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Defect structure and electrical conductivity in the pseudo-binary system Bi_3TaO_7–Bi_3NbO_7

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ABSTRACT

A study of electrical and structural characteristics of compositions in the $Bi_3Ta_{1-x}Nb_xO_7$ system, using X-ray and neutron powder diffraction and AC impedance spectroscopy, is presented. The electrical conductivity increases with increasing niobium content. A full solid solution is observed which adopts an incommensurately ordered pseudo-cubic fluorite structure (type II). Analysis of the defect structure of the $x = 0.50$ composition shows chains of niobate/tantalate octahedra as a likely structural motif. A small degree of non-linearity in the thermal expansion of the cubic subcell lattice parameter is observed.

1. Introduction

The disordered defect fluorite phase, δ-Bi_2O_3, exhibits the highest oxide ion conductivity of any known material [1], but is only stable over a narrow temperature range, from *ca.* 730 °C to its melting point at *ca.* 825 °C. Solid-solution formation with other oxides allows for stabilisation of fluorite based phases to room temperature [2–6]. However, many of these phases show a degree of superlattice ordering or distortions away from regular cubic symmetry, with a consequent lowering of electrical conductivity.

The binary systems of Bi_2O_3–M_2O_5, where M = Nb or Ta, have been studied by a number of investigators [7–16]. At compositions with Bi:M ratios of 3:1 and above, a number of ordered fluorite type phases have been identified. Zhou [10] classified the phases that appear in these systems into four principal types (I to IV). At the 3:1 Bi:M ratio, both Bi_3NbO_7 and Bi_3TaO_7 exhibit type-II pseudo-cubic fluorite phases. Bi_3NbO_7 is known to exhibit unusual polymorphism, with a tetragonally ordered phase (type-III) existing between 800 °C and 900 °C and the pseudo-cubic type-II phase stable above and below this temperature range [17,18]. There is no indication of similar polymorphism in Bi_3TaO_7, despite the fact that Nb and Ta oxides often exhibit similar chemistries.

We have recently reported on the defect structures of type-II forms of Bi_3NbO_7 [19] and Bi_3TaO_7 [20]. Both structures exhibit an incommensurate superlattice characteristic of the type-II phase. In a detailed analysis of the structure of Bi_3TaO_7, using neutron diffraction, we were able to propose the existence of chains of tantalate octahedra as a key structural motif in the system. Using electron diffraction, Tang and Zhou [21] were able to propose models for the type II bismuth niobate solid solution involving Nb_7O_{30} and $Nb_{18}O_{72}$ pyrochlore like clusters. Later work by Withers et al. [16], summarised by Ling [12] characterised the incommensurate nature of the type II structure

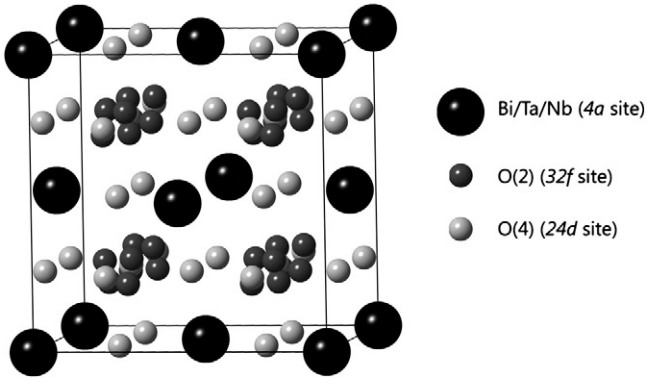

Fig. 1. Structure of $Bi_3Ta_{1-x}Nb_xO_7$ showing the location of Bi/Ta/Nb cations and oxide ion sites.

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Table 1
Crystal and refinement parameters for $Bi_3Ta_{0.5}Nb_{0.5}O_7$.

Temperature	23 °C	800 °C
Chemical formula	$Bi_3Ta_{0.5}Nb_{0.5}O_7$	$Bi_3Ta_{0.5}Nb_{0.5}O_7$
Formula weight	875.86	875.86
Crystal system	Cubic	Cubic
Space group	*Fm*-3*m*	*Fm*-3*m*
Unit cell dimension	$a = 5.45918(3)$ Å	$a = 5.50668(4)$ Å
Volume	162.698(3) Å^3	166.982(4) Å^3
Z	1	1
Density (calculated)	8.939 g cm^{-3}	8.710 g cm^{-3}
Incommensurate modulation parameter, ε	0.388	0.386
R-factors[a]	(a) Neutron backscattering $R_{wp} = 0.0226$, $R_p = 0.0342$ $R_{ex} = 0.0033$, $R_F2 = 0.1707$ (b) Neutron low angle $R_{wp} = 0.0587$, $R_p = 0.0409$ $R_{ex} = 0.0131$, $R_F2 = 0.1205$ (c) X-ray $R_{wp} = 0.0683$, $R_p = 0.0440$ $R_{ex} = 0.0218$, $R_F2 = 0.0307$	(a) Neutron backscattering $R_{wp} = 0.0126$, $R_p = 0.0257$, $R_{ex} = 0.0062$, $R_F2 = 0.1794$ (b) Neutron low angle $R_{wp} = 0.0503$, $R_p = 0.0403$, $R_{ex} = 0.0260$, $R_F2 = 0.1309$ (c) X-ray $R_{wp} = 0.0495$, $R_p = 0.0348$, $R_{ex} = 0.0257$, $R_F2 = 0.0231$
Total no. of variables	118	118
No of profile points used	4199 (neutron backscattering) 4641 (neutron low angle) 6281 (X-ray)	4199 (neutron backscattering) 4641 (neutron low angle) 6268 (X-ray)

[a] For definition of R-factors see reference [26].

in the bismuth niobates and bismuth tantalates using superspace symmetry, with a model involving both chains and clusters of tantalate/niobate octahedra. Interestingly, superlattice ordering is lost on subvalent substitution of Nb^{5+} with Y^{3+} as seen in the pseudo-binary system Bi_3NbO_7–Bi_3YO_6, where stabilisation of the disordered δ-type phase is observed [19].

An investigation of the pseudo-binary system Bi_3NbO_7–Bi_3TaO_7, synthesised by mechanochemical routes, has shown a full solid solution range [22]. More recently, research on this system has focused on characterisation of dielectric properties [23,24]. In the present study, we examine the thermal dependence of defect structure and compositional dependence of electrical conductivity in this system.

Table 3
Significant contact distances (Å) for $Bi_3Ta_{0.5}Nb_{0.5}O_7$. Estimated standard deviations are given in parentheses.

Temperature	23 °C	800 °C
Bi/Nb/Ta-O(2)	2.2680(4)	2.2797(4)
Bi/Nb/Ta-O(4)	1.93011(1)	1.94691(1)

2. Experimental

2.1. Sample preparations

Samples of general composition $Bi_3Ta_{1-x}Nb_xO_7$ ($x = 0.25$, 0.50 and 0.75) were prepared using stoichiometric amounts of Bi_2O_3 (Aldrich, 99.9%), Nb_2O_5 (Aldrich, 99.9%) and Ta_2O_5 (Aldrich, 99.9%). Starting mixtures were ground in ethanol using a planetary ball mill. The dried mixtures were heated initially at 750 °C for 24 h, then cooled, reground and pelletised. Pellets were pressed isostatically at a pressure of 400 MPa, then sintered at 800 °C for 10 h, before slow cooling in air to room temperature, over a period of approximately 12 h.

2.2. Electrical measurements

Electrical parameters were determined by impedance spectroscopy, using a fully automated Solartron 1255/1286 system, in the frequency range 1 Hz to 5×10^5 Hz (18 frequencies per decade). Samples for impedance measurements were rectangular blocks (*ca.* $6\times3\times3$ mm^3) cut from sintered pellets using a diamond saw. Platinum electrodes were sputtered by cathodic discharge on the two smallest flat polished parallel faces of the sample. Impedance spectra were recorded during heating and cooling ramps between *ca.* 300 °C

Table 2
Refined structural parameters for $Bi_3Ta_{0.5}Nb_{0.5}O_7$ at (a) 23 °C and (b) 800 °C. Estimated standard deviations are given in parentheses.

(a)

Atom	Wyc.	*x*	*y*	*z*	Occ.	$U_{iso/eqv}$ (Å^2)[b]
Bi	4*a*	0.0(−)	0.0(−)	0.0(−)	0.75(−)	0.0197(2)
Nb	4*a*	0.0(−)	0.0(−)	0.0(−)	0.125(−)	0.0197(2)
Ta	4*a*	0.0(−)	0.0(−)	0.0(−)	0.125(−)	0.0197(2)
O(2)	32*f*	0.2889(3)	0.2889(3)	0.2889(3)	0.193(1)	0.073(1)
O(4)	24*d*	0.5(−)	0.25(−)	0.25(−)	0.034(1)	0.073(1)

Anisotropic thermal parameters(Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi/Nb/Ta	0.0197(2)	0.0197(2)	0.0197(2)	0.0(−)	0.0(−)	0.0(−)
O(2)	0.073(1)	0.073(1)	0.073(1)	−0.0081(5)	−0.0081(5)	−0.0081(5)

(b)

Atom	Wyc.	*x*	*y*	*z*	Occ.	$U_{iso/eqv}$ (Å^2)[b]
Bi	4*a*	0.0(−)	0.0(−)	0.0(−)	0.75(−)	0.0454(2)
Nb	4*a*	0.0(−)	0.0(−)	0.0(−)	0.125(−)	0.0454(2)
Ta	4*a*	0.0(−)	0.0(−)	0.0(−)	0.125(−)	0.0454(2)
O(2)	32*f*	0.2937(3)	0.2937(3)	0.2937(3)	0.187(1)	0.077(1)
O(4)	24*d*	0.5(−)	0.25(−)	0.25(−)	0.042(1)	0.077(1)

Anisotropic thermal parameters(Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi/Nb/Ta	0.0454(2)	0.0454(2)	0.0454(2)	0.0(−)	0.0(−)	0.0(−)
O(2)	0.077(1)	0.077(1)	0.077(1)	−0.0062(5)	−0.0062(5)	−0.0062(5)

[b] $U_{eqv} = (U_{11} + U_{22} + U_{33})/3$.