

Synthesis, Crystal Structure, and Oxide Ion Conductivity in $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$

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A novel bismuth calcium vanadate, $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$, has been synthesized. Its crystal structure has been determined by synchrotron X-ray diffraction. The compound crystallizes in orthorhombic space group $Pnmm$, with cell parameters $a = 11.930(2)$ Å, $b = 16.030(3)$ Å, and $c = 11.500(2)$ Å. The crystal structure can be viewed as consisting of fluorite-like slabs of edge-sharing OA_4 ($\text{A} = \text{Bi}, \text{Ca}$) tetrahedra that extend along the c axis of the crystal and interspersed disordered VO_4 groups. Bi and Ca atoms undergo site disorder, with Bi preferentially occupying locations with low site symmetry and irregular coordination environments. Variable temperature powder diffraction measurements reveal a change in the thermal expansion coefficient of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ above 600 °C and this coincides with the change in conductivity as revealed by a.c. impedance measurements.

Introduction

Bismuth oxide Bi_2O_3 exhibits four polymorphs in its stability range.¹ The high-temperature form, δ - Bi_2O_3 , is one of the best oxide ion conductors known,^{2,3} but it is thermodynamically stable only between 730 and 825 °C. Oxide ion conductors are an important class of materials, as they find applications in oxygen sensors and pumps, membranes for oxygen separation, and electrolyte materials in solid oxide fuel cells.^{4–6} This technologically important aspect has driven a substantial amount of research in the field of inorganic oxides toward finding materials with high oxide ion conductivity at device operating temperatures. The attractive conductivity properties of δ - Bi_2O_3 are associated with its structural features, namely, the simultaneous presence of a highly polarizable cation network and an intrinsically disordered oxide ion sublattice with vacant sites. It has been shown that the structure of δ - Bi_2O_3 can be stabilized down to room temperature by partial substitution of Bi^{3+} by numerous cations. This approach has given rise to the discovery of high oxide ion conductivity in a large number of novel materials.^{7,8}

Experimental Section

Polycrystalline samples of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ were prepared by a solid-state reaction of stoichiometric quantities of Bi_2O_3 (99.999%, Alfa Aesar), CaCO_3 (analytical grade, BDH Chemicals Ltd.), and NH_4VO_3 (99.93%, Alfa Aesar). The mixture was thoroughly ground and heated at 880 °C for 5 days in an alumina crucible. A small quantity of the obtained powder was melted at 1050 °C, cooled to 600 °C at a rate of 3 °C/h, and then furnace-cooled to room temperature, yielding yellow crystals of prismatic habit.

A single crystal of approximate dimensions of $0.05 \times 0.10 \times 0.18$ mm³ was mounted on a glass fiber for data collection. The X-ray diffraction experiment was performed at Station 9.8 of the Synchrotron Radiation Source at Daresbury Laboratory. The data were collected at 100 K on a Bruker AXS SMART three-circle diffractometer with a CCD detector. A wavelength of 0.4901 Å was used to minimize absorption. A hemisphere of data was collected with a frame width of 0.1° and a counting time of 3 s. A multiscan absorption correction⁹ was applied to the raw data and the resulting R_{int} was 2.14%. Frames were integrated using the program SAINT.¹⁰

Variable temperature powder X-ray diffraction data were collected using a Bruker AXS D8 Advance diffractometer equipped with an Anton Paar HTK1200 high-temperature stage. Starting from 30 °C, a data collection was performed every 10 °C up to 800 °C. The heating rate between temperatures was 0.2 °C/s, 2θ range between 10 and 90°, step size 0.0143°, and step time 0.3 s, resulting in a data collection time of 28 min/temperature. A small amount of Al_2O_3 was added to the sample as an internal standard for temperature calibration.

\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5} and details of the single-crystal data collection are given in Table 1.

The conductivity of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ was measured by a.c. impedance. A Schlumberger Solartron 1260 Frequency Re-

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Table 1. Crystallographic Details for $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$

chemical formula	$\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$
molecular weight (amu)	1256.93
crystal system	orthorhombic
space group	$Pnmm$
a (Å)	11.930(2)
b (Å)	16.030(3)
c (Å)	11.500(2)
V (Å ³)	2199.2(3)
Z	8
calculated density (g/cm ⁻³)	7.590
wavelength (Å)	0.4901
temperature (K)	100(1)
μ (mm ⁻¹)	22.12
total number of reflections	7156
number of unique reflections	2268
R_{int} (%)	2.14
number of parameters	186
$\Delta\rho_{\text{min}}$ (e ⁻ /Å ³)	-8.45
$\Delta\rho_{\text{max}}$ (e ⁻ /Å ³)	+5.49
R (%)	7.70
wR (%)	9.10
goodness-of-fit	1.024

sponse Analyser coupled with a 1287 Electrochemical Interface controlled by Z-plot electrochemical impedance software was used over the frequency range 1 MHz to 100 mHz. The pellet was fired at 850 °C for 3 h and then coated with organ-gold pastes electrodes. These were dried at 200 °C and fired at 600 °C for 1 h to form fairly dense gold electrodes before the measurements. Platinum electrodes were not used as too high a final firing temperature would be required. Measurements were performed in laboratory air.

Results

Single-Crystal Structure Determination. Preliminary single-crystal diffraction experiments indicated an orthorhombic unit cell for $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$, with cell parameters of $a \sim 11.9$ Å, $b \sim 16.0$ Å, and $c \sim 11.5$ Å. This cell was recognized as an orthorhombic distortion of a tetragonal cell related to cubic $\delta\text{-Bi}_2\text{O}_3$ by the transformation matrix:

$$\begin{matrix} 3/2 & 3/2 & 0 \\ 0 & 0 & 3 \\ -3/2 & 3/2 & 0 \end{matrix}$$

However, attempts to refine the structure from a starting model obtained by the transformation of the $\delta\text{-Bi}_2\text{O}_3$ structure were not successful due to high correlations of the positional parameters. The structure was instead solved by the Patterson method using the Shelx-97 software suite.¹¹ Fifteen different peaks from the sharpened Patterson map were used as superposition vectors. The residuals for the obtained solutions were calculated by refining the scale factor and the overall temperature factor only and they fell within the $\pm 5\%$ range. The solution with the lowest R factor was selected as a starting model for structure refinement. All structure refinements were performed using the Oxford Crystals suite.¹² Initially, the coordinates and isotropic displacement parameters of the ten Bi atoms in the starting model were refined. Two crystallographically unique vanadium atoms were easily identified from the geometry of the surrounding peaks in the difference Fourier map. The values of the displacement parameters obtained for Bi atoms on a number of sites indicated that they were probably partially occupied by Ca. Consequently, Bi and Ca atoms were disordered over eight crystallographically unique sites (herein

referred to as the A sites) and their occupancies were allowed to refine. A total of 14 oxygen sites were found from difference Fourier maps: 8 that bond to Bi and Ca atoms and 6 that form the VO_4 tetrahedra. A full anisotropic refinement yielded slightly elongated anisotropic displacement parameters for the latter. The two unique VO_4 groups were then refined isotropically and a single subsequent difference Fourier map revealed peaks between the existing oxygen positions. VO_4 groups were therefore split into two statically disordered positions. In the final cycles of refinement, a total of 186 parameters were varied: all coordinates, equated isotropic temperature factors for the disordered VO_4 groups and anisotropic displacement parameters for the rest of the structure, Bi/Ca occupancies of the site disordered positions, an extinction parameter, and a scale factor. The refinement of the A sites occupancies with the restraint that each individual site remain fully occupied, but without any restraints pertaining to the Bi/Ca ratio or the overall charge balance, gave a composition of $\text{Bi}_{4.80(7)}\text{Ca}_{0.95(7)}\text{VO}_{10.5}$. When a charge-balancing restraint was introduced, the formula $\text{Bi}_{4.66(2)}\text{Ca}_{1.09(2)}\text{VO}_{10.5}$ was obtained. All data tabulated herein pertain to the latter model. The structure refinement details and the final agreement factors are summarized in Table 1.

Variable Temperature Powder XRD. The model obtained from single-crystal data was used to carry out Rietveld refinements of the 156 variable temperature powder patterns.¹³ The only structural parameters refined were the cell parameters and an overall temperature factor for $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ and the internal standard Al_2O_3 . The other parameters refined were sample displacement, six background terms, and six terms describing a pseudo-Voigt profile function. Temperature calibration was performed by correcting the obtained thermal expansion data for alumina on the basis of literature values given by Taylor.¹⁴ The plots of the cell parameters of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ as a function of temperature are given in Figure 1. They show that although the individual cell axes behave differently, the overall effect on the cell volume is that it displays two linear regions, with a slight increase in slope just below 650 °C. However, the diffracted intensities do not appear to differ appreciably below and above this temperature, indicating a subtle structural modification that most likely involves oxygen atoms only.

a.c. Impedance Measurement. Two principal features are observed in the complex impedance plane, Z^* , plots, a single flattened semicircular arc and a low-frequency inclined spike (Figure 2). The semicircular arc is associated with a capacitance of about 7 pF cm⁻¹ and is hence consistent with a grain response. The flattening may indicate that a grain boundary contribution is also present; however, it seems more likely that there is a distributed bulk response arising from microstructural features. The low-frequency part of the response in Figure 2 consists of an inclined spike, reminiscent of Warburg-type diffusion. At higher temperatures the

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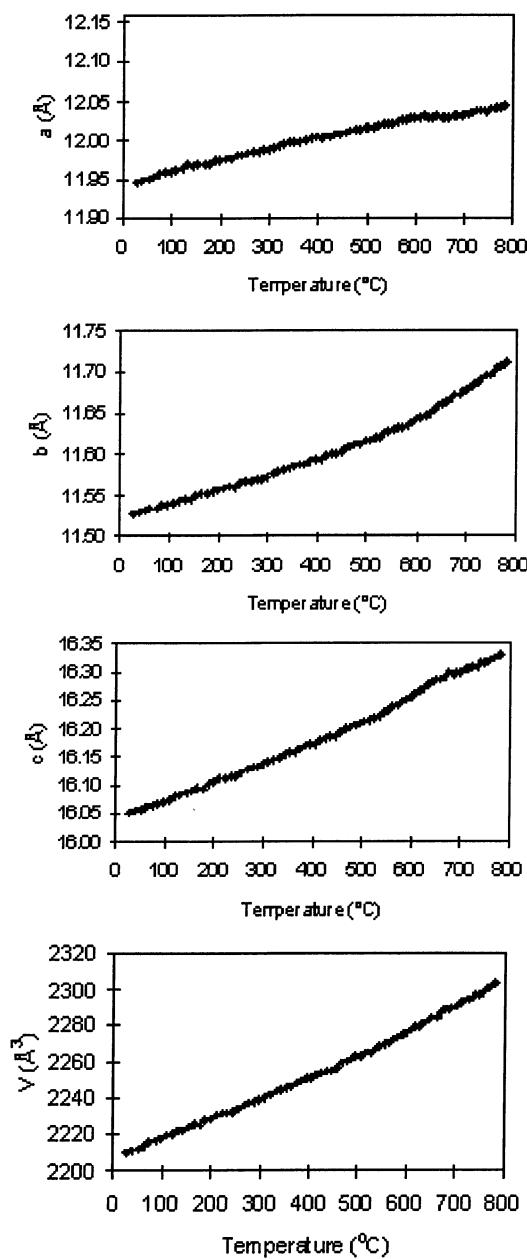


Figure 1. Variation of the a , b , and c axes and the unit cell volume of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ as a function of temperature (°C).

spike curves over, indicating that an electrochemical reaction is taking place at the electrode. Such features strongly indicate that conduction in $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ is predominantly oxide-ionic, as might be expected for such a fluorite-related bismuth oxide. The Arrhenius plot of the total conductivity of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ as a function of temperature is displayed in Figure 3.

Discussion

The obtained positional parameters and displacement parameters for $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ are given in Table 2. All bond lengths and angles are given in the CIF file submitted as Supporting Information. A polyhedral representation of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ is shown in Figure 4. Eight crystallographically unique oxygen atoms are tetrahedrally coordinated by Bi and Ca metals. The pattern of edge-sharing OA_4 ($\text{A} = \text{Bi}, \text{Ca}$) tetrahedra in $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ is very similar to that in $\delta\text{-Bi}_2\text{O}_3$, as

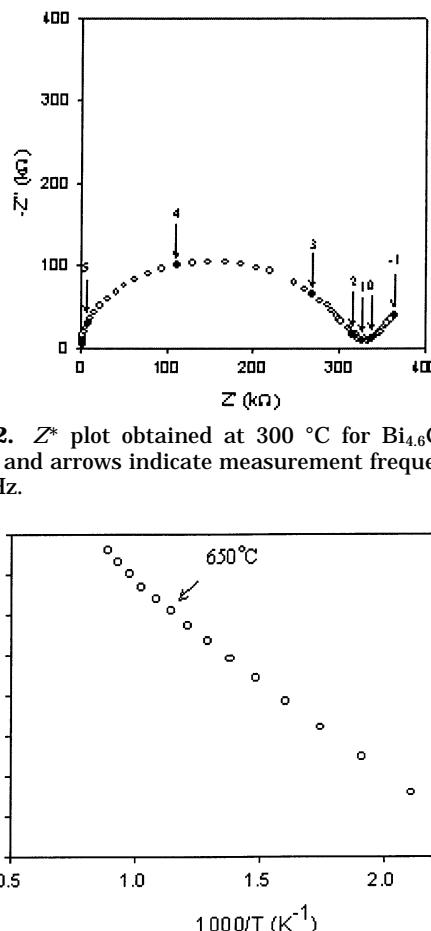


Figure 2. Z^* plot obtained at 300 °C for $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$; numbers and arrows indicate measurement frequency points as $\log f/\text{Hz}$.

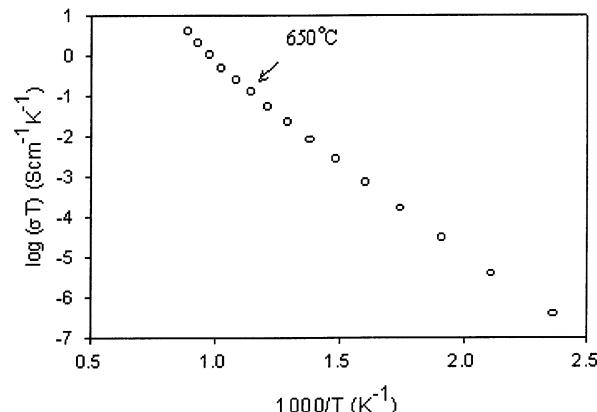


Figure 3. Arrhenius plot of conductivity of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ versus temperature.

shown in parts a and b, respectively, of Figure 5. The three-dimensional connectivity of the tetrahedra found in the parent structure type is broken in $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ due to the existence of disordered VO_4 groups. In this case, the slabs of edge-sharing OA_4 tetrahedra extend along the crystallographic c axis, which corresponds to a face diagonal in cubic $\delta\text{-Bi}_2\text{O}_3$.

The type of fluorite-based supercell exhibited by the title compound has been reported for $\text{Pb}_5\text{Bi}_{18}\text{P}_4\text{O}_{42}$ by Giraud et al.¹⁵ They found that $\text{Pb}_5\text{Bi}_{18}\text{P}_4\text{O}_{42}$ crystallizes in body-centered monoclinic space group $I\bar{2}m$, with cell parameters of $a = 11.885(2)$ Å, $b = 11.540(2)$ Å, $c = 15.636(3)$ Å, and $\beta = 90.23(3)$ °. The formula for both this compound and the title phase can be written as $\text{A}_{23}\text{B}_4\text{O}_{42}$ ($\text{A} = \text{Bi}, \text{Ca}/\text{Pb}, \text{B} = \text{V}/\text{P}$), and given the similarity of their cell parameters, one may expect the two phases to be isostructural. However, Giraud et al. point out that the results of EDAX analysis of $\text{Pb}_5\text{Bi}_{18}\text{P}_4\text{O}_{42}$ were inconclusive and the composition of their sample was deduced from X-ray diffraction. The atomic scattering factors for Bi and Pb are so similar and these two species are known to undergo site disorder, so any stoichiometry determined from X-ray diffraction only should be treated with caution.

The occurrence of Bi/Ca site disorder has been reported in a number of Bi/Ca/V/O phases.^{16–19} The ionic

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Table 2. Atomic Parameters for $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$

atom	x/a	y/b	z/c	$U_{\text{iso,eq}}$	occupancy
Bi(1)	0.81916(8)	0.49828(5)	0.33610(6)	0.0202(1)	1.000(6)
Ca(1)	0.81916(8)	0.49828(5)	0.33610(6)	0.0202(1)	0.000(6)
Bi(2)	0.65582(7)	0.67179(5)	0.16368(6)	0.0169(1)	0.958(5)
Ca(2)	0.65582(7)	0.67179(5)	0.16368(6)	0.0169(1)	0.042(5)
Bi(3)	0.49500(5)	0.83689(4)	0.33962(6)	0.0107(1)	1.000(5)
Ca(3)	0.49500(5)	0.83689(4)	0.33962(6)	0.0107(1)	0.000(5)
Bi(4)	0.34171(6)	0.66694(4)	-0.17865(7)	0.0164(1)	0.981(5)
Ca(4)	0.34171(6)	0.66694(4)	-0.17865(7)	0.0164(1)	0.019(5)
Bi(5)	0.5	0.5	0	0.0310(1)	0.44(1)
Ca(5)	0.5	0.5	0	0.0310(1)	0.56(1)
Bi(6)	0.6653(1)	0.65695(9)	0.5	0.0337(1)	0.832(7)
Ca(6)	0.6653(1)	0.65695(9)	0.5	0.0337(1)	0.168(7)
Bi(7)	0.6492(3)	0.3361(2)	0.5	0.0325(1)	0.291(9)
Ca(7)	0.6492(3)	0.3361(2)	0.5	0.0325(1)	0.709(9)
Bi(8)	0	0	0.1683(3)	0.0252(1)	0.102(9)
Ca(8)	0	0	0.1683(3)	0.0252(1)	0.898(9)
V(9)	0.8112(5)	0.4991(3)	0	0.0199(1)	1
V(10)	0.5118(4)	0.8398(3)	0	0.0193(1)	1
O(1)	0.181(1)	0.0845(9)	0.179(1)	0.0299(2)	1
O(2)	0.746(1)	0.022(1)	0	0.0288(2)	1
O(3)	0.982(2)	0.274(1)	0	0.0349(2)	1
O(4)	0.979(2)	0.092(1)	0	0.0323(2)	1
O(5)	0.138(2)	0.251(1)	0.180(1)	0.0542(2)	1
O(6)	0.798 (2)	0.095(1)	0.194(1)	0.0493(2)	1
O(7)	0.875(2)	0.251(2)	0.204(2)	0.0759(2)	1
O(8)	0.499(1)	0.402(2)	0.163(2)	0.0665(2)	1
O(910)	0.149(4)	0.398(1)	0	0.112(8)	0.5
O(911)	0.082(4)	0.428(3)	0	0.112(8)	0.5
O(920)	0.3327(6)	0.507(4)	0	0.112(8)	0.5
O(921)	0.316(3)	0.450(4)	0	0.112(8)	0.5
O(930)	0.863(3)	0.450(2)	0.1222(7)	0.112(8)	0.5
O(931)	0.821(3)	0.4376(8)	0.1222(7)	0.112(8)	0.5
O(1010)	0.494(5)	0.2674(3)	0	0.112(8)	0.5
O(1011)	0.359(2)	0.208(3)	0	0.112(8)	0.5
O(1020)	0.351(2)	0.128(4)	0	0.112(8)	0.5
O(1021)	0.470(5)	0.0537(6)	0	0.112(8)	0.5
O(1030)	0.554(3)	0.123(2)	0.1221(7)	0.112(8)	0.5
O(1031)	0.562(2)	0.189(2)	0.1221(7)	0.112(8)	0.5

radii of Bi and Ca are very similar (1.17 and 1.14 Å for 6-fold coordination, respectively²⁰), but their bonding preferences are different and present the main factor that determines their distribution over the different A sites in the structure. Data in Table 2 show that Bi atoms fully or almost fully occupy the four general positions among the A sites. These sites have a coordination environment consisting of a mix of short (2.0–2.2 Å) and long (2.6–2.9 Å) oxygen contacts, characteristic of a lone pair cation. On the other hand, metal sites occupied predominantly by Ca (A7 and A8) exhibit a more uniform coordination geometry, with six to seven oxygen atoms at distances between 2.4 and 2.6 Å.

The analysis of variable temperature X-ray powder diffraction data suggests the absence of a major structural phase transition in $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ between room temperature and its melting point. However, a change of slope in the variation of cell volume as a function of temperature occurs just above 600 °C and it corresponds to a change in the linear thermal expansion coefficient from 1.70×10^{-5} 1/K below the critical temperature to 2.16×10^{-5} 1/K above it. The results of the conductivity measurements show that between 600 and 650 °C there is a change of slope in the Arrhenius plots of conductivity as a function of temperature. Calculated activation energies for the conduction process are 0.91(2) eV in the

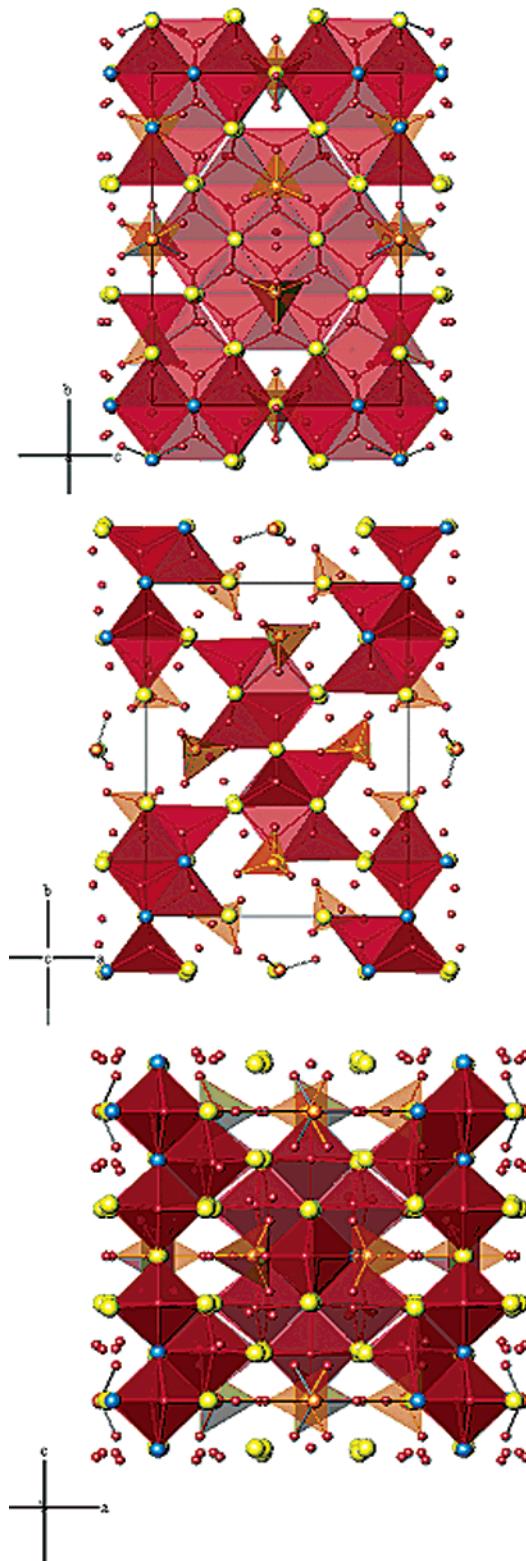


Figure 4. A polyhedral representation of the $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ structure in bc , ab , and ac views: red tetrahedra represent OA_4 groups, light brown tetrahedra represent VO_4 groups (only one set, for clarity), red circles represent oxygen atoms, light brown circles represent vanadium atoms, yellow circles represent sites with majority Bi occupancy, and blue circles represent sites with majority Ca occupancy.

temperature range between 150 and 650 °C and 1.24(1) eV between 650 and 850 °C. The ionic conductivity of $\text{Bi}_{4.6}\text{Ca}_{1.1}\text{VO}_{10.5}$ at 600 °C is 1.47×10^{-4} S/cm, 2

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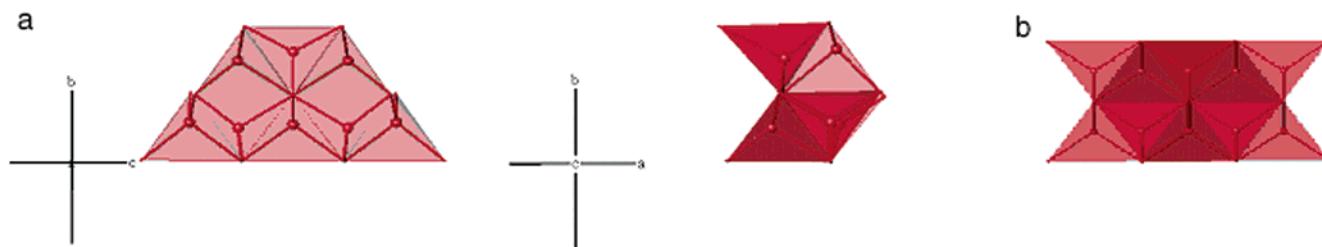


Figure 5. (a) OA₄ tetrahedra edge-sharing pattern in Bi_{4.6}Ca_{1.1}VO_{10.5} viewed perpendicular to the *a* axis and the *c* axis. (b) OBi₄ tetrahedra edge-sharing pattern in δ -Bi₂O₃ viewed perpendicular to the cubic face diagonal.

orders of magnitude smaller than that of YSZ²¹ and comparable to NaBi₃V₂O₁₀.²²

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Supporting Information Available: A crystallographic information file (CIF) file has been submitted as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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