

A (3 + 3)-Dimensional “Hypercubic” Oxide-Ionic Conductor: Type II $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$

C.D. Ling¹, S. Schmid¹, P.E.R. Blanchard¹, V. Petříček², G.J. McIntyre³, N. Sharma¹, A. Maljuk⁴, A.A. Yaremchenko⁵, V.V. Kharton⁵, M. Gutmann⁶, Ray L. Withers⁷

¹ — School of Chemistry, The University of Sydney, Australia
² — Institute of Physics, ASCR, v.v.i., The Academy of Sciences of the Czech Republic
³ — Institut Laue-Langevin, Grenoble, France
⁴ — Leibniz Institute for Solid State and Materials Research Dresden, Germany
⁵ — Department of Materials and Ceramic Engineering & CICECO, University of Aveiro
⁶ — ISIS, Science and Technology Facilities Council, Rutherford Appleton Laboratory, United Kingdom
⁷ — Research School of Chemistry, Australian National University, Canberra, Australia

FIGURE 1
 Refined structure of Type II $(\text{Bi}_2\text{O}_3)_{0.795}(\text{Nb}_2\text{O}_5)_{0.205}$, view along the $\langle 110000 \rangle$ direction, drawn over $8 \times 8 \times 8$ fluorite-type subcells. Bi atoms are purple, and Nb atoms and polyhedra are green.

FIGURE 2
 Partial oxide-ionic (σ_o) and electronic (σ_e) conductivities for the ceramic samples of Type II and Type III $(\text{Bi}_2\text{O}_3)_{0.76}(\text{Nb}_2\text{O}_5)_{0.24}$.

The high-temperature cubic form of bismuth oxide, $\delta\text{-Bi}_2\text{O}_3$, is the best intermediate-temperature oxide-ionic conductor known. The well-established way of stabilizing $\delta\text{-Bi}_2\text{O}_3$ to room temperature, while preserving a large part of its conductivity, is by doping with higher valent transition metals to create wide solid-solutions fields with exceedingly rare and complex (3+3)-dimensional incommensurately modulated “hypercubic” Type II structures. These materials remain poorly understood because no such structure has ever been quantitatively solved and refined, due to the complexity of the problem and lack of adequate experimental data. In the present work, this was addressed by growing a large (centimeter scale) crystal using a novel refluxing floating-zone method, collecting high-quality single-crystal neutron diffraction data, and treating its structure together with X-ray diffraction data within the superspace symmetry formalism.¹ The Type II structure can be understood as an “inflated” pyrochlore, in which the corner-connected NbO_6 octahedral chains move smoothly apart to accommodate the solid solution. While some oxide vacancies are ordered in these chains, others are dis-

tributed throughout a continuous three-dimensional network of wide $\delta\text{-Bi}_2\text{O}_3$ -like channels (Figure 1), explaining the superior oxide-ionic conductivity of incommensurate Type II phase compared to commensurately modulated Type III phases in the same pseudobinary system (Figure 2).

REFERENCES

[1] C.D. Ling, S. Schmid, P.E.R. Blanchard, V. Petříček, G.J. McIntyre, N. Sharma, A. Maljuk, A.A. Yaremchenko, V.V. Kharton, M. Gutmann, R. L. Withers⁷, *J. Am. Chem. Soc.*, 2013, **135**, 6477–6484. DOI: 10.1021/ja3109328

