa_9V_7O_{28}$ shows efficient second harmonic generation.[6] $BiCa_4V_3O_{13}$ and $BiCa_2VO_6$ crystallize in non-centrosymmetric polar space groups and thus may be expected to exhibit nonlinear optical properties and are potential ferroelectrics. In this paper we report the synthesis and structure of a new phase in this system, $Bi_3Ca_9V_{11}O_{41}$. This phase contains Bi/Ca atoms disordered over a total of 12 different A cation sites in the asymmetric unit and three distinct types of V_nO_m coordination polyhedra: VO_4, V_2O_7 and V_4O_{14}, giving a structural formula $Bi_3Ca_9(VO_4)_5$-$(V_2O_7)(V_4O_{14})$.

Experimental

Single crystals of $Bi_3Ca_9V_{11}O_{41}$ were grown from a congruently melting powder. A bright orange-yellow polycrystalline sample of $Bi_3Ca_9V_{11}O_{41}$ was prepared from a stoichiometric mixture of Bi_2O_3, $CaCO_3$ and NH_4VO_3. 1.0000 g (2.15×10^{-3} mol) of Bi_2O_3, 1.2912 g (0.0129 mol) of $CaCO_3$ and 1.8444 g (0.0158 mol) of NH_4VO_3 were thoroughly ground and heated in an alumina crucible at 900 °C for 48 hours. The powder was then melted at 950 °C, slow-cooled to 600 °C at a rate of 3 °C per hour and cooled to room temperature at a rate of 5 °C per minute. The crystals obtained were bright orange and rod-like in shape.

A single crystal of approximate dimensions $0.12\times0.12\times0.36$ mm^3 was mounted on a glass fibre for 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 349 reflections. An absorption correction was applied to the data based on the 010, $0\bar{1}0$, 001, $00\bar{1}$, 101 and $\bar{1}0\bar{1}$ faces of the crystal using the program XPREP,[7] and data integrated using the SAINT program.[8] Details about the crystal and data collection are given in Table 1.

Structure solution

The structure was solved by direct methods using the XS routine within the SHELXTL suite.[9] A total of 23 cation sites were found in the asymmetric unit. Initial attempts to assign the metal types to individual crystallographic sites proved unsuccessful, presumably due to the Ca/Bi site disorder present. Given the expected Ca : Bi ratio of 3 : 1 and the ratio of atomic numbers of 83 : 20, scattering from these sites (hereafter referred to as A cation sites) was initially modeled using Br atoms as an average of the scattering power. Vanadium sites were easily distinguished from the A sites by the distance to adjacent peaks in difference Fourier maps. During the initial stages of the refinement, all cation temperature factors U_{iso} were fixed at 0.01 Å^2. All positional parameters and A site occupancies were refined until a stable model was reached. A total of 41 oxygen sites were then found from a single difference Fourier map. A full anisotropic refinement of this model (589 parameters) gave an agreement factor of $R_F=4.00\%$.

The Bi/Ca site disorder was then modeled by placing both atom types on each A site and refining their occupancies. The necessary constraints were introduced on positional and thermal parameters for these sites. In the final cycles, all positional parameters were refined, as well as anisotropic displacement parameters and Bi and Ca occupancies. This corresponds to a total of 589 variables and led to an agreement factor of $R_F=3.93\%$.

All calculations were performed within the Oxford CRYS-

Table 1 Crystallographic details for $Bi_3Ca_9V_{11}O_{41}$

Chemical formula	$Bi_3Ca_9V_{11}O_{41}$
Molecular weight/amu	2204
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.4099(5)
b/Å	10.0036(6)
c/Å	18.881(1)
α/°	79.891(2)
β/°	85.382(2)
γ/°	89.057(2)
V/Å^3	1744.0(3)
Z	2
Calculated density/g cm^{-3}	4.197
Temperature/K	120
μ/mm^{-1}	19.33
Total number of reflections	22871
Number of unique reflections	9637
R_{int} (%)	3.75

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Table 2 Structure refinement details for $Bi_3Ca_9V_{11}O_{41}$

A site model	Br	Bi/Ca
Number of parameters	589	589
$\Delta\rho_{max}/e^- A^{-3}$	4.75	4.64
$\Delta\rho_{min}/e^- A^{-3}$	−2.53	−2.27
R (%)	4.00	3.93
wR (%)	4.21	4.11

TALS[10] suite of programs running under Red Hat Linux 5.2. Details of the structure refinement are given in Table 2.

CCDC reference number 1145/227.

See http://www.rsc.org/suppdata/jm/b0/b002857f/ for crystallographic files in .cif format.

Discussion

$Bi_3Ca_9V_{11}O_{41}$ was first identified as an impurity obtained during attempts to grow single crystals of $BiCa_9V_7O_{28}$. The stoichiometry of the phase was suggested by electron microprobe analysis and confirmed by preliminary single crystal investigations. A pure polycrystalline sample was then successfully prepared, from which the single crystals used in this study were grown. A view of the structure is given in Fig. 1, fractional atomic coordinates in Table 3 and selected bond distances and angles in Table 4. It can be seen from Fig. 1, and perhaps more clearly from the coordinates of Table 3, that the structure of $Bi_3Ca_9V_{11}O_{41}$ displays a pseudo symmetry that corresponds to an approximate face centering. For most metal positions, related sites are found at approximately +(1/2,0,0), +(0,1/2,0) and +(1/2,1/2,0).

There are 11 crystallographically unique vanadium sites giving rise to three different types of V_nO_m groups, namely VO_4, V_2O_7 and V_4O_{14}. In order to investigate the frequency of occurrence and the geometries of these oxovanadate groups in other structurally characterized phases, a custom database comprising all vanadium containing oxides in the ICSD[11] database was created using the program Prequest[12] and searched using the program Quest.[12]

In $Bi_3Ca_9V_{11}O_{41}$ there are ten isolated VO_4 tetrahedra per unit cell. O–V–O tetrahedral bond angles are uniformly distributed around 109.5°, with a minimum and maximum angle of 98.0 and 120.2°. In Fig. 2 we compare the distributions of the O–V–O tetrahedral angles in $Bi_3Ca_9V_{11}O_{41}$ with those found in our database of vanadates. The appearance of the two distributions is fairly similar in terms of the range of angles they include. The smallest tetrahedral angle in $Bi_3Ca_9V_{11}O_{41}$ is 98.0°; similar angles are found in $Pb_2V_2O_7$[13] and $Fe_2V_4O_{13}$.[14] The maximum value for a tetrahedral angle in $Bi_3Ca_9V_{11}O_{41}$ is 120.2° and such angles also exist in $Fe_2V_4O_{13}$,[14] Nb_9VO_{25}[15] and $Bi_6V_3O_{16}$.[16] It does, however, appear that the spread of O–V–O angles in the present phase is somewhat broader than in VO_4 tetrahedra as a whole. This is presumably related to Bi/Ca site disorder in this material (see below).

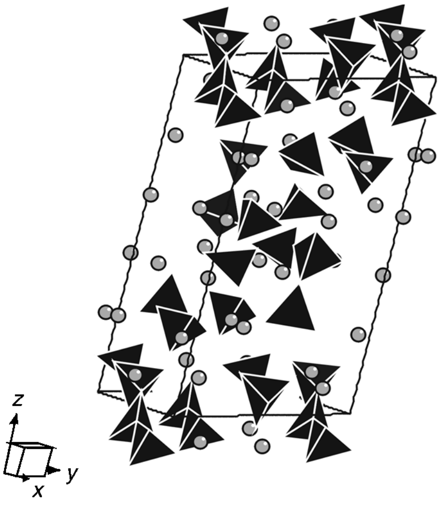

Fig. 1 A view of the structure of $Bi_3Ca_9V_{11}O_{41}$. Dark polyhedra are V centred, light grey spheres are disordered Bi/Ca A cation sites.

V_2O_7 groups are formed by pairs of VO_4 tetrahedra sharing a corner, as shown in Fig. 3(a). There are two such groups per unit cell. The V–O–V bridging angle of the V_2O_7 groups is 121.2°. A database search for phases containing V_2O_7 groups showed that the distribution of V–O–V bridging angles shows two maxima, one around 120° and the other around 140°. Compounds containing V–O–V bridging angles similar to those found in $Bi_3Ca_9V_{11}O_{41}$ are α-$Sr_2V_2O_7$ (121.2° and 123.0°),[17] β-$Sr_2V_2O_7$ (123 and 124°),[18] $Pb_2V_2O_7$ (122.2°),[13] $Ni_2V_2O_7$ (117.6°),[19] $Co_2V_2O_7$ (117.5°)[19] and $BiSr_2V_3O_{11}$ (125.3°).[20]

There are two V_4O_{14} groups per unit cell of $Bi_3Ca_9V_{11}O_{41}$. This motif is more unusual and it is depicted in Fig. 3(b). It consists of a pair of edge-sharing VO_5 square pyramids each sharing a corner with a VO_4 tetrahedron. In both the VO_4 tetrahedra and VO_5 square pyramids, the longest V–O bond involves the oxygen shared between these units. The shortest V–O bond in all VO_5 square pyramids is to the apical oxygen. In addition, the apices are oriented towards opposite sides of the shared edge. V–V contacts across the shared edge are 2.877(4) and 2.883(4) Å in the two unique V_4O_{14} groups. A feature worth mentioning is the short O–O distances along the shared edge, which are 2.38(1) and 2.41(1) Å in the two groups. This short distance is presumably due to the tendency of the two V^{5+} cations to maximize their separation and thus decrease mutual repulsion. Short O–O contacts of comparable length are found in edge sharing VO_5 groups in a number of phases. Examples include V_2O_5,[21] with O–O contacts of 2.386 Å, V_3O_7[22] (2.36 and 2.37 Å), as well as vanadium bronzes $Cs_xV_3O_7$, $x \approx 0.35$[23] (2.44 Å) and $Cs_xV_2O_5$, $x \approx 0.3$[24] (2.40 Å).

In order to get an insight into the frequency of occurrence of V_4O_{14} groups, we carried out a database search for this motif. No V_4O_{14} groups were found and we conclude that this polyhedral arrangement is, to the best of our knowledge, unique among structurally characterized vanadates.

In general, the ability of V_nO_m groups to catenate is well established in both the solid state and aqueous solutions. Typical examples include: AVO_3 (A = Na, K, NH_4) phases, which contain infinite chains of corner sharing tetrahedra;[25,26,27] $K_3V_5O_{14}$, which contains infinite layers of corner sharing VO_5 square pyramids and VO_4 tetrahedra;[28] V_2O_5 itself can be thought of as layers of edge and corner sharing VO_5 groups, themselves forming distorted square pyramids.[21]

Bi/Ca site disorder

As discussed in the previous section, the V_nO_m polyhedra are arranged in the unit cell so as to give 12 potential A cation sites. The ionic radii of Bi and Ca are very similar (1.17 *vs.* 1.14 Å for 6 fold coordination)[29] and there are several known examples of Bi/Ca site disorder in Bi/Ca/V/O phases and other systems.[1,2]

In the two methods used to model the A sites, the relative scattering density of these 12 sites was constant. The freely refined scattering power in terms of numbers of electrons was 421 (3Bi + 9Ca = 429 electrons), while the freely refined Bi and Ca occupancies gave a Bi : Ca ratio of 1 : 3.004(9), thus confirming the stoichiometry of the compound.

For the purpose of an analysis of Bi and Ca cation distribution on the A sites, all contacts up to 3.5 Å in length were considered. Coordination numbers range from 7 to 10, with bond lengths from 2.17 to 3.45 Å. Average A–O distances for these sites are fairly constant and they are depicted in Fig. 4.

Table 3 Atomic parameters for $Bi_3Ca_9V_{11}O_{41}$. Sites A(*n*) contain both Bi(*n*) and Ca(*n*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{iso, eq}$	Occupancy[a]	Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{iso, eq}$
A(1)	0.89434(5)	0.31883(5)	0.25414(3)	0.0102(1)	0.618(3)	O(10)	0.5847(7)	0.9733(7)	0.0441(3)	0.012(4)
A(2)	1.37747(6)	−0.17470(6)	0.25822(3)	0.0102(1)	0.576(3)	O(11)	0.8103(7)	0.6115(7)	0.3799(3)	0.009(4)
A(3)	1.49962(7)	−0.57744(7)	0.24533(3)	0.0063(2)	0.405(3)	O(12)	0.0448(7)	0.1733(7)	0.1495(4)	0.014(4)
A(4)	1.47060(7)	−0.06599(7)	0.41570(4)	0.0118(2)	0.381(3)	O(13)	0.2360(6)	0.0003(6)	0.2540(3)	0.009(4)
A(5)	1.00589(9)	−0.07101(9)	0.23698(5)	0.0084(2)	0.243(3)	O(14)	0.9206(7)	0.6572(6)	0.0971(4)	0.009(4)
A(6)	1.3828(1)	−0.4562(1)	0.41586(7)	0.0095(3)	0.087(3)	O(15)	0.3198(6)	0.8982(7)	0.1124(3)	0.010(4)
A(7)	1.2646(1)	−0.6674(1)	0.11091(6)	0.0100(3)	0.171(3)	O(16)	0.3833(7)	0.6709(6)	0.0314(3)	0.010(4)
A(8)	0.8948(1)	0.0367(1)	0.40605(7)	0.0105(3)	0.118(3)	O(17)	0.0767(7)	0.6160(7)	0.4408(4)	0.014(4)
A(9)	1.0388(1)	−0.4215(1)	0.57641(7)	0.0143(3)	0.154(3)	O(18)	0.0183(7)	0.8621(7)	0.3568(3)	0.010(4)
A(10)	1.7615(1)	−0.1659(1)	0.10697(6)	0.0082(3)	0.131(3)	O(19)	0.3163(7)	0.2746(7)	0.2400(3)	0.010(4)
A(11)	1.6538(1)	−0.7566(1)	0.08818(7)	0.0084(3)	0.070(3)	O(20)	0.4905(7)	0.4297(7)	0.1127(3)	0.010(4)
A(12)	2.1537(1)	−0.2622(1)	0.08969(7)	0.0093(3)	0.081(3)	O(21)	0.0867(7)	0.4746(7)	0.0442(4)	0.014(4)
V(1)	1.1256(2)	−0.2185(2)	0.4177(1)	0.0062(8)		O(22)	0.5626(7)	0.6717(7)	0.3126(4)	0.011(4)
V(2)	1.2683(2)	−0.6928(2)	0.54465(8)	0.0089(8)		O(23)	0.5195(7)	0.3702(7)	0.3676(4)	0.011(4)
V(3)	0.6452(2)	0.2824(2)	0.41805(8)	0.0060(8)		O(24)	0.8195(7)	0.0512(7)	0.2894(4)	0.011(4)
V(4)	1.1608(2)	−0.4360(2)	0.24959(8)	0.0049(8)		O(25)	0.5952(8)	0.1178(7)	0.4555(4)	0.017(4)
V(5)	0.6672(1)	0.0655(1)	0.24498(8)	0.0049(8)		O(26)	0.3101(7)	0.5501(7)	0.2964(4)	0.012(4)
V(6)	1.7359(1)	−0.3597(1)	0.29350(8)	0.0050(8)		O(27)	0.6386(7)	0.2380(6)	0.2255(3)	0.008(4)
V(7)	1.2376(2)	0.1391(1)	0.29885(8)	0.0065(8)		O(28)	0.7399(7)	0.4965(6)	0.2544(3)	0.008(4)
V(8)	1.5249(2)	−0.3995(2)	0.07713(8)	0.0070(8)		O(29)	0.6911(7)	0.6126(7)	0.0251(4)	0.015(4)
V(9)	1.0262(2)	0.1021(2)	0.07513(8)	0.0060(8)		O(30)	0.7048(7)	0.0238(6)	0.1634(4)	0.011(4)
V(10)	1.8928(2)	−0.4723(2)	0.05435(8)	0.0100(8)		O(31)	0.8078(7)	0.2699(7)	0.3658(3)	0.010(4)
V(11)	1.3930(2)	0.0274(2)	0.05470(8)	0.0085(8)		O(32)	0.4221(7)	0.1570(6)	0.0978(4)	0.010(4)
O(1)	0.1371(7)	0.7380(6)	0.2247(3)	0.008(4)		O(33)	0.5432(8)	0.6774(7)	0.1490(4)	0.015(4)
O(2)	0.0195(7)	0.4720(7)	0.2986(3)	0.010(4)		O(34)	0.8856(7)	0.1751(7)	0.0296(3)	0.010(4)
O(3)	0.5269(7)	0.9693(7)	0.2927(3)	0.011(4)		O(35)	0.1930(7)	0.1152(7)	0.0248(3)	0.012(4)
O(4)	0.3064(7)	0.7855(7)	0.3764(4)	0.018(4)		O(36)	0.1957(7)	0.5163(7)	0.1690(3)	0.012(4)
O(5)	0.3169(7)	0.0985(7)	0.3776(4)	0.013(4)		O(37)	0.1925(7)	0.3651(7)	0.4673(4)	0.013(4)
O(6)	0.8114(7)	0.7737(7)	0.2348(3)	0.010(4)		O(38)	0.7061(7)	0.3706(7)	0.4775(3)	0.013(4)
O(7)	0.8206(6)	0.3978(6)	0.1124(3)	0.009(4)		O(39)	−0.0844(8)	0.1409(8)	0.5103(4)	0.019(4)
O(8)	−0.0072(6)	0.9303(6)	0.1082(3)	0.008(4)		O(40)	0.7263(7)	0.8659(7)	0.4328(4)	0.016(4)
O(9)	0.0614(7)	0.1760(7)	0.3204(4)	0.013(4)		O(41)	0.5621(7)	0.6402(7)	0.4724(4)	0.015(4)

[a] Occupancy quoted is that of Bi(*n*), the site occupancy of Ca(*n*) is 1−Occupancy(Bi(*n*)).

It is, however, of relevance to consider the factors that determine the Bi/Ca distribution at the different sites in this structure. One way to approach this question is by applying the concept of bond valence.[30,31] Fig. 5(a) shows how the valence around two given A sites (here site 2 and site 9) in the lattice depends upon the number of oxygen neighbours. From such a curve it is possible to calculate the number of neighbors required to supply a given percentage of the total valence of a specific site. We define *n*(50) and *n*(75) as the number of neighbors required to supply 50% and 75%, respectively, of the total valence of a given A site. These numbers can be extracted from Fig. 5(a) by simple interpolation between the experimental data points, or by solving the equations obtained by nonlinear least squares fitting of the experimental data. Clearly a non-fractional coordination number, such as those derived in this manner, has no real physical significance. This approach does, however, provide a simple one parameter method for describing a range of non-equivalent coordination sites such as are present in this structure.

In Fig. 5(b) we plot *n*(50) and *n*(75) against the fraction of Bi at a given site. It can be seen from this figure that 50% of the valence of a given A site is provided by between 3 and 4 nearest

Table 4 Selected bond lengths (Å) and angles (°) for $Bi_3Ca_9V_{11}O_{41}$

A site	Distances to neighbouring oxygens									
A(1)	2.172(6)	2.261(7)	2.278(6)	2.386(7)	2.677(7)	2.733(7)	2.793(7)	2.919(7)		
A(2)	2.176(6)	2.241(7)	2.245(7)	2.469(6)	2.602(6)	2.791(7)	2.816(7)	3.058(7)		
A(3)	2.291(7)	2.311(7)	2.311(6)	2.412(6)	2.419(6)	2.501(6)	2.874(7)	3.077(7)	3.352(7)	
A(4)	2.234(7)	2.306(6)	2.406(7)	2.427(7)	2.453(7)	2.521(7)	3.080(7)			
A(5)	2.255(7)	2.294(6)	2.355(6)	2.371(6)	2.428(7)	2.442(6)	2.711(7)	3.225(7)	3.308(7)	
A(6)	2.3713(7)	2.399(7)	2.407(7)	2.408(7)	2.513(7)	2.562(7)	2.625(7)	2.640(7)	2.978(7)	
A(7)	2.313(6)	2.357(7)	2.358(6)	2.457(7)	2.490(7)	2.531(7)	2.608(7)	3.048(7)		
A(8)	2.312(7)	2.356(7)	2.365(6)	2.405(7)	2.426(7)	2.471(6)	2.864(8)	3.040(7)		
A(9)	2.329(7)	2.347(7)	2.413(7)	2.420(7)	2.518(7)	2.546(7)	2.554(6)	3.009(8)	3.442(7)	3.468(7)
A(10)	2.322(6)	2.368(6)	2.398(6)	2.403(7)	2.455(7)	2.464(7)	2.591(7)	3.026(8)		
A(11)	2.322(6)	2.340(7)	2.347(7)	2.459(7)	2.479(6)	2.504(6)	2.576(6)	3.058(7)		
A(12)	2.325(6)	2.335(7)	2.373(7)	2.481(6)	2.485(6)	2.492(7)	2.541(6)	3.001(7)		
V(1)	1.681(7)	1.698(7)	1.698(7)	1.811(6)						
V(2)	1.677(7)	1.683(7)	1.710(7)	1.858(6)						
V(3)	1.683(7)	1.712(7)	1.731(7)	1.768(6)						
V(4)	1.679(6)	1.711(7)	1.736(7)	1.737(6)						
V(5)	1.675(7)	1.710(7)	1.722(6)	1.739(6)						
V(6)	1.678(6)	1.703(6)	1.726(6)	1.802(7)						
V(7)	1.700(7)	1.725(6)	1.730(6)	1.749(6)						
V(8)	1.694(7)	1.720 (7	1.748(7)	1.773(7)						
V(9)	1.704(7)	1.719(7)	1.747(6)	1.762(6)						
V(10)	1.661(6)	1.677(7)	1.859(7)	1.897(7)	2.140(7)					
V(11)	1.657(6)	1.685(7)	1.861(6)	1.880(7)	2.139(7)					

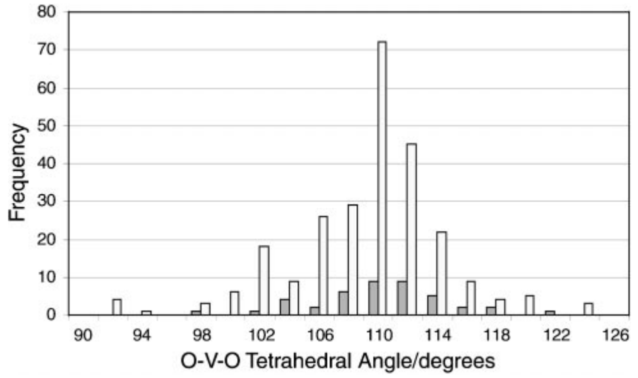

Fig. 2 Distribution of O–V–O tetrahedral angles: light colored bars represent the database entries, dark bars the title compound.

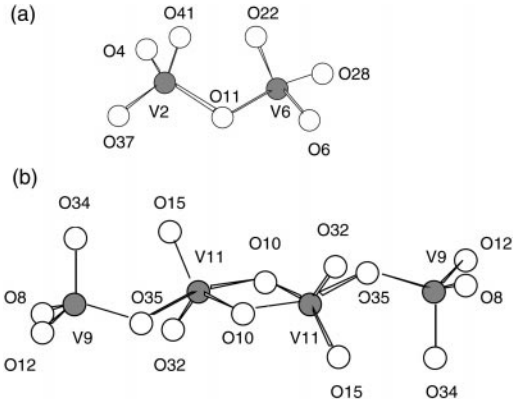

Fig. 3 Oxovanadate groups in $Bi_3Ca_9V_{11}O_{41}$: (a) V_2O_7 group; (b) V_4O_{14} group.

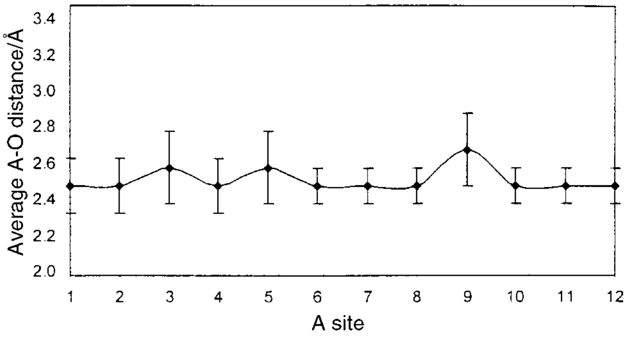

Fig. 4 Average A–O bond lengths for the 12 A sites. Error bars represent the standard deviations of the distances at individual sites.

oxygens; 75% of the valence is provided by between 5 and 6 neighbors. The negative slope of both the $n(50)$ and $n(75)$ plots reveals the preference of Bi for more distorted A sites, that is those containing at least a portion of very short A–O bonds.

This conclusion can be checked against the actual site coordination geometries and bond length data obtained from the structure refinement. Even though the average A–O distance for the twelve sites remains essentially constant, as shown in Fig. 4, details of the coordination environments vary significantly. Sites 1 and 2 are the only two A sites with 4 fairly close oxygen neighbors; the coordination sphere is then completed by 4 more oxygens at much larger distances. They are also the only sites with bonds to oxygen atoms shorter than 2.3 Å. Sites 1 and 2 are the only A sites with Bi occupancy greater than 50%. The distributions of A–O bond lengths for sites with Bi occupancies above and below 50% are shown in Figs. 6(a) and 6(b), respectively. The first distribution ($Bi_{occ} > 50\%$) shows two maxima, one for short and one for

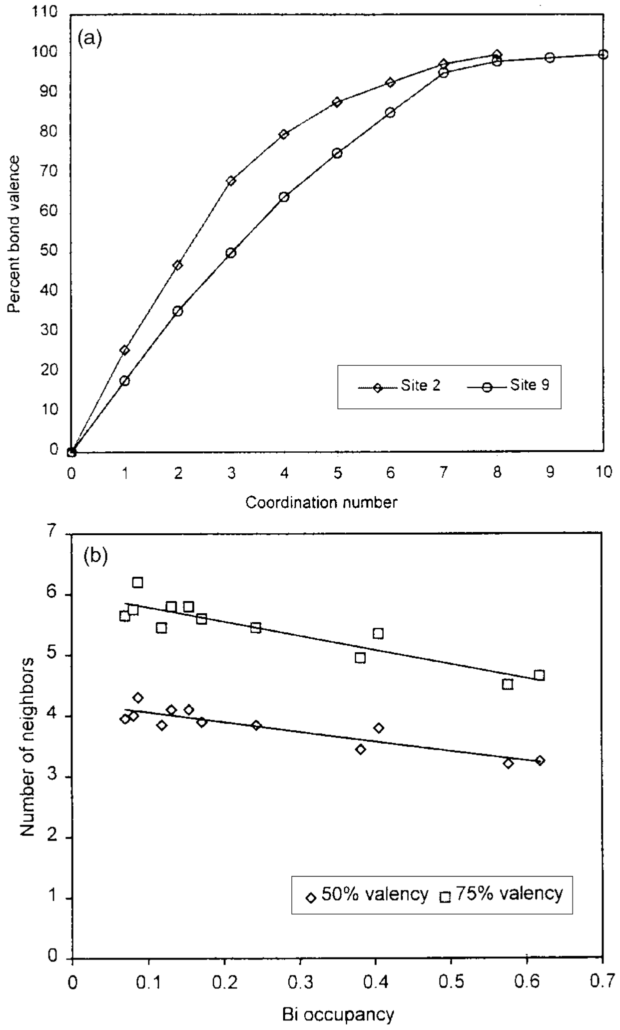

Fig. 5 (a) The dependence of the valence of two A sites on the number of nearest oxygen neighbors (diamonds represent site 2 (Bi rich) and circles represent site 9 (Bi poor)); (b) dependence of $n(50)$ and $n(75)$ on Bi occupancy for each of the 12 A sites in the lattice (see text).

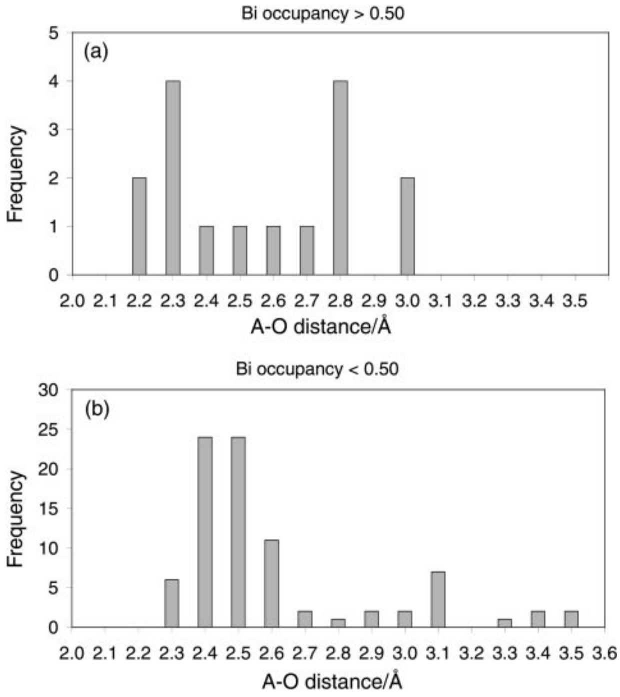

Fig. 6 Distribution of (a) A–O bond lengths for sites with $Bi_{occ} > 50\%$; and (b) A–O bond lengths for sites with $Bi_{occ} < 50\%$.

long A–O bonds. The second distribution ($Bi_{occ} < 50\%$) has one pronounced maximum at intermediate A–O bond lengths.

This analysis supports the conclusion of bond valence considerations that Bi exhibits a preference for more distorted sites with a mixture of short and long bonds to oxygen. This behavior is presumably related to the stereochemical activity of the Bi lone pair.

Conclusion

The present work shows the structural complexities possible in the Bi/Ca/V/O system. $Bi_3Ca_9V_{11}O_{41}$ contains three distinct types of $V_nO_m^{(2m-5n)-}$ polyhedral building blocks, the $V_4O_{14}^{8-}$ group being reported for the first time. This complexity is presumably imparted by both the Bi/Ca site disorder, which leads to non-uniform charge distribution over the 12 A cation sites, and the preference of Bi for structurally less symmetric coordination sites. Clearly the presence of Bi(III) rather than Ca(II) at any individual cation site will cause some local structural distortions, and will influence the geometry of both adjacent V_nO_m groups and the site occupancy of nearby A sites. Such modulations, which are modeled only indirectly in the current work, presumably also influence the stability of $Bi_3Ca_9V_{11}O_{41}$.

Acknowledgements

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References

1 J. Huang, J. S. O. Evans and A. W. Sleight, in preparation.
2 J. Huang and A. W. Sleight, *J. Solid State Chem.*, 1993, **104**, 52.
3 I. Radosavljevic, J. S. O. Evans and A. W. Sleight, *J. Solid State Chem.*, 1998, **137**, 143.
4 J. Boje and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.*, 1993, **619**, 521.
5 J. S. O. Evans and A. W. Sleight, *Int. J. Inorg.Mater.*, 2000, in press.
6 A. W. Sleight and J. Huang, US Patent No. 5202891, 1993.
7 *XPREP*, version 5.00, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1995.
8 *SAINT*, version 5.00, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1995.
9 *SHELX97*, G. M. Sheldrick, University of Goettingen, 1997.
10 *Oxford CRYSTALS*, D. J. Watkin, J. D. Carruthers and P. W. Betteridge, Chemical Crystallography Laboratory, University of Oxford, 1992.
11 Inorganic Crystal Structure Data ICSD, Release 9901, 1999.
12 Prequest and Quest Programs, 3D Search and Research Using the Cambridge Structural Database: F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.
13 R. D. Shannon and C. Calvo, *Can. J. Chem.*, 1973, **51**, 70.
14 L. Permer and Y. Laligant, *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 41.
15 M. T. Casais, E. Gutierrez-Puebla, M. A. Monge and I. Rasines, *J. Solid State Chem.*, 1993, **102**, 261.
16 O. Joubert, A. Jouanneaux and M. Ganne, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1995, **97**, 119.
17 J. Huang and A. W. Sleight, *Mater. Res. Bull.*, 1992, **27**, 581.
18 J. A. Baglio and J. N. Dann, *J. Solid State Chem.*, 1972, **4**, 87.
19 E. E. Sauerbrei, E. Faggiani and C. Calvo, *Acta Crystallogr., Sect. B*, 1974, **30**, 2907.
20 J. Huang and A. W. Sleight, *J. Solid State Chem.*, 1992, **97**, 228.
21 R. Enjalbert and J. Galy, *Acta Crystallogr., Sect. C*, 1986, **42**, 1467.
22 K. Waltersson, B. Forslund, K. A. Wilhelmi, S. Andersson and J. Galy, *Acta Crystallogr., Sect. B*, 1974, **30**, 2644.
23 K. Waltersson and B. Forslund, *Acta Crystallogr., Sect. B*, 1977, **33**, 775.
24 K. Waltersson and B. Forslund, *Acta Crystallogr., Sect. B*, 1977, **33**, 780.
25 F. C. Hawthorne and C. Calvo, *J. Solid State Chem.*, 1977, **22**, 157.
26 F. Marumo, M. Isobe and S. I. Iwani, *Acta Crystallogr., Sect. B*, 1974, **30**, 1628.
27 H. T. Evans, *Z. Kristallogr.*, 1960, **114**, 257.
28 H. T. Evans and A. M. Brusewitz, *Acta Chem. Scand.*, 1994, **48**, 533.
29 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
30 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
31 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **47**, 192.