Synthesis, phase stability and electrical characterisation of BINAVOX solid solutions

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The compositional range of '$Bi_4V_2O_{11}$' solid solutions containing Na has been determined by means of a phase diagram study using X-ray diffraction and electron probe microanalysis. The locus of the solid solution indicates that Na replaces V in the crystal structure and the BINAVOX family has the overall formula $Bi_{4+y}V_{2-y-x}Na_xO_{11-y-2x}$. The solid solution limits are temperature dependent and for samples prepared and air-cooled from 830 °C the limits are defined as $0.00 < x < 0.18$ and $0.05 < y < 0.19$. BINAVOX compositions with $x > 0.10$ are thermodynamically unstable below *ca.* 720 °C but can be stabilised kinetically by rapid cooling from temperatures above *ca.* 750 °C. ac Impedance measurements demonstrate that BINAVOX materials are electrically inhomogeneous, exhibit temperature- and time-dependent conductivities and do not offer any significant advantages over the parent solid solution.

The bismuth vanadate, $Bi_{4+y}V_{2-y}O_{11-y}$ has attracted a lot of attention as the parent phase for a family of oxide ion conductors known as BIMEVOX.[1–4] $Bi_{4+y}V_{2-y}O_{11-y}$ is a solid-solution phase whose compositional limits are highly temperature dependent, covering a compositional range from *ca.* $0 < y \leqslant 0.22$ at 880 °C.[5] Three polymorphs are known to exist and the high-temperature γ polymorph exhibits high conductivity mainly due to oxide ions. The explanation for the high conductivity is that the γ polymorph has a layered structure of alternating $Bi_2O_2^{2+}$ and $VO_{3.5}^{2-}$ layers and the perovskite-like layers $VO_{3.5}\square_{0.5}^{2-}$ are oxygen deficient.

Transformation to the β and α polymorphs at lower temperatures results in ordering of the oxygen vacancies and the conductivity decreases markedly. Partial substitution of Cu or Ni for V suppresses the $\gamma \rightarrow \beta/\alpha$ transitions thus stabilising the high-temperature γ polymorph of $Bi_{4+y}V_{2-y}O_{11-y}$, giving conductivities as high as $1 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 240 °C.[1]

The crystal chemistry of $Bi_{4+y}V_{2-y}O_{11-y}$ is still not clearly resolved owing to problems associated with stoichiometry, polymorphism, twinning[6] and incommensurate supercells.[3] Recently, Huve *et al.*[7] reported that the symmetry of the α polymorph depends on the purity of the V_2O_5 employed in the synthesis. High-purity V_2O_5, free from Na/K contamination gave rise to a monoclinic cell, space group *A2/m*, whereas reagents with trace amounts of Na/K result in the commonly reported orthorhombic cell, space group *Amam.*

Despite the complexities associated with the crystal chemistry of $Bi_{4+y}V_{2-y}O_{11-y}$ the number of BINAVOX materials has grown considerably with over seventeen different families being reported. In this paper we describe, for the first time, the BINAVOX family. The solid-solution limits at 830 °C are determined *via* a combination of X-ray diffraction (XRD) results and electron probe microanalysis (EPMA) and the thermal stability and electrical properties of the BINAVOX materials are also discussed. Low levels of Na-doping, *ca.* 3 mol%, are effective for kinetic stabilisation of the γ polymorph on rapid cooling from 830 °C, but these materials are metastable and transform slowly to the α polymorph on post-annealing at, *e.g.* 350 °C. On slow cooling or annealing at *ca.* 650–720 °C for *ca.* 48 h the γ-BINAVOX solid solutions decompose into a three-phase mixture containing α-BINAVOX. ac Impedance spectroscopy measurements show the bulk conductivity behaviour of BINAVOX materials to be electrically inhomogeneous and very dependent on thermal history.

Experimental

Bi_2O_3 (99.99%), V_2O_5 (99.6%) and Na_2CO_3 (99.99%) reagents were dried at 300 °C overnight and stored in a desiccator prior to use. Reaction mixtures totalling 3–4 g were weighed and mixed into a paste with acetone using an agate mortar and pestle. In order to limit volatilisation of the reagents, approximately two thirds of the powder for each sample was cold-pressed into pellets, placed in Au foil boats and covered with the remaining powder. A heating sequence of 500 °C for 2 h, 650 °C for 2 h, 800 °C for 12 h, regrinding and repelletising, then 750 °C for 2 h and 830 °C for 12 h was found to be adequate to obtain equilibrium. Pellets for EPMA and ac impedance measurements were cold-pressed, covered with powder of similar composition and sintered at 830 °C for a further 12 h.

Phase purity was determined by X-ray diffraction using a Hagg Guinier camera or a Stoe-Stadi diffractometer using Cu-Kα_1 radiation. The final composition of the BiNaVOX materials was determined using a Cameca SX51 electron microprobe analyser with an incident beam energy of 20 kV and a current of 50 nA. All samples were polished to $< 1\ \mu m$ and carbon coated. The standards used were Bi_2CuO_4 for Bi-Lα, V_2O_5 for V-Kα and $NaAlSi_3O_8$ for Na-Kα. Oxygen was calculated by stoichiometry. ac Impedance measurements from *ca.* 25 to 800 °C were conducted using a Hewlett Packard 4192A impedance analyser over the frequency range 5 Hz–5 MHz with an applied voltage of 100 mV. Electrodes were fabricated from Pt organopaste; electroded pellets were fired at 800 °C overnight to decompose the paste and harden the Pt residue. Pellets were attached to the Pt measuring leads of a conductivity jig and placed in a horizontal tube furnace whose temperature was controlled and measured within ±3 °C.

Results and Discussion

The compositions studied have general formula $Bi_{4+y}V_{2-y-x}Na_xO_{11-y-2x}$. Although XRD was adequate to determine whether any given composition was single phase, EPMA was employed to determine the final composition(s) of the phases present in selected samples. Combining both sets of results enabled the solid-solution area at 830 °C in air to be determined, as shown on the composition triangle Bi_2O_3–Na_2O–V_2O_5 in Fig. 1. Closed circles represent the final compositions of single-phase BiNaVOX samples, half-filled circles represent the starting composition of samples which were determined to be phase mixtures and filled triangles represent the final composition of the BINAVOX phase within phase mixtures (half-filled circles). EPMA established that there were no significant problems associated with volatility of the reagents. For example, a sample of nominal starting

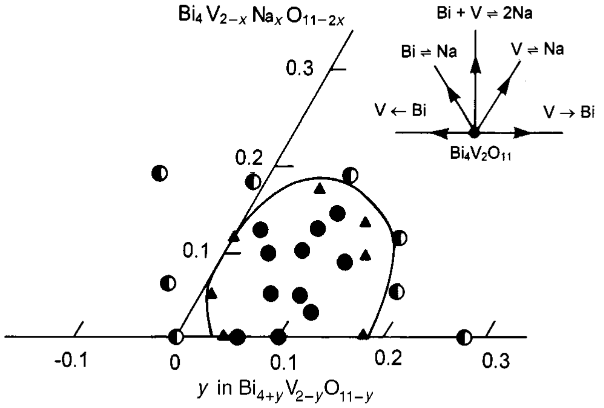

Fig. 1 Compositional extent of BINAVOX by EPMA for samples prepared and air-cooled from 830 °C. Closed circles represent phase-pure compositions, half-filled circles represent phase mixtures and closed triangles represent the composition of BINAVOX in phase mixtures. The inset shows the loci of solid solutions for different substitution mechanisms.

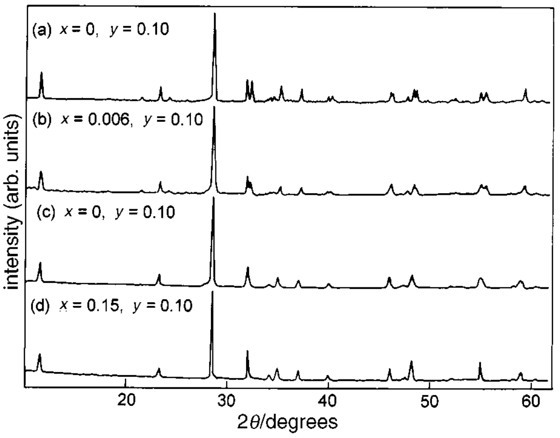

Fig. 2 X-Ray diffractograms of $Bi_{4+y}V_{2-x-y}Na_yO_{11-x-2y}$ solid solutions prepared and air-cooled from 830 °C

composition, $Bi_{4.08}V_{1.77}Na_{0.15}O_{10.62}$ was analysed to have a final composition of $Bi_{4.10(2)}V_{1.76(2)}Na_{0.15(2)}O_{\delta}$. The results clearly indicate that Na has been incorporated into the crystal lattice and that the solid-solution limits can be defined as $0<x<0.18$ and $0.05<y<0.19$ for samples prepared and air-cooled from 830 °C.

Several interesting features emerge from the results. First, phase-pure, stoichiometric $Bi_4V_2O_{11}$ ($y=0$) cannot be prepared in air at 830 °C. The parent phase of the sample with the stoichiometric composition, $y=0$, was found by EPMA to be Bi-rich with $y=0.05$ and trace amounts of a secondary phase $BiVO_4$ were detected. This confirms the work of Lee *et al.*[4] who established that excess Bi is always required to prepare single-phase $Bi_{4+y}V_{2-y}O_{11-y}$ below *ca.* 850 °C.

Secondly, on the basis of the solid solution locus, Fig. 1, the phase diagram results suggest that Na is predominantly incorporated onto V rather than Bi sites within the crystal lattice. There is considerable disorder in the coordination of oxygen ions around the V-sites within the lattice and the possibility exists that the large Na ions are located in distorted tetrahedral sites within the perovskite-like layers. Nevertheless, this result is rather surprising given the large difference in ionic radii of V^{5+} and Na, 0.54 and 1.13 Å,[8] respectively and needs confirmation by crystallographic studies. The low solubility limit of Na in $Bi_{4+y}V_{2-y}O_{11-y}$ makes it is difficult to use the phase diagram to establish the precise substitution mechanism, however, it is clear that the BINAVOX phase diagram differs significantly from those obtained with other large dopant cations such as Sr^{2+} and Pb^{2+}. Such diagrams[9] show extensive solid solutions extending in the $-y$ direction, inferring that large divalent cations substitute onto the Bi sites.

The α and γ polymorphs can usually be distinguished by XRD in the range 2θ 31–33°. The presence of a doublet at *ca.* 32° is ascribed to (020) and (200) reflections of the lower symmetry, orthorhombic α polymorph whereas a singlet at *ca.* 32.5° is assigned to the (110) reflection of the higher symmetry, tetragonal γ polymorph. For samples with $y=0.1$, it is clear from XRD that increasing the Na content (x value) is effective in stabilising the γ polymorph on air-cooling from 830 °C, as shown by the convergence of the (020)–(200) doublet at *ca.* 31–33° for $x=0$, Fig. 2(a), into a singlet for $x=0.15$, Fig. 2(d).

In general, samples with high x values could be satisfactorily indexed as γ polymorphs and the unit cell expands in the c direction compared with undoped materials. For example, the lattice parameters of γ-$Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ ($x=0.15$ and $y=0.1$) are $a=3.941(9)$ and $c=15.349(5)$ Å, compared with $a=5.518(2)$, $b=5.593(2)$ and $c=15.239(5)$ Å for α-$Bi_{4.10(2)}V_{1.90(2)}O_{10.90}$ ($x=0$, $y=0.1$). This is consistent with the suggested substitution mechanism of replacing small V ions by larger Na ions. Compositions with $0.05<x<0.15$ could not be indexed satisfactorily on any single polymorph, owing to variations in peak intensities and problems associated with peak convergence/asymmetry, such as shown for the doublet at *ca.* 32° for $x=0.06$ and 0.10, Fig. 2(b) and (c), respectively. Compositions with $x \leqslant 0.05$ indexed as α polymorphs and differential thermal analysis (DTA) showed the presence of an exotherm at *ca.* 450 °C on heating and an endotherm at *ca.* 350 °C on cooling, consistent with a reversible $\alpha \rightleftharpoons \gamma$ transition. No thermal event was detected by DTA between 25 and 700 °C for samples with $x>0.05$. These results indicate a gradual change in polymorphism from α to γ on increasing x.

XRD patterns obtained for BINAVOX solid solutions with intermediate values of x, *ca.* $0.05<x<0.15$ depend on thermal history, as shown for $Bi_{4.13(2)}V_{1.78(2)}Na_{0.09(2)}O_{10.69}$ ($x=0.13$, $y=0.09$) in Fig. 3. Rapid cooling from elevated temperatures enables the γ polymorph to be 'preserved' at *ca.* 25 °C, as shown by the single peak at *ca.* 32°, Fig. 3(a). Annealing the same sample for 5 days at 350 °C leads to a clear doublet at *ca.* 31–33°, Fig. 3(b), consistent with the existence of the α polymorph. No change in phase assemblage was detected by EPMA for any BINAVOX material prepared at 830 °C and subsequently annealed below *ca.* 600 °C. These results clearly demonstrate that the γ polymorph of BINAVOX materials with $x>0.05$ in samples quenched from high temperature transform to the more stable α polymorph on low-temperature annealing, typically at *ca.* 350 °C. Without undertaking extensive crystallographic studies on samples subjected to a variety of heat treatments, it is difficult to determine whether the change from α to γ on increasing x is continuous or if a two-phase region exists at intermediate x which separates α and γ regions at low and high x values, respectively.

The above comments on polymorphism refer to materials

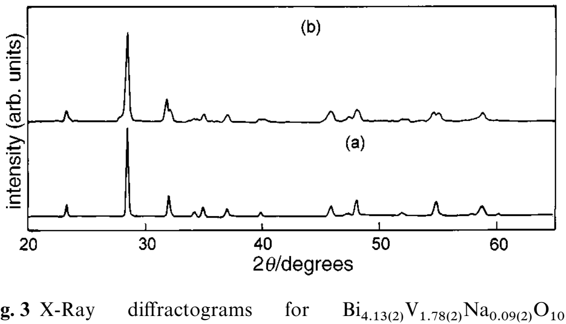

Fig. 3 X-Ray diffractograms for $Bi_{4.13(2)}V_{1.78(2)}Na_{0.09(2)}O_{10.69}$ quenched from 850 °C (a) and post-annealed for five days at 350 °C (b)

quenched from high temperature and subsequently annealed at relatively low temperature, 350 °C. At intermediate temperatures, different behaviour occurs.

Unlike many other BIMEVOX families, γ-BINAVOX solid solutions with $x > 0.10$ decompose on annealing between 650 and 720 °C into a mixture of phases containing α-BINAVOX of low x values. XRD results for $Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ ($x = 0.15$) quenched onto a brass block from 830 °C, Fig. 4(a), and annealed at 650 °C for 72 h, Fig. 4(b), clearly demonstrate a mixture of α-BINAVOX and peaks associated with secondary phases.

EPMA revealed the presence of three phases in the decomposed sample as shown by the back-scattered image in Fig. 5. Table 1 lists the atom% of Bi, V and Na for the single-phase γ polymorph and for the decomposition products including α-BiNAVOX. It is clear that Na is exsolved from γ-$Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ on annealing at 650–720 °C to form a phase mixture including α-$Bi_{4.02(5)}V_{1.88(4)}Na_{0.10(4)}O_{10.78}$. Good quality analysis of the impurity phases was restricted because of their small grain size, Fig. 5, however, both are Bi-rich with respect to the BINAVOX materials. Further details of these phases are discussed elsewhere.[10]

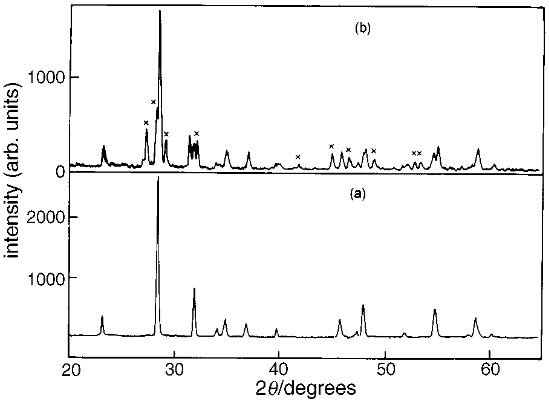

Fig. 4 X-Ray diffractograms for $Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ quenched from 830 °C (a) and post-annealed at 650 °C for 72 h (b). × indicate unindexed peaks associated with secondary phases.

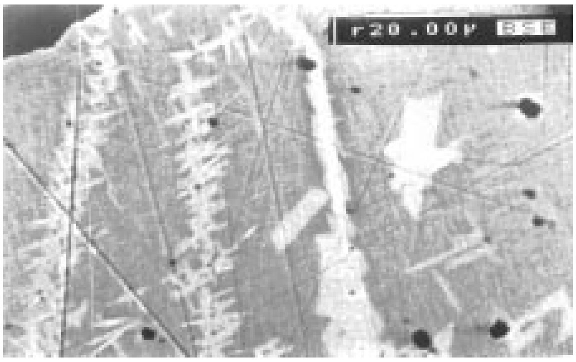

Fig. 5 A back-scattered electron image of the composition $Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ after being annealed at 650 °C for 72 h. Dark regions are α-$Bi_{4.02(2)}V_{1.88(2)}Na_{0.10(2)}O_{10.78}$; grey and white regions are the minor phases 1 and 2, respectively.

Table 1 Composition analysis (atom%) before and after the decomposition of a γ-BINAVOX solid solution at 650 °C[a]

	before decomposition		after decomposition			
	γ-BINAVOX		α-BINAVOX		minor 1	minor 2
element	av.	σ	av.	σ	av.	av.
Bi	24.68	0.07	23.98	0.25	25.63	26.87
V	10.56	0.04	11.20	0.18	9.75	9.35
Na	0.89	0.05	0.56	0.04	1.20	0.06
O	63.87	0.03	64.26	0.08	63.42	63.71

[a] atom% shown here is normalised to give total % = 100. Actual total mass% was 99.64 and 100.83 for the γ- and α-BINAVOX phases, respectively. Data of ten points were averaged in determining the composition of the BINAVOX phases; σ is standard deviation.

The decomposition of BINAVOX materials with $x > 0.10$ takes place only over a narrow temperature range, *ca.* 650–720 °C and is fully reversible: reheating above *ca.* 720 °C for 1 h results in reformation of single-phase BINAVOX. This suggests that BINAVOX materials with $x > 0.10$ are thermodynamically stable only above *ca.* 720 °C but may be preserved to room temperature, where they are kinetically stable, by rapid cooling. BINAVOX materials with $x < 0.10$ did not decompose on prolonged annealing between *ca.* 650 and 720 °C, suggesting that α-BINAVOX materials are thermodynamically stable under the conditions tested. Given the obvious complexity associated with stability and polymorphism in the BINAVOX system, we chose not to indicate the polymorphs on the phase diagram, Fig. 1 and stress that this diagram is relevant only for materials which have been air-cooled from 830 °C. Like many other BIMEVOX systems, the BINAVOX solid solution limits are highly temperature dependent with the maximum solubility in the γ polymorph occurring close to melting temperatures.

Three types of conductivity data set were collected for the BINAVOX solid solutions; (i) above 720 °C where all samples were thermodynamically stable γ polymorphs, (ii) between *ca.* 150 and 650 °C for samples air-cooled from 800 °C, and (iii) as a function of time at *ca.* 250 °C for samples quenched from 800 °C.

In general, impedance plane plots below 400 °C consist of a single, semicircular arc and a low-frequency 'spike'. There was no evidence of a grain boundary arc and the low-frequency effects are attributable to ionic polarisation and diffusion-limited phenomena at the electrode and support the idea that conduction is mainly by means of ions. The inclined spike is similar to that expected for a Warburg impedance with an ideal slope of 45°.

(i) Conductivity data above 720 °C

Total conductivities for single-phase BINAVOX solid solutions were extracted from the inverse of the low-frequency intercept of the electrode spike with the real axis of impedance plane plots at 725, 750, 775 and 800 °C. The results demonstrated that all single-phase compositions had similar but slightly lower conductivity values and similar activation energies to the γ polymorph in undoped materials, as shown for a variety of compositions in Fig. 6. Thus, Na-doping does not enhance the high-temperature conductivity of γ-$Bi_{4+y}V_{2-y}O_{11-y}$ materials.

(ii) Conductivity data between 150 and 650 °C

The conductivity changes irreversibly on thermal cycling between 150 and 600 °C, Fig. 7. The high conductivity values obtained below *ca.* 400 °C on the initial heating cycle of γ-BINAVOX materials are not reproduced on subsequent cooling and reheating. Given the metastable nature of BINAVOX materials with $x > 0.10$ and the tendency to transform from the γ to the α polymorph at 350 °C, as shown by the XRD results in Fig. 3, it is not surprising that conductivities depend on thermal treatment.

Conductivities of $Bi_{4.13(2)}V_{1.78(2)}Na_{0.09(2)}O_{10.69}$ and γ-$Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ are shown in Fig. 7 (conductivities for undoped α-$Bi_{4.06(2)}V_{1.94(2)}O_{10.94}$ are indicated as a dotted line for comparison). It is clear from the Arrhenius plots in Fig. 7 that the samples have similar conductivities and acti-

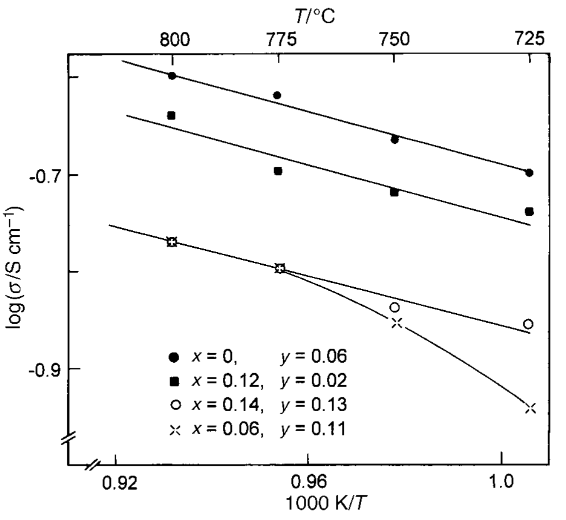

Fig. 6 Arrhenius plots for various BINAVOX materials above 725 °C

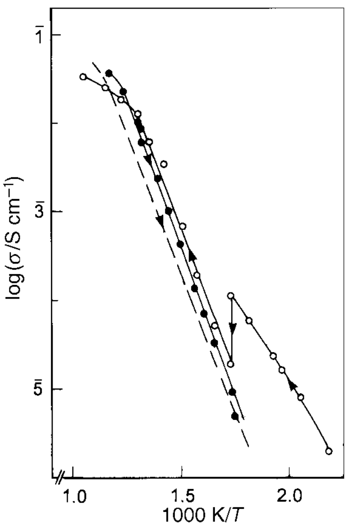

Fig. 7 Arrhenius plots for various BINAVOX materials over the temperature range 150 to 650 °C (–, cooling cycle: $x=0$, $y=0.06$; ●, cooling cycle: $x=0.09$, $y=0.13$; ○, initial heating cycle: $x=0.15$, $y=0.10$)

vation energies over the temperature range *ca.* 320–650 °C. Similar results were obtained for all single-phase BINAVOX compositions.

Initial heating-cycle data for γ-$Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ below 300 °C demonstrate a characteristic feature of BINAVOX materials with $x>0.10$, namely enhanced, low-temperature conductivity values which are time dependent and irreproducible on thermal cycling. For ac impedance measurements, samples are allowed to equilibrate for *ca.* 1 h between successive temperatures and are therefore maintained at elevated temperatures for long periods during thermal cycling. The conductivity of γ-$Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ below *ca.* 300 °C was over an order of magnitude higher on the initial heating cycle compared with that on any subsequent heating or cooling cycle and at 305 °C on the initial heating cycle decreased from 0.11 to 0.018 mS cm^{-1} overnight, *ca.* 12 h, Fig. 7. This time dependent decrease is clearly associated with the metastable nature of these materials and is probably associated with their tendency to undergo oxygen re-ordering at low temperatures. In order to further investigate this phenomenon, samples were rapidly quenched from 800 °C and variations in the bulk conductivity monitored as a function of time at *ca.* 250 °C.

(iii) Conductivity data at *ca.* 250 °C for samples quenched from 800 °C

The bulk conductivity at *ca.* 250 °C for a pellet of γ-$Bi_{4.10(2)}V_{1.81(2)}Na_{0.15(2)}O_{10.60}$ which had been rapidly quenched from 800 °C was extracted from the inverse of the low-frequency intercept of the asymmetric semicircular arc on the real axis of impedance plane plots, Fig. 8. The associated capacitance of the arc was calculated to be 33 pF cm^{-1} using the relationship $\omega RC=1$ (where $\omega=2\pi f$ and is the angular frequency) at the arc maximum and is consistent with a bulk or intragranular response. The bulk arc resistivity increased as a function of time and Fig. 9 shows the smooth decrease in bulk conductivity from 20 to 4.5 μS cm^{-1} over a period of *ca.* 150 h. Conductivity measurements are clearly very sensitive to oxygen ordering as the highly conducting metastable γ polymorph transforms, albeit rather slowly, to the α polymorph. This decrease in conductivity is consistent with the observed line broadening/splitting in XRD patterns when annealing rapidly quenched γ-BINAVOX materials at moderate temperatures, as shown in Fig. 3 for $Bi_{4.13(2)}V_{1.78(2)}Na_{0.09(2)}O_{10.69}$.

In order to further investigate the bulk conductivity characteristics of BINAVOX materials, ac impedance data were replotted in the form of combined spectroscopic plots of the imaginary components of the complex impedance and electric modulus formalisms, Z'' and M'', respectively. Such plots are well established for probing the electrical homogeneity of many electroceramics[11] and reveal that the bulk characteristics of BINAVOX materials are inhomogeneous. Fig. 10 shows a

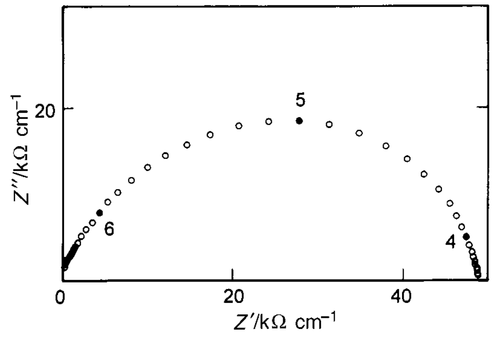

Fig. 8 Complex impedance plane plot for $Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ quenched from 800 °C and annealed at 253 °C for 143 h. Closed circles identify selected frequencies on a logarithmic scale, *e.g.* $5=10^5$ Hz.

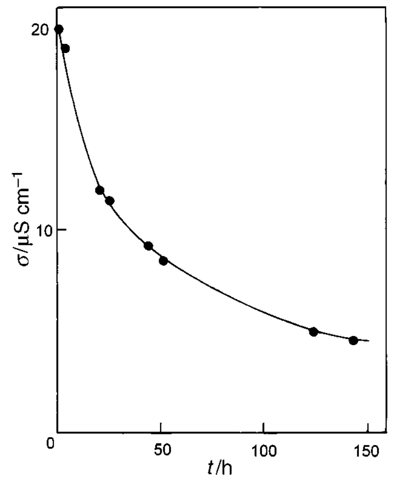

Fig. 9 Variation in conductivity as a function of time for $Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ quenched from 800 °C and annealed at *ca.* 250 °C

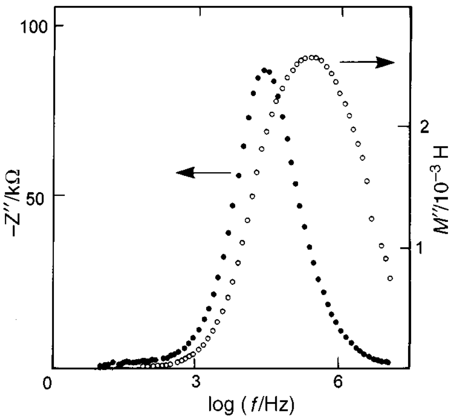

Fig. 10 A combined Z'' and M'' spectroscopic plot for $Bi_{4.10(2)}V_{1.75(2)}Na_{0.15(2)}O_{10.60}$ quenched from 800 °C and annealed at 253 °C for 143 h

combined Z'' and M'' plot for γ-$Bi_{4.10(2)}V_{1.81}Na_{0.15}O_{10.60}$ after *ca.* 143 h at 250 °C on quenching from 800 °C. For an ideal Debye response, the frequency maxima of Z'' and M'' peaks should be coincident and the half-height peak widths 1.14 decades on a log(f) scale. Although it is not uncommon for the f_{max} values of Z'' and M'' to be separated by up to one order of magnitude in good solid electrolytes such as Na-β-Al_2O_3 [12] it can clearly be seen that the M'' peak is exceptionally broad, with a half-height peak width of *ca.* 2.56 decades on a log(f) scale. Such a response could be associated with the metastability of the BINAVOX materials as they transform from the disordered γ to the ordered α polymorph on low-temperature annealing or it may be associated with the intrinsic, anisotropic nature of the conduction properties of BIMEVOX materials, as shown in single-crystal studies.[13] Further studies are in progress to clarify the origin of the extremely broad M'' spectra but such plots clearly show the bulk conductivity characteristics in these materials to be complex and inhomogeneous.

In conclusion, although Na can be incorporated into the $Bi_{4+y}V_{2-y}O_{11-y}$ lattice the BINAVOX family exhibit complex thermal stability behaviour and are unsuitable for producing stable, high oxide-ion conducting materials for practical applications.

The authors would like to thank the University of Aberdeen for an M.Sc. studentship for C.J.W., EPSRC for financial support for the EPMA facility and Professor Tony West for helpful discussions.

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Paper 7/03629I; *Received* 27*th May*, 1997