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Oxygen vacancy control in the defect $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ pyrochlore: a way to tune the electronic bandwidth

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Abstract. An oxygen deficient $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ pyrochlore has been prepared by heating mixtures of Bi_2O_3 and RuO_2 at 1000°C in air and a subsequent treatment under Ar atmosphere. This material is metallic between 4 and 290 K, showing an increased resistivity, by one order of magnitude at 300 K, with respect to stoichiometric $\text{Bi}_2\text{Ru}_2\text{O}_7$. The structure is cubic, $a = 10.2991(7) \text{ \AA}$, and can be described in the space group $Fd\bar{3}m$. A profile refinement of neutron diffraction data indicates a significant oxygen vacancy content of $y = 0.20(2)$, with the vacancies distributed at random over the 8a positions. From accurate Ru–O and Bi–O interatomic distances, a bond-valence study suggests an oxidation state lower than 4+ for Ru cations, which is consistent with the presence of oxygen vacancies in the structure, and with the increase of the lattice parameter with respect to stoichiometric $\text{Bi}_2\text{Ru}_2\text{O}_7$. With respect to other ruthenate pyrochlores, the very short bonds between Bi^{3+} and the special O' oxygens, in which the $6s^2$ electron lone pair of Bi^{3+} are probably involved, account for the comparatively weak remaining six Bi–O bonds, giving rise to a shift of the O positions and indirectly opening the Ru–O–Ru angles. These angles control the transfer integral between Ru t_{2g} and O 2p orbitals, strongly related to the t_{2g} -block bandwidth and, thus, to the electronic delocalization across the solid. The control of the O' content in $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ (y depending on the final annealing conditions of the material) may be, therefore, a clean way to tune the bandwidth of this technologically important electronic material.

1. Introduction

Most commercial, air-fired thick film resistors [1] are based either on RuO_2 with the rutile structure, or bismuth or lead ruthenate ($\text{Bi}_2\text{Ru}_2\text{O}_7$ or $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$) with the pyrochlore structure. Both ruthenate pyrochlores are characterized by high electronic conductivity (10 to $1000 \text{ \Omega}^{-1} \text{ cm}^{-1}$ at room temperature) and also show technological importance as electrode materials [2–4]. Moreover, ruthenium pyrochlores $\text{A}_2\text{Ru}_2\text{O}_7$ show unusual electronic properties [5–7], since Ru 4d electrons are borderline between localized and itinerant, and depending on the nature of the A-type cation the materials are either metallic Pauli paramagnets, e.g. $\text{Bi}_2\text{Ru}_2\text{O}_7$, or semiconductors with a spontaneous ruthenium localized ionic moment, e.g. $\text{Y}_2\text{Ru}_2\text{O}_7$. The electrochemical activity of these materials is believed to be related to the variable oxidation states available to ruthenium, and consequently to the oxygen stoichiometry. These fascinating properties account for the renewed interest on the study of the ruthenium pyrochlores [8, 9] in the last few years.

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The pyrochlore structure, of general stoichiometry $A_2B_2O_6O'$, can be described as two interpenetrating networks [10]. The smaller B cations are octahedrally coordinated to O-type oxygens, the BO_6 octahedra sharing corners to give a B_2O_6 sublattice, which can be considered as the back-bone of the structure. The cage-like holes of this network contain a second sublattice A_2O' , not essential for the stability of the structure: both A and O' atoms may be partially or totally absent, as happens in certain families of defect pyrochlores AB_2O_6 [10]. Most pyrochlores are cubic, and crystallize in the space group $Fd\bar{3}m$ (No 227). Setting the origin at $\bar{3}m$, the pyrochlore structure can be described with A cations at 16c (0, 0, 0) positions, B cations at 16d (1/2, 1/2, 1/2), O at 48f (u , 1/8, 1/8) and O' at 8a (1/8, 1/8, 1/8) positions.

Some oxygen deficient pyrochlores such as $Pb_2Ru_2O_{6.5}$ exhibit a long-distance ordering of the oxygen vacancies: the observation of weak (420) and (640) reflections in the neutron diffraction patterns [11], forbidden in the space group $Fd\bar{3}m$, makes it necessary to describe the structure in the acentric $F\bar{4}3m$, in which O' occupy a positions of multiplicity 4. This behaviour has also been observed in other Pb-containing pyrochlores, such as $Pb_2(SbTi)O_{6.5}$ [12], in which it appears that the oxygen vacancy ordering is driven by the presence of the stereochemically active Pb^{2+} electron lone pair, which physically 'occupies' the vacancy positions in the structure. Subsequently, a similar vacancy mechanism has been suggested [13] for $Bi_2Ru_2O_7$, although simple valence arguments would appear to discount this. However, a neutron diffraction redetermination of the $Bi_2Ru_2O_7$ structure [14] concluded that there is no appreciable oxygen non-stoichiometry for this pyrochlore.

This work aims to show that, depending on the preparation conditions, metallic $Bi_2Ru_2O_{7-y}$ pyrochlores with a significant oxygen vacancy content can be isolated. Accurate Bi–O and Ru–O distances from a neutron powder diffraction study are discussed on the light of the bond-valence theory [15], and the transport properties of the defect pyrochlore are correlated to the observed structural features.

2. Experiment

Black polycrystalline $Bi_2Ru_2O_7$ was prepared by heating stoichiometric mixtures of Bi_2O_3 and RuO_2 at 1000 °C in air for 24 h. The product was reground, and the process repeated several times to ensure homogeneity. Oxygen deficient $Bi_2Ru_2O_{7-y}$ was prepared after a final annealing at 1000 °C for 12 h under Ar atmosphere. Sintered pellets for resistivity measurements were also annealed either in air or in Ar.

The materials were characterized by x-ray diffraction (XRD) using Cu $K\alpha$ radiation, to assess for phase purity. A neutron powder diffraction (NPD) pattern of $Bi_2Ru_2O_{7-y}$ was collected at room temperature in the multidetector DN5 diffractometer at the Siloé reactor of the Centre d'Etudes Nucléaires, Grenoble. A wavelength of 1.345 Å was selected from a Cu monochromator. The 800 detectors covered a 2Θ range of 80°, from $2\Theta_i = 11^\circ$. The counting time was about 4 h, using 10 g of sample contained in a vanadium can.

The NPD pattern was analysed by the Rietveld method, using the FULLPROF program [16]. The line shape of the diffraction peaks was generated by a pseudo-Voigt function, and the background refined to a fifth-degree polynomial. The coherent scattering lengths for Bi, Ru and O were, respectively, 8.532, 7.030 and 5.803 fm. In the final run the following parameters were refined: background coefficients, zero-point, half-width, pseudo-Voigt and asymmetry parameters for the peak shape; scale factor, positional, occupancy factors for Bi and O' , thermal isotropic factors for Ru, O and O' and anisotropic for Bi and unit-cell parameters.

DC resistivity measurements were performed by the standard four probe technique in the temperature range 4 to 400 K.

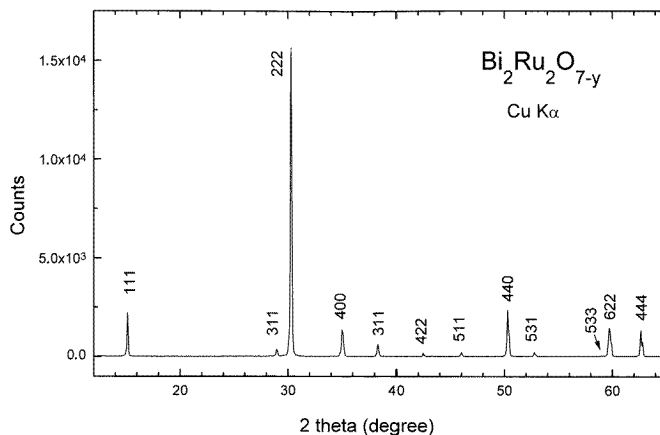


Figure 1. X-ray diffraction pattern of $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$, indexed in a cubic unit cell with $a = 10.2991(8)$ Å.

Table 1. Crystallographic parameters for $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ after the Rietveld refinement^a of NPD data at room temperature. Space group $Fd\bar{3}m$, $a = 10.2991(8)$ Å.

Atom	Site	x	y	z	B_{iso} (Å ²)	Occup. factor
Bi	16c	0	0	0	1.7(1) ^b	0.974(14)
Ru	16d	1/2	1/2	1/2	0.2(1)	1.0
O	48f	0.4229(3)	1/8	1/8	0.93(7)	1.0
O'	8a	1/8	1/8	1/8	0.3(3)	0.80(2)

^a Discrepancy factors: $R_p = 3.13$, $R_{wp} = 4.19$, $R_I = 6.30\%$.

^b Anisotropic thermal factors ($\times 10^4$): $\beta_{11} = \beta_{22} = \beta_{33} = 40(2)$, $\beta_{12} = \beta_{13} = \beta_{23} = -6(3)$.

3. Results

3.1. Structural features

$\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ was obtained as a well crystallized powder, whose XRD diagram was characteristic of a pyrochlore structure. Figure 1 shows the indexed XRD diagram in a cubic unit cell with $a = 10.2991(8)$ Å, slightly larger than that given in [14] for $\text{Bi}_2\text{Ru}_2\text{O}_7$ of $10.2957(1)$ Å. The structural refinement from NPD data of $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ was performed by the Rietveld method in the space group $Fd\bar{3}m$, taking as starting parameters those of $\text{Pb}_2(\text{TiSb})\text{O}_{6.5}$ [12]. The final atomic coordinates, unit-cell parameters and discrepancy factors after the refinement are included in table 1. This structural model assumes the random distribution of the oxygen vacancies at 8a positions. The results of the refinement indicate a significant non-stoichiometry in the O' sublattice. The occupancy of the Bi positions must be considered as complete, within two standard deviations. According to this, the crystallographic formula of this pyrochlore should be written as $\text{Bi}_2\text{Ru}_2\text{O}_{6.80(2)}$. Figure 2 shows the agreement between observed and calculated NPD profiles for $\text{Bi}_2\text{Ru}_2\text{O}_{6.8}$. If we assume a formal valence of 3+ for Bi cations, the oxygen deficiency would imply a reduction in the valence of Ru, probably in the $\text{Ru}^{4+}\text{-Ru}^{3+}$ mixed valence form.

The possibility of long range ordering of the O' vacancies was studied in a second refinement in the acentric space group $F43m$. Figure 3 illustrates the difference between refinements in both $Fd\bar{3}m$ and $F43m$ space groups. In the latter situation, assuming vacancy

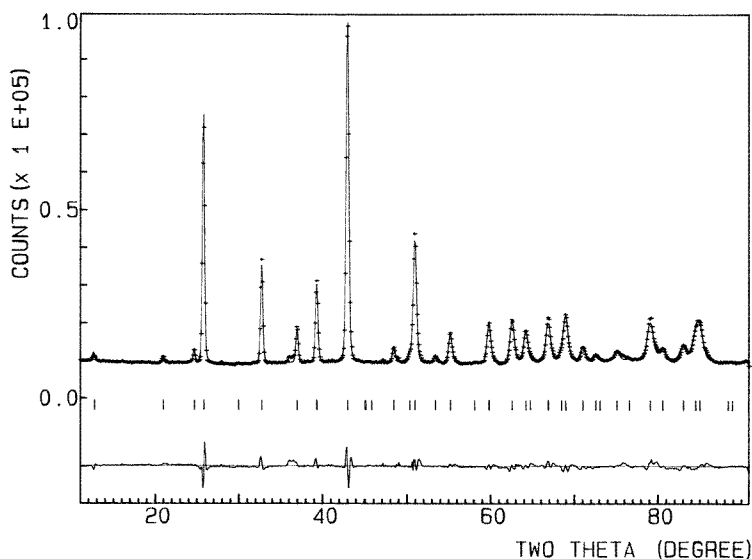


Figure 2. Observed (crosses), calculated (solid line) and difference (beneath) NPD profiles for $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ at 295 K in the space group $Fd\bar{3}m$.

Table 2. Selected atomic distances (\AA) and angles ($^\circ$) for $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$.

BiO ₈ scalenohedra		RuO ₆ octahedra	
Bi–O × 6	2.546(1)	Ru–O × 6	1.986(1)
Bi–O' × 2	2.2298(1)		
O1–Bi–O1	116.83(5)	O1–Ru–O1	95.7(1)
O1–Bi–O1	63.17(6)	O1–Ru–O1	84.35(7)
O1–Bi–O2	100.38(8)		
O1–Bi–O2	79.62(3)		
Bi–O1–Bi	91.29(6)	Ru–O1–Ru	132.85(5)
Bi–O2–Bi	9.471(9)		

ordering, the calculated pattern (solid line) very clearly shows superstructure reflections (420) and (640), which are not present in the observed pattern (dotted line). Thus, the ordering of O' atoms versus vacancies must be excluded.

Table 2 contains a selected list of distances and angles for $\text{Bi}_2\text{Ru}_2\text{O}_{6.8}$, and a view of the structure is shown in figure 4. Bi^{3+} cations are coordinated to eight oxygens ($6\text{O} + 2\text{O}'$) placed in the corners of a distorted cube, better described as a scalenohedron. Notice the very short Bi–O' distances, of 2.23 \AA , much smaller than the Shannon [17] ionic radii sum, of 2.36 \AA . In contrast, Bi–O (2.54 \AA) are larger than expected. During the refinement, the isotropic thermal factor of Bi atoms was found to be much larger than those of Ru and oxygens (see table 2), thus the anisotropic refinement for Bi was performed. The magnitudes of the anisotropic vibrations of the Bi atom (U -eigenvalues) parallel and perpendicular to the [1 1 1] direction, are 0.015 and 0.025 \AA^2 , respectively, which shows that movement along the threefold axis is inhibited.

Ru^{4+} cations are coordinated to six O-type oxygens in slightly distorted octahedra, showing Ru–O bondlengths of 1.987(1) \AA . This value is slightly larger than that given in [14] for

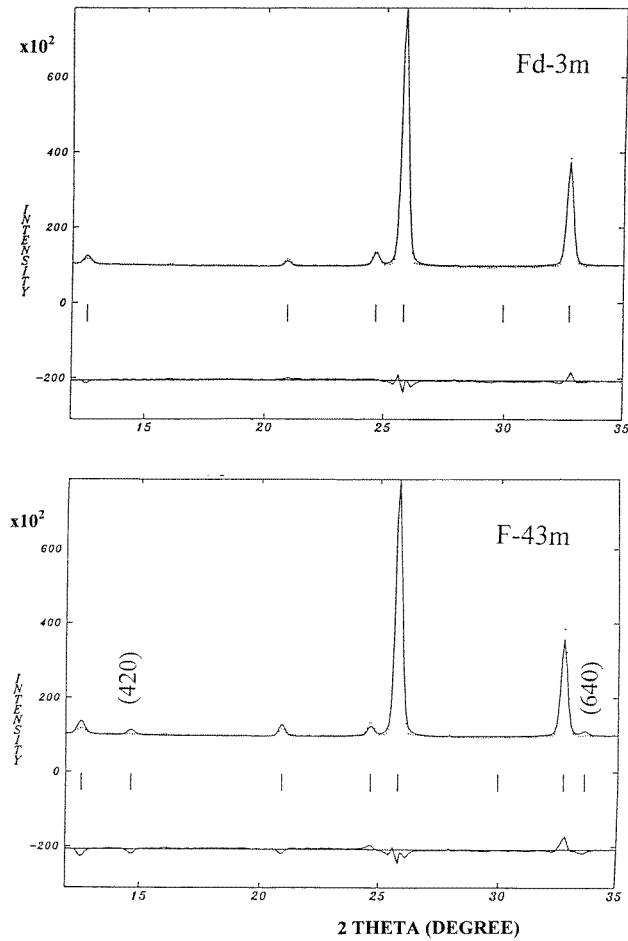


Figure 3. Comparison of the NPD profiles for $Fd\bar{3}m$ and $F\bar{4}3m$ models. The (420) and (640) superstructure reflections (calculated pattern for $F\bar{4}3m$) are not experimentally observed.

$\text{Bi}_2\text{Ru}_2\text{O}_7$, of 1.984(1) Å. This larger Ru–O bondlength is consistent with a slightly lower valence for Ru, which would be expected to balance the presence of oxygen vacancies in the O' sublattice. Ru–O–Ru angles in the Ru_2O_6 network are 132.8° , also slightly lower than the value of 133.1° given in [14] for $\text{Bi}_2\text{Ru}_2\text{O}_7$.

3.2. Transport measurements

Figure 5 shows the resistivity behaviour of $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ ($y = 0.2$) (annealed in Ar). A metallic-like behaviour is observed below 290 K. Room temperature resistivity is $\rho(300 \text{ K}) = 2.85 \times 10^{-3} \Omega \text{ cm}$. A maximum in the resistivity curve at 290 K suggests the presence of an insulator-to-metal transition, observed when cooling from 380 K. Data for stoichiometric $\text{Bi}_2\text{Ru}_2\text{O}_7$ (annealed in air) are given for the sake of comparison. The inset of figure 5 shows in detail the resistivity behaviour of $\text{Bi}_2\text{Ru}_2\text{O}_7$, with $\rho(300 \text{ K}) = 5.25 \times 10^{-4} \Omega \text{ cm}$ in the cooling run. An insulator-to-metal transition is also observed at lower temperatures, with a maximum in resistivity at 110 K. The difference between cooling and heating resistivity data is probably

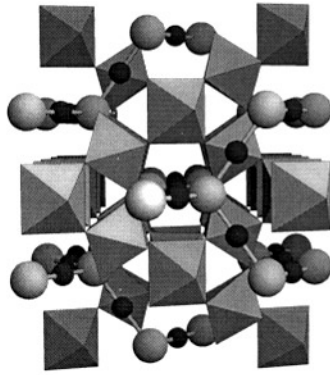


Figure 4. Projection of the pyrochlore structure along $[110]$ direction, showing the vertex-sharing network of RuO_6 octahedra and the independent Bi-O' sublattice (dark (Bi) and light (O') spheres).

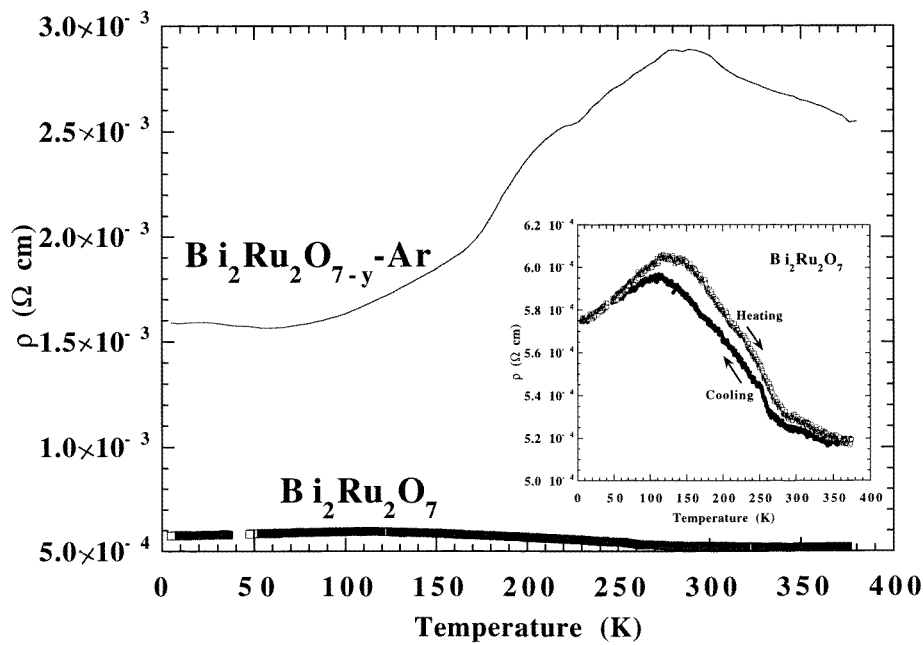


Figure 5. Resistivity-temperature plots for $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$, annealed under Ar atmosphere, and $\text{Bi}_2\text{Ru}_2\text{O}_7$, annealed in air. The inset shows in detail the resistivity variation of the latter.

due to the dynamic regime of the data collection, although a partial hysteretic effect associated with the insulator-to-metal transition must not be ruled out. These data are in good agreement with those previously reported for stoichiometric $\text{Bi}_2\text{Ru}_2\text{O}_7$; for instance a value of $\rho(300 \text{ K})$ ($7.0 \times 10^{-4} \Omega \text{ cm}$ is given in [18], in which a resistivity maximum at 170 K is also described. As shown in figure 5, the resistivity of the defect pyrochlore $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ annealed under Ar is higher than that of the stoichiometric compound in the whole temperature range: at room temperature, this difference is of almost one order of magnitude.

Table 3. Bond valences^a (s_i) for Bi–O and Ru–O bonds, multiplicity of the bonds [m] and valences ($\sum s_i$) for Bi, Ru and O atoms within the respective coordination polyhedra in the $\text{Bi}_2\text{Ru}_2\text{O}_{6.8}$ structure.

Atom	s_i [m]	$\sum s_i$
Bi	0.303(1) [6] 0.568(1) [2]	2.954(3)
Ru	0.661(2) [6]	3.966(7)
O	0.294(2) [2] 0.661(2) [2]	1.910(4)
O'	0.693(1) [4]	2.772(1)

^a Bond valences are calculated as $s_i = \exp[(r_0 - r_i)/B]$; $B = 0.37$; $r_0(\text{Bi}) = 2.094$, $r_0(\text{Ru}) = 1.834 \text{ \AA}$ for the $\text{Bi}^{\text{III}}\text{--O}^{2-}$ and $\text{Ru}^{\text{IV}}\text{--O}^{2-}$ pairs, respectively (from [18]). Individual Bi–O and Ru–O distances are taken from table 2. Partial occupancy for Bi and O' sites have been taken account in the calculation of s_i .

4. Discussion

The presence of either possible structural stresses or covalency effects in the crystal can be estimated through the calculation of the valence of the cations and anions present in the solid, by means of the Brown bond valence model [15, 19]. This model gives a phenomenological relationship between the formal valence of a bond and the corresponding bond length. In perfect nonstrained structures the bond valence sum (BVS) rule states that the formal charge of the cation (anion) is equal to the sum of the bond valences around this cation (anion). The departure from the BVS rule is a measure of the existing stress in the bonds of the structure and indicates the presence of covalent interactions.

Table 3 lists the valences calculated for Bi, Ru and O from the individual Bi–O and Ru–O distances of table 2. Ru cations shows a valence less than +4 in $\text{Bi}_2\text{Ru}_2\text{O}_{6.8}$: this is consistent with the presence of oxygen vacancies in the structure. Bi cations exhibit a valence significantly lower than that expected of +3. Notice, however, the huge valence exhibited by O', of -2.77 , due to the extremely short bond length Bi–O'. The strong interaction observed in the Bi–O' bond suggests the probable participation of the $6s^2$ lone pair of Bi^{3+} . In contrast with $\text{A}_2\text{Bi}_2\text{O}_7$ ruthenates with lone-pair free A^{3+} cations, e.g. rare earths, the smaller cubic unit-cell parameter observed in $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ could be related to this strong covalent bonding between Bi and O'. It appears that the Bi^{3+} bonding power is almost exhausted in the 'extra' bonds to O', in such a way that the remaining six Bi–O bonds are significantly weakened. This results in a displacement of the O atoms (increasing the x atomic parameter in 48f positions) giving rise to a greater Ru–O–Ru angle, much larger than that expected from the Bi^{3+} ionic radius [17].

The Ru–O–Ru angle is closely correlated to the transport properties of ruthenate pyrochlores. As discussed in more detail elsewhere [20, 21], it is believed that metallic conductivity in ruthenate pyrochlores requires an 'opening up' of the Ru–O–Ru angle. From the study of a number of $\text{A}_2\text{Ru}_2\text{O}_7$ ($\text{A} = \text{rare earths, Tl, Bi}$), Kennedy and Vogt [8] conclude that if the Ru–O–Ru angle is less than 133° the compound will be a semiconductor and if it is greater it will be a metallic oxide, provided that the Ru–O distance is acceptably small. The 'extra' opening of the Ru–O–Ru angles in $\text{Bi}_2\text{Ru}_2\text{O}_7$, indirectly due to the strong covalent bonding between Bi and O' oxygens, accounts for the metallic behaviour observed in the Bi pyrochlore in contrast with other $\text{A}_2\text{Ru}_2\text{O}_7$ pyrochlores (A : rare earths), which are electrical insulators.

The behaviour of the defect $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ pyrochlore prepared by annealing under Ar is consistent with the ideas discussed above; the presence of a significant number of oxygen vacancies is related with the observed increase in resistivity, as follows. The O' oxygen

content in the structure is 20% lower; therefore the Bi–O' bonds are, on average, somewhat weaker than those present in the stoichiometric compound. As a result, Bi–O bonds are comparatively stronger (shorter); compare $d_{\text{Bi-O}} = 2.546(1)$ Å for the defect pyrochlore with $d_{\text{Bi-O}} = 2.567(1)$ Å for the stoichiometric phase [14]. This shortening is achieved by means of a shift of the O positions; compare $u = 0.4229(3)$ for the defect pyrochlore with $u = 0.4234(1)$ for the stoichiometric compound [14]. Finally, the oxygen shift leads to a closing of the Ru–O–Ru angles: as indicated above, Ru–O–Ru angles are slightly lower in oxygen defective $\text{Bi}_2\text{Ru}_2\text{O}_{6.8}$ than in stoichiometric $\text{Bi}_2\text{Ru}_2\text{O}_7$, thus reducing the overlapping between Ru and O orbitals. The observed increase in resistivity by almost one order of magnitude in the former compound is therefore consistent with the slightly lower Ru–O–Ru angle determined for the defective compound. This effect is predominant over the carrier injection (electron doping) associated with the creation of oxygen vacancies. In summary, it appears that the presence of O' vacancies in $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ is mainly responsible for the reduction of the t_{2g} -block band-width, through the displacement of the O atoms in 48f positions and closing of the Ru–O–Ru angle. Thus, the electronic properties of this technologically important compound can be modified in a very clean way, avoiding chemical doping with cationic substitutions, by carefully controlling the annealing atmosphere and, therefore, the O' content of the pyrochlore. New synthetic routes to prepare more strongly reduced, monophased $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ pyrochlores are currently under study.

5. Conclusions

Metallic $\text{Bi}_2\text{Ru}_2\text{O}_{7-y}$ pyrochlores with significant y oxygen vacancies content can be prepared by thermal annealings under inert atmosphere. An NPD study reveals significant differences with respect to stoichiometric $\text{Bi}_2\text{Ru}_2\text{O}_7$: in $\text{Bi}_2\text{Ru}_2\text{O}_{6.8}$ the cubic unit-cell parameter is larger, as well as the Ru–O bond-lengths; both facts are consistent with a lower oxidation state for Ru cations. Moreover, a bond valence study demonstrates that Ru valence is lower than 4+, as expected. The very short Bi–O' bond lengths suggest a strong covalent bonding in which the 6s electron lone pair of Bi^{3+} is probably involved, giving a special stability to the structure. The abnormally high strength of Bi–O' bonds is probably related to the metallic character exhibited by this material: the bonding power of Bi^{3+} , exhausted in the two Bi–O' bonds, is correspondingly weak for the remaining six Bi–O bonds. This results in a larger 'effective' ionic size for Bi^{3+} , which indirectly leads to an opening of the Ru–O–Ru angles with respect to other insulating $\text{A}_2\text{Ru}_2\text{O}_7$ pyrochlores. This opening increases the overall t_{2g} -block band-width allowing the Mott–Hubbard mechanism of electron delocalization [9]. The occupancy factor of O' determines, thus, the strength of the six Bi–O bonds, the O positions and, finally, the Ru–O–Ru angles. The control of the O' content (depending on the final annealing conditions of the material) may be, therefore, a clean way to tune the bandwidth of this technologically important electronic material.

Acknowledgments

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