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Structure of $NaBi_3V_2O_{10}$ and Implications for Ionic Conductivity

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The compound $NaBi_3V_2O_{10}$ is reported to be a good oxygen ion conductor.[1] Two reports on the structure of this compound agree on the unit cell but give a very different arrangement of atoms[2,3] We have re-examined the structure of $NaBi_3V_2O_{10}$ using both single-crystal X-ray and powder neutron diffraction data. Although we confirm the cation positions of one report,[3] we find substantial differences in oxygen positions. Most importantly, our analysis indicates that the oxygen conductivity is likely due to a small amount of interstitial oxygen rather than oxygen deficiency at one site as previously suggested.[3]

Polycrystalline $NaBi_3V_2O_{10}$ was prepared from a 1:3:2 mixture of Na_2CO_3 (Aldrich), Bi_2O_3 (Cerac), and V_2O_5 (Johnson Matthey). An intimate mixture of these reactants was heated in air at 625 °C for 24 h, reground, heated for another 15 h at 625 °C, and cooled to room temperature at 5°/min. Single crystals of $NaBi_3V_2O_{10}$ were obtained from a 3:3:2 mixture of Na_2CO_3, V_2O_5, and Bi_2O_3 heated to 800 °C for 15 h and then cooled to room temperature at 0.05 °C/min. Single-crystal X-ray diffraction data were obtained at room temperature on a Rigaku AFC6R diffractometer with monochromatic Mo Kα radiation ($\lambda = 0.71069$ Å). No decay in intensity was noted during data collection. The observed intensities were corrected for Lorentz polarization and absorption. Data reduction was carried out using a local program, capable of creating a data file containing the crystal-dependent direction cosines of the diffracted and reverse incident beam, for purposes of correction of absorption anisotropy problems. Correction for the effects of absorption anisotropy was carried out using the program SORTAV,[4] as programmed in the software collection WinGX v1.64.02.[5] Structure solution was carried out using Patterson map interpretation as programmed in SHELXS-90 and refined using full-matrix least-squares refinement on F^2 using the program SHELXL-97.[6]

Table 1. Comparison of Atomic Positions for $NaBi_3V_2O_{10}$

atom	data type	*x*	*y*	*z*
Bi1	published[a]	0.082(1)	0.759(1)	0.526(5)
	single Crystal	0.0838(1)	0.7574(1)	0.5283(1)
	neutron	0.0816(6)	0.7598(4)	0.5288(5)
Bi2/Na	published	0.3168(5)	0.379(2)	0.2070(2)
	single crystal	0.3134(2)	0.3822(2)	0.2103(2)
	neutron	0.3091(8)	0.3794(7)	0.2004(8)
V	published	0.346(1)	0.847(3)	0.1444(3)
	single crystal	0.3446(6)	0.8440(4)	0.1446(4)
	neutron	0.3446(6)	0.8440(4)	0.1446(4)
O1	published (O4)	0.178(3)	0.7(2)	0.233(3)
	single crystal	0.159(3)	0.690(2)	0.217(2)
	neutron	0.1562(9)	0.6926(6)	0.2170(7)
O2	published (O5)	0.150(2)	0.79(1)	0.86(2)
	single crystal	0.147(3)	0.803(2)	0.875(2)
	neutron	0.1460(9)	0.8043(7)	0.8800(7)
O3	published (O1)	0.24(2)	0.48(2)	0.546(4)
	single crystal	0.252(3)	0.500(2)	0.527(2)
	neutron	0.2552(9)	0.4988(6)	0.5333(7)
O4	published (O2)	0.59(1)	0.900(9)	0.718(5)
	single crystal	0.566(3)	0.895(2)	0.693(2)
	neutron	0.5660(9)	0.8970(6)	0.6949(7)
O5	published (O3)	0.401(3)	0.245(4)	0.82(6)
	single crystal	0.380(3)	0.235(2)	0.833(3)
	neutron	0.377(1)	0.2362(8)	0.8333(9)

[a] Reference 3.

A structure for $NaBi_3V_2O_{10}$ was obtained in space group $P\bar{1}$ with $a = 5.5364(1)$ Å, $b = 7.0628(2)$ Å, $c = 7.1418(2)$ Å, $\alpha = 107.882(2)°$, $\beta = 112.047(2)°$, $\gamma = 95.550(2)°$, and $Z = 1$. Powder neutron diffraction data were collected on BT-1 at the NIST Center for Neutron Research using a wavelength of 1.5402 Å. Refined positional parameters for both our X-ray and neutron data are given in Table 1. For the refinement of the neutron diffraction data, the vanadium parameters were fixed at the values obtained from our X-ray refinement. Supporting Information is available for the crystallographic details.

Both previous reports[2,3] had used a triclinic cell with $a = 7.20$ Å, $b = 7.06$ Å, $c = 5.53$ Å, $\alpha = 84.5°$, $\beta = 113.3°$, and $\gamma = 112.3°$, which is a nonstandard setting. We therefore transformed this reported unit cell and positional parameters to allow a direct comparison of the reported structure with the structure we obtained. The transformed positional parameters of one of the reported[3] structures are also given in Table 1. All three refinements presented in Table 1 give very similar positional parameters for the cations, and there is also good agreement between oxygen parameters obtained from our X-ray and neutron data. However, there is poor agreement between our results and the reported oxygen positions. This difference is as great as 0.24 Å (Table 2). This of course results in very different bond lengths and calculated valences[7] (Table 3). For example, this reported structure[3] gives a very distorted VO_4 tetrahedron with V−O distances varying from 1.56 to 1.88 Å, whereas we find a much more regular VO_4 tetrahedron with V−O distances varying from 1.65 to 1.74 Å. Valences calculated for our refined structure are generally closer to the expected values with the exception of the site occupied by both Bi and Na. Good agreement is

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Table 2. Differences of Atomic Positions for $NaBi_3V_2O_{10}$

atom	single crystal vs neutron difference in position (Å)	published vs neutron difference in position (Å)
Bi1	0.0005	0.0003
Bi2/Na	0.0610	0.0507
V	0.0000	0.0249
O1	0.0252	0.2420
O2	0.0366	0.1441
O3	0.0454	0.1934
O4	0.0003	0.1560
O5	0.0003	0.1842

Table 3. Bond Distances and Valences[a]

atoms	bond length (Å)	bond valence	bond valence totals
Bi(1)−O(1)	2.331(6)	0.527	
	2.258(23)	*0.642*	
Bi(1)−O(2)	2.311(5)	0.556	
	2.229(28)	*0.694*	
Bi(1)−O(3)	2.163(6)	0.830	
	2.119(30)	*0.935*	
Bi(1)−O(3)	2.287(5)	0.592	
	2.204(38)	*0.743*	
Bi(1)−O(4)	2.438(6)	0.396	
	2.542(29)	*0.298*	
Bi(1)−O(5)	2.876(6)	0.121	total Bi(1) = 3.022
	2.882(41)	*0.119*	*3.431*
Bi(2)/Na−O(1)	2.429(7)	0.404/0.184	
	2.231(32)	*0.691/0.315*	
Bi(2)/Na−O(2)	2.487(7)	0.346/0.157	
	2.519(32)	*0.317/0.144*	
Bi(2)/Na−O(3)	2.408(8)	0.427/0.194	
	2.509(23)	*0.326/0.148*	
Bi(2)/Na−O(3)	2.308(6)	0.562/0.256	total Bi only = 2.414
	2.310(35)	*0.558/0.254*	
Bi(2)/Na−O(4)	2.370(6)	0.474/0.216	total Na only = 1.099
	2.252(32)	*0.652/0.297*	
Bi(2)/Na−O(5)	2.689(7)	0.200/0.091	mean sum[b] = 1.783
	2.825(25)	*0.139/0.063*	*1.952*
V−O(1)	1.738(4)	1.186	
	1.876(29)	*0.821*	
V−O(2)	1.711(4)	1.296	
	1.761(32)	*1.120*	
V−O(4)	1.738(4)	1.195	
	1.667(25)	*1.444*	
V−O(5)	1.655(5)	1.472	total V = 5.149
	1.565(42)	*1.903*	*5.288*

[a] Values in italics are from ref 3. [b] Mean bond valence sum calculated as weighted average of 0.52 occupancy of Bi.

not expected at this site because local relaxation is expected to give somewhat different bond lengths depending on whether Na or Bi actually occupies the site. The most important discrepancy between our results and those reported[3] lies in the occupation parameters for the oxygen atoms. We find that all five oxygen sites are fully occupied. The reported structure[3] claims that one such site (O1 in Table 1 or O3 in their paper) is only 90% occupied. Porob and Guru Row suggest that the high oxygen ion conductivity is related to this partial occupancy.[3]

All three structure refinements for $NaBi_3V_2O_{10}$ presented in Table 1 agree that the Bi:Na ratio on the Bi/Na site is not 1.0. Instead this site is Bi-rich by a small but significant amount, which was also confirmed by our electron microprobe analysis of crystals. The reported structure[3] gives this Bi:Na ratio as 56:44. We find 52:48 from both our X-ray and neutron data, and this agreement is good evidence for a lack of substantial vacancies at this site. We conclude that the oxygen conductivity in $NaBi_3V_2O_{10}$ is likely due to a small concentration of oxygen intersitials given by the formula $Na_{0.96}Bi_{3.04}V_2O_{10.04}$. Assuming that all the interstitial oxygen occupies one general position site, this would mean searching for a site only 2% occupied. There is no possibility that such a small amount of interstitial oxygen could be found using our X-ray or neutron diffraction data.

There is an inconsistency in the paper by Porob and Guru Row.[3] From their refinement of the Bi:Na ratio, they would have a formula of $Na_{0.88}Bi_{3.12}V_2O_{10.12}$, assuming Bi(III), Na(I), and V(V), which seem clearly to be the correct oxidation states. However, they claim an oxygen content of 9.80 instead of 10.00 or 10.12. We conclude that their analysis of their X-ray powder diffraction data gave them reasonable cation positions but gave unreliable positions and occupancies for oxygen atoms. An entirely different structure with the same unit cell was proposed by Sinclair et al.[2] using an analogy to the structure of $Pb_2Bi_2V_2O_{10}$. Although it seems unlikely that there are two entirely different structures with the same unit cell, we measured the oxygen conductivity on a sintered pellet of our $Na_{0.96}Bi_{3.04}V_2O_{10.04}$ sample. The results were in good agreement with those reported by Sinclair et al.[1,2] We thus conclude that we have studied the same compound originally reported by Sinclair et al.[1] to be a good oxygen ion conductor.

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Supporting Information Available: Crystallographic data for $Na_{0.96}Bi_{3.04}V_2O_{10.04}$ (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.

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