Journal of Solid State Chemistry **144,** 467–469 (1999)
Article ID jssc.1999.8171, available online at http://www.idealibrary.com on IDEAL®

BRIEF COMMUNICATION

Temperature-Dependent Structural Behavior of $Bi_{0.5}Nd_{1.5}Ru_2O_7$

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Received October 22, 1998; accepted January 21, 1999

The structure of the Bi-doped pyrochlore, $Bi_{0.5}Nd_{1.5}Ru_2O_7$ has been studied between 20 and 300 K using powder synchrotron diffraction methods. The structure shows an abupt change in the Bi(Nd)–O and and Ru–O contacts near 200 K as a consequence of a metal–semiconductor transition. There is a marked hysteresis in the structural parameters upon rewarming the sample. © **1999 Academic Press**

The electronic properties of ruthenium pyrochlores $A_2Ru_2O_{7-y}$ (A = Bi, Pb, Ln, etc.) are of both fundamental interest and technological significance (1). The behavior of the Ru 4*d* electrons in these materials can, depending on the *A* cation, range from localized to itinerant behavior so that these can be either metals or magnetic semiconductors (2–4). For example, $Nd_2Ru_2O_7$ is a semiconductor that becomes metallic upon replacing the Nd with Bi. Recent structural studies (2–4), supported by electronic band structure calculations (5, 6), have identified the conditions necessary for metallic conductivity in the ruthenate pyrochlores, namely that the Ru–O–Ru bond angle is greater than 133° and that there is a shortening of the Ru–O bond distance. Intriguingly, a number of ruthenate pyrochlores also exhibit unusual temperature-dependent magnetic or electronic properties. For example, $Tl_2Ru_2O_7$ undergoes a metal-to-nonmetal (MNM) transition near 120 K (7) and $Cd_2Ru_2O_7$ displays anomalous electronic and magnetic properties around 100 K (8). Unlike the well-documented structural changes at the MNM transition with *A* cation doping, studies of these materials have not provided any evidence for structural changes upon cooling, and it was suggested for $Cd_2Ru_2O_7$ that the low-temperature behavior was purely electronic in origin (8). At low Bi levels some of the quaternary $Bi_{2-x}Nd_xRu_2O_7$ oxides also undergo a MNM transition upon cooling (3). In the present work, we have used synchrotron x-ray diffraction methods to probe the temperature dependent structural changes in one such oxide, $Bi_{0.5}Nd_{1.5}Ru_2O_7$.

A sample of $Bi_{0.5}Nd_{1.5}Ru_2O_7$ was prepared from Bi_2O_3, Nd_2O_3, and Ru metal. The starting mixture was fired at 650°C for 12 h, 800°C for 72 h, and 950°C for 12 h with periodic regrinding. It was finally annealed in air at 1100°C for 36 h followed by furnace cooling to room temperature. The variable-temperature synchrotron powder-diffraction patterns were collected on beam line X7A at the National Synchrotron Light Source at Brookhaven National Laboratory. Monochromatic wavelength of 0.7981 Å was obtained using a channel-cut double crystal Ge(111) monochromator. The samples were loaded into 0.2-mm glass capillaries, which were oriented and mounted into a displex which was rocked 15° to minimize preferred orientation effects. A linear position sensitive detector (PSD) (9) was used to collect data during runs of approximately 1 h per temperature. Room temperature neutron diffraction data were collected on the HRPD at the high flux Australian reactor (10). The Rietveld refinements were carried out using the program LHPM (11).

At room temperature, $Bi_{0.5}Nd_{1.5}Ru_2O_7$ adopts a regular pyrochlore type structure with the Bi and Nd both occupying the 16*d* sites at $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ (12). Careful examination of the

0022-4596/99 $30.00

profiles revealed a handful of extremely weak reflections that could not be indexed within the cubic pyrochlore cell. The intensity of the strongest of these reflections was less than 0.7% of the intensity of the strongest pyrochlore peak and the relative positions and intensities of these did not significantly change during cooling. There were an insufficient number of these weak reflections to enable us to identify the species responsible for these and accordingly the regions involving these were excluded during the structural refinements. No additional reflections or indication of peak splitting or broadening was observed on cooling and the structure was refined using the same crystallographic model at all temperatures (12).

Cooling the sample results in a monotonic decrease in the cubic cell parameter until around 70 K, below which it is essentially constant. This behavior is very similar to that presented for $Cd_2Ru_2O_7$ (8). There is no evidence in the temperature dependence of the lattice parameter to suggest the occurrence of any unusual effects, although we note that it is not generally possible to distinguish between the metallic and nonmetallic states by the lattice parameters alone. At room temperature, the Ru–O bond distance is 1.984(8) Å and the Ru–O–Ru bond angle is 134.3(6)°. These values have been confirmed using powder neutron diffraction data and are consistent with the reported metallic properties of $Bi_{0.5}Nd_{1.5}Ru_2O_7$. Examination of the temperature dependence of the Ru–O and Bi–O bond distances are more instructive. Despite the relatively high estimated standard deviations in the bond distances, ca 0.007 Å, in the structural refinements employing the synchrotron diffraction data, it is clear that cooling results in abrupt changes in the Bi–O and Ru–O bond distances near 210 K. These are simultaneously accompanied by a decrease in the Ru–O–Ru bond angles. These observed structural changes are consistent with the transition from a metallic state to a nonmetallic state with decreasing temperature.

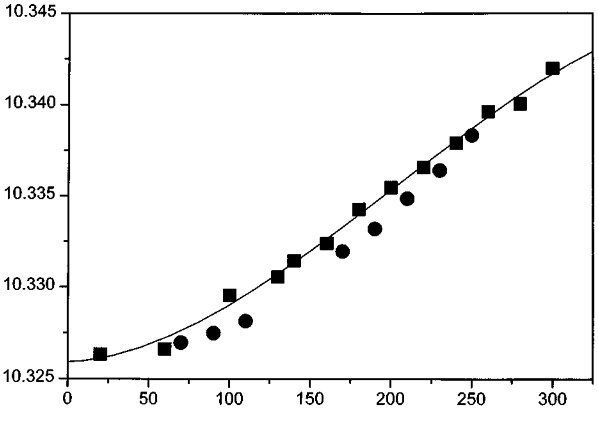

FIG. 1. Temperature dependence of the cubic lattice parameter for $Bi_{0.5}Nd_{1.5}Ru_2O_7$. The temperatures represented by the square symbols were obtained while cooling the sample and those represented by the circles were obtained while reheating the sample. The solid line is drawn as a guide.

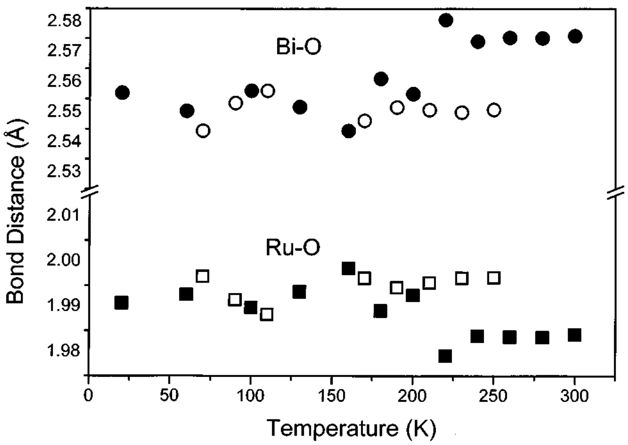

FIG. 2. Temperature dependence of the Bi–O and Ru–O bond distances. The temperatures represented by the closed symbols were obtained while cooling the sample and those represented by the open symbols were obtained while reheating the sample.

In the $A_2Ru_2O_6O'$ pyrochlores each *A*-type cation is surrounded by six O and two O′ atoms in a compressed scalehedron (1). The *A*–O′ distance is dependent only on the cell dimension, whereas the *A*–O distance is a function of both the oxygen position (x, 1/8 1/8) and the lattice parameter. Each O atom is surrounded by two Ru and two *A* cations in a distorted tetrahedron. The abrupt changes in the Ru–O distance and Ru–O–Ru angle at the MNM transition results in a contraction in the *A*–O distance. It has been shown previously that there is a linear dependence of the Ru–O–Ru angle on the ionic radii of the *A*-type cation due to overlap repulsion between the filled shells of the *A* cation and the O^{2-} anions (5, 6). This repulsion is reduced by the presence of vacancies in the O sublattice. Such vacancies are an intrinsic feature of the metallic ruthenium pyrochlores (2,6). The present results suggest that altering the nature of the Ru–O bonding changes the degree of repulsion between the *A* cation and the O^{2-} anions, without altering the number of O vacancies.

The conductivity measurements of Yamamoto *et al.* have demonstrated that $Bi_{0.5}Nd_{1.5}Ru_2O_7$ undergoes a MNM transition near 70 K (3). These authors also showed that the MNM transition temperature in $Bi_{2-x}Nd_xRu_2O_7$ is sensitive to the precise composition of the sample. The MNM transition temperature is also expected to be dependent on the number of oxygen vacancies. XPS studies have shown that the surface of pure $Bi_2Ru_2O_{6.9}$ is bismuth poor, whereas that of $Nd_2Ru_2O_7$ is stoichiometric. We speculate that the difference between the MNM transition temperature observed by Yamamoto *et al.* and that deduced here from the structural variations is a result of small changes in the surface composition of the pellet Yamamoto *et al.* used for their electrical resistivity measurements.

A further interesting observation in the system is the hysteresis in the observed structural changes. On initial cooling below 200 K there is an expansion in the Ru–O distance from about 1.98 to around 2.00 Å. This distance, like the Bi–O distance and Ru–O–Ru angle, then remains essentially constant down to 20 K. Upon rewarming the sample to 250 K the Ru–O distance, and other structural features, remains constant. This could be explained by a first-order structural transition but more detailed studies, including neutron diffraction measurements, are needed to understand this effect.

ACKNOWLEDGMENTS

The support of the Australian Institute of Nuclear Science and Engineering for the neutron scattering experiments is gratefully acknowledged. Brookhaven National Laboratory is operated by Brookhaven Science Associated for the U.S. Department of Energy under Contract DE-AC02-98-CH10886.

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