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$NaBi_3V_2O_{10}$: a new oxide ion conductor

Derek C. Sinclair, Craig J. Watson, R. Alan Howie, Janet M. S. Skakle, Alison M. Coats, Caroline A. Kirk, Eric E. Lachowski and James Marr

Chemistry Department, University of Aberdeen, Meston Walk, Aberdeen, UK, AB24 3UE

The new phase $NaBi_3V_2O_{10}$ is reported; it was synthesised by oxide reaction at 600 °C and is triclinic with $a = 7.2026(10)$, $b = 7.0600(9)$, $c = 5.5312(6)$ Å, $\alpha = 84.542(12)$, $\beta = 113.318(11)$ and $\gamma = 112.267(12)°$; it is an oxide ion conductor with conductivity of *ca.* 1.5 mS cm^{-1} at 675 °C.

Yttria-stabilised zirconia (YSZ) is commonly employed as a solid electrolyte in many technological applications such as solid oxide fuel cells and oxygen pumps.[1] Although YSZ is an excellent solid electrolyte there remains much interest, from both a fundamental and an industrial view point, in trying to find new oxide ion conductors[2,3] which have superior electrical properties compared with YSZ. Over the last eight years, there has been considerable interest in doped $Bi_{4+y}V_{2-y}O_{11-y}$ solid solutions[4,5] known by the acronym BIMEVOX, where ME corresponds to the dopant ion, owing to their high oxide ion conductivity. During a phase diagram study of the compositional range of BINAVOX solid solutions[6] within the Na_2O–Bi_2O_3–V_2O_5 ternary system, we discovered a new phase, whose composition was determined *via* electron probe microanalysis (EPMA) to be $NaBi_3V_2O_{10}$.[7] Here, we report the synthesis of this new phase, a fully indexed X-ray pattern based on a primitive, triclinic cell and preliminary conductivity data that suggests $NaBi_3V_2O_{10}$ is an oxide ion conductor.

$NaBi_3V_2O_{10}$ was prepared by conventional solid state synthesis. 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. A reaction mixture of stoichiometry $NaBi_3V_2O_{10}$ totalling 3–4 g was weighed from the starting reagents and mixed into a paste with acetone using an agate mortar and pestle, dried and fired in Au foil boats. A combination of X-ray powder diffraction (XRD) data and EPMA results showed that a single phase yellow powder could be prepared by heating the reaction mixture at 600 °C for 24 h, with an intermediate regrind after 12 h. EPMA analysis showed that there was no evidence of any secondary or unreacted phases on a micrometre scale. Quantitative EPMA analysis on twenty seven points of a sintered pellet determined the composition to be 15.9 mol% Na_2O, 33.6 mol% V_2O_5 and 50.5 mol% Bi_2O_3 which is in good agreement with the starting composition of $NaBi_3V_2O_{10}$.

On heating above *ca.* 700 °C, the yellow powder became brown and extra reflections associated with a secondary phase appeared in the XRD patterns. The reaction mixture melted at *ca.* 755 °C and formed a purple–brown coloured solid on cooling. XRD analysis showed the minor phase in powders heated above 700 °C and the major phase cooled from the melt to be a γ-polymorph of the BINAVOX solid solution. Detailed phase studies are currently in progress and will be reported elsewhere.

The program VISSER[8] was used in an attempt to index the XRD pattern of $NaBi_3V_2O_{10}$; results suggested that the most probable solution was a primitive triclinic cell, which was refined to give a unit cell, $a = 7.2026(10)$, $b = 7.0600(9)$, $c = 5.5312(6)$ Å, $\alpha = 84.542(12)$, $\beta = 113.318(11)$ and $\gamma = 112.267(12)°$. Table 1 shows the first thirty lines of the indexed powder pattern. Given that the volume of an oxygen ion can be estimated as *ca.* 22 Å^3, the cell volume of 238.53(4) Å^3 is in good agreement with that expected for the proposed formula with $Z = 1$, giving support to the suggested unit cell. In addition, selected area electron diffraction (SAED) studies have also been found to be consistent the unit cell proposed by the VISSER program.

Differential thermal analysis showed the presence of a large endotherm at 575 °C on heating which was fully reversible on thermal cycling, suggesting $NaBi_3V_2O_{10}$ undergoes a polymorphic phase transition at this temperature. Although this has been confirmed by high temperature XRD, as yet, we have no information on the symmetry or crystal structure of the high temperature polymorph.

ac Impedance measurements on a pellet sintered at 675 °C and coated with Au paste electrodes were collected on both heating and cooling in air between 25–675 °C. Complex impedance plane, Z^*, plots consisted of a single, semi-circular arc and a low frequency electrode 'spike', as shown in Fig. 1. The associated capacitance of the arc was calculated to be *ca.* 3–5 pF cm^{-1} using the relationship $\omega RC = 1$ (where $\omega = 2\pi f$ and is the angular frequency) at the arc maximum. This capacitance

Table 1 Indexed X-ray diffraction pattern for triclinic $NaBi_3V_2O_{10}$ with $a = 7.2026(10)$, $b = 7.0600(9)$, $c = 5.5312(6)$ Å, $\alpha = 84.542(12)$, $\beta = 113.318(11)$ and $\gamma = 112.267(12)$, $V = 238.53(4)$ Å^3. A full listing (101 lines) is available from the authors on request

d_{obs}	d_{calc}	h	k	l	I/I_0	$\Delta(2\theta)$
6.5256	6.5199	0	1	0	15.3	−0.0119
6.1454	6.1361	1	0	0	72.4	−0.0220
5.6451	5.6415	−1	1	0	19.5	−0.0103
5.0719	5.0688	0	0	1	14.6	−0.0105
4.9816	4.9773	−1	0	1	22.6	−0.0156
4.5150	4.5113	−1	1	1	9.5	−0.0162
4.1327	4.1332	0	−1	1	29.2	0.0025
3.8844	3.8821	0	1	1	1.1	−0.0139
3.8137	3.8139	1	1	0	9.1	0.0013
3.5657	3.5659	−1	−1	1	8.7	0.0008
3.4631	3.4641	−1	2	0	6.8	0.0078
3.4278	3.4293	−2	1	1	22.6	0.0109
3.3195	3.3224	1	0	1	96.7	0.0235
3.2867	3.2891	−2	1	0	29.2	0.0203
3.2479	3.2456	−2	0	1	100.0	−0.0197
3.0836	3.0867	−1	2	1	71.1	0.0298
3.0650	3.0681	2	0	0	9.2	0.0300
2.8577	2.8607	−2	2	1	15.7	0.0338
2.8180	2.8207	−2	2	0	86.5	0.0309
2.7531	2.7523	−1	0	2	41.8	−0.0100
2.7041	2.7048	1	1	1	12.7	0.0090
2.6775	2.6769	1	−2	1	18.6	−0.0074
2.6268	2.6289	−1	1	2	15.9	0.0285
2.5671	2.5660	−2	−1	1	2.1	−0.0152
2.5326	2.5344	0	0	2	19.3	0.0266
2.5133	2.5159	1	2	0	36.8	0.0386
2.4877	2.4886	−2	0	2	5.2	0.0149
2.4458	2.4464	2	1	0	17.5	0.0101
2.3952	2.3969	−3	1	1	5.2	0.0286

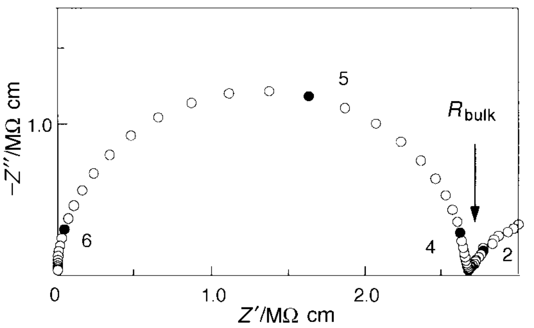

Fig. 1 Z^* plot for $NaBi_3V_2O_{10}$ in air at 505 °C. Selected frequencies in filled circles are identified by the logarithm of the frequency, *e.g.* $2 = 10^2$ Hz.

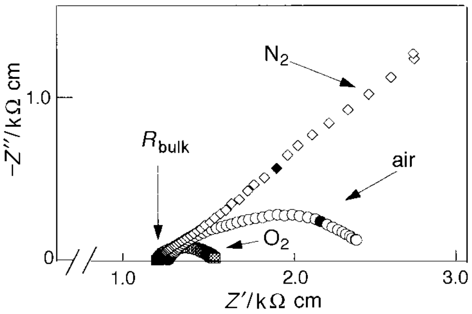

Fig. 2 Z^* plots for $NaBi_3V_2O_{10}$ in various atmospheres at 650 °C. 0.3 Hz is identified by the filled symbol in N_2 and air data.

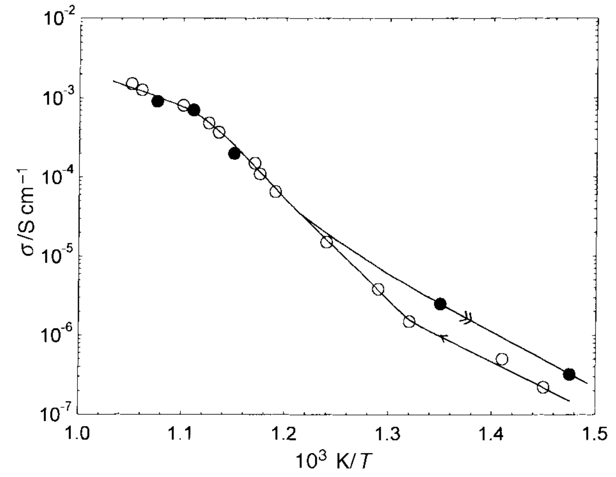

Fig. 3 Arrhenius plot of the bulk conductivity in air. Open and closed circles represent heating and cooling data, respectively.

value was temperature independent over the measured range and is consistent with a bulk or intra-granular response.

The presence of a low frequency spike with an associated capacitance of 1–5 μF in Fig. 1 is attributable to ionic polarisation and diffusion-limited phenomena at the electrode and supports the idea that the conduction is mainly by means of ions. At higher temperatures in air, *ca.* 600 °C, the low frequency response consists of a broad semi-circular arc with an associated capacitance of *ca.* 10^{-5} F, consistent with a charge transfer reaction occurring at the sample/electrode interface. The resistance associated with this process can be estimated from the diameter of the low frequency semi-circular arc in Z^* plots.

In order to establish if the material was an oxide ion conductor the gas atmosphere at 650 °C was changed sequentially from laboratory air to flowing oxygen to flowing nitrogen before reverting to laboratory air. The oxygen partial pressure of the atmosphere had a dramatic effect on the low frequency response, as shown in Fig. 2. On changing the atmosphere from laboratory air to flowing oxygen the resistance associated with the charge transfer process occurring at the electrode/sample interface decreased from a value of *ca.* 1.25 kΩ to a (constant) value of *ca.* 0.25 kΩ after *ca.* 1 h. In flowing N_2 the resistance associated with the charge transfer process increased rapidly and after 1 h the low frequency response consisted of an inclined-spike at an angle of *ca.* 45°. Such a response is indicative of a Warburg-like response and suggests that the rate-limiting step controlling the overall impedance at low frequencies involves the diffusion of electroactive species to/from the electrode/sample interface. Given the dependence of this process on oxygen partial pressure in the surrounding atmosphere, the diffusing species must be oxygen-based, presumably O_2 molecules. This therefore indicates that $NaBi_3V_2O_{10}$ is predominantly an O^{2-} ion (rather than an Na^+ ion) conductor.

The changes in electrode behaviour were reproducible on switching between the various atmospheres whereas the bulk resistivity was independent of oxygen partial pressure, as shown by the high frequency, non-zero intercept in Fig. 2. Although we need to perform concentration (emf) cell measurements in order to prove that $NaBi_3V_2O_{10}$ is an oxide ion conductor, the impedance behaviour described above is compelling evidence that this material is predominantly an oxide-ion conductor.

Bulk conductivity values were calculated from the reciprocal of the low frequency intercept of the high frequency semi-circular arc with the Z' axis of Z^* plots and are shown in the form of an Arrhenius plot, Fig. 3. There is no discontinuity in the Arrhenius plot around the transition temperature at *ca.* 575 °C, instead the data yield a sigmoidal curve which is nearly fully reversible on thermal cycling. As the data do not obey the Arrhenius law it is difficult to calculate any activation energy for the bulk conduction process, however, the data clearly start to approach a plateau above 600 °C.

The bulk conductivity of $NaBi_3V_2O_{10}$ is two orders of magnitude lower than that of YSZ at *ca.* 600 °C;[1] as yet, however, we have only studied the parent material. It may be possible to enhance the conductivity of $NaBi_3V_2O_{10}$, especially below the phase transition temperature of 575 °C by stabilising the high temperature polymorph *via* chemical doping, as is the case with ZrO_2- and BIMEVOX-based solid electrolytes.

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