Metal Oxides

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Pressure-Induced Intersite Bi–M (M = Ru, Ir) Valence Transitions in Hexagonal Perovskites**

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Abstract: *Pressure-induced charge transfer from Bi to Ir/Ru is observed in the hexagonal perovskites $Ba_{3+n}BiM_{2+n}O_{9+3n}$ ($n = 0,1$; $M = Ir,Ru$). These compounds show first-order, circa 1% volume contractions at room temperature above 5 GPa, which are due to the large reduction in the effective ionic radius of Bi when the 6s shell is emptied on oxidation, compared to the relatively negligible effect of reduction on the radii of Ir or Ru. They are the first such transitions involving 4d and 5d compounds, and they double the total number of cases known. Ab initio calculations suggest that magnetic interactions through very short (ca. 2.6 Å) M–M bonds contribute to the finely balanced nature of their electronic states.*

Solid-state compounds such as oxides are generally thought of as consisting of ions with well-defined formal oxidation states. Although in reality all ionic compounds have some degree of covalent bonding character, the ionic approximation is usually sufficient to understand their "crystal chemistry" in conjunction with quantitative empirical concepts, such as bond valence sum (BVS)[1] and effective ionic radius (IR).[2] IR values predict that the effective size of an atom in an ionic solid will decrease as its oxidation state increases. IR changes gradually as electrons are removed from a shell: for example, $IR(Ir^{3+}) = 0.68$, $IR(Ir^{4+}) = 0.625$, $IR(Ir^{5+}) = 0.57$ Å in six-fold coordination. However, when removing an electron completely empties a shell, the change is more pronounced: for example, $IR(Bi^{3+}) = 1.03$, $IR(Bi^{5+}) = 0.76$ Å. Consequently, for ionic solids containing suitable combinations of cations, a net reduction in volume could be achieved by transferring an electron from one cation to another; changes in temperature and/or pressure could make such a valence state transition favorable. When both cations are of the same element, this is thought of as a charge-ordering transition, of which there are many examples (such as the Verwey transition in Fe_3O_4[3]). However, cases involving different elements are extremely rare. We are aware of three, all involving 3d transition metals: $(Bi^{3+}_{0.5}Bi^{5+}_{0.5})Ni^{2+}O_3 \rightarrow Bi^{3+}Ni^{3+}O_3$, marked by a 2.6% volume reduction at about 3.5 GPa[4] (this can be shifted to ambient pressure by La-doping[5]); $LaCu^{2+}_3Fe^{3.75+}_4O_{12} \rightarrow LaCu^{3+}_3Fe^{3+}_4O_{12}$, on cooling to about 400 K, also marked by negative thermal expansion;[6] and $Fe^{2+}Ti^{4+}O_3 \rightarrow Fe^{3+}Ti^{3+}O_3$, which occurs gradually over 2–4 GPa.[7] The rarity of these transitions suggests that the electronic state of a compound must be particularly finely balanced for temperature or pressure to change its ground state in this way.

We recently reported a series of unusual first-order magnetostructural transitions in the hexagonal 6H-type perovskites $Ba_3BiIr_2O_9$[8] and $Ba_3BiRu_2O_9$[9] and 12L-type $Ba_4BiIr_3O_{12}$,[10] where the unit cell volumes increases on cooling through a low-temperature transition T^*. The structures of the Ir phases are shown in Figure 1 ($Ba_3BiRu_2O_9$ is isostructural with $Ba_3BiIr_2O_9$). Note the face-sharing octahe-

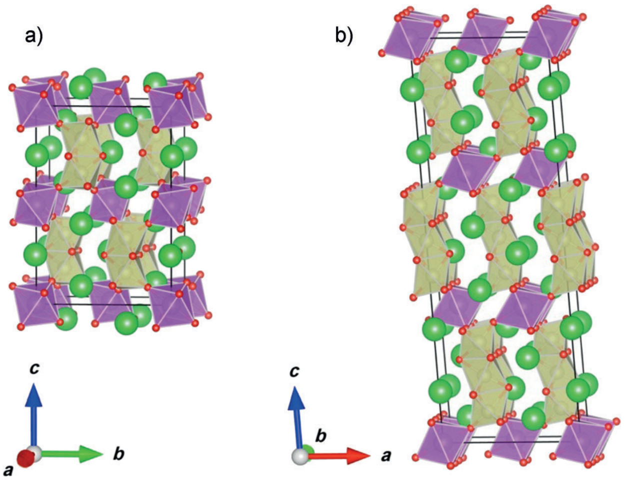

Figure 1. Structures of a) $Ba_3BiIr_2O_9$ and b) $Ba_4BiIr_3O_{12}$. O small red spheres, Ba large green spheres; isolated BiO_6 octahedra are purple, face-sharing IrO_6 octahedra are gold.

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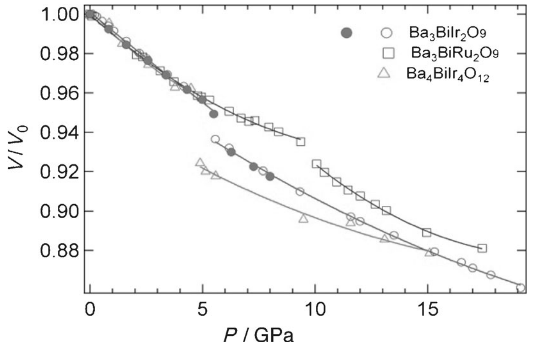

Figure 2. Unit cell volume versus pressure for $Ba_3BiIr_2O_9$, $Ba_3BiRu_2O_9$, and $Ba_4BiIr_3O_{12}$ from S-XRD data collected at the AS (open symbols) and ESRF (closed symbols). Errors are smaller than the symbols; lines are guides to the eye.

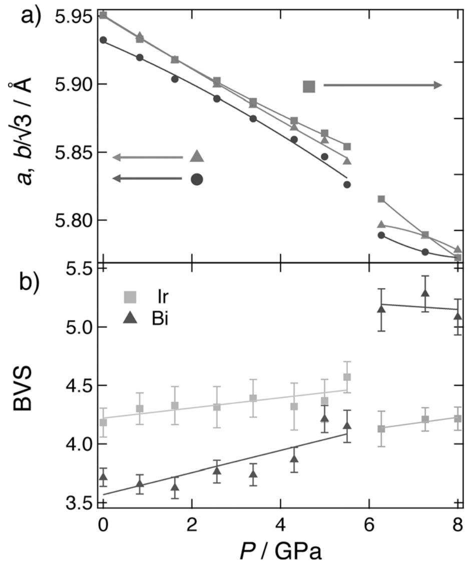

Figure 3. a) Unit cell edges (error bars are smaller than symbols) and b) BVS for Bi/Ir versus pressure for $Ba_3BiIr_2O_9$ from NPD data. Lines are guides to the eye.

dral Ir_2O_9 or Ir_3O_{12} units containing short (ca. 2.6 Å) Ir–Ir bonds, bridged by corner-shared BiO_6 octahedra.

For $Ba_3BiIr_2O_9$, the negative thermal expansion is very large (1.0 %), which led us to investigate the effects of applied pressure on these compounds. Figure 2 shows unit cell volume as a function of pressure for all three samples, determined by synchrotron X-ray powder diffraction (S-XRD) in a diamond-anvil cell (DAC). Note that the limited number of crystallites in the beam when using a DAC, combined with the relative insensitivity of x-rays to light oxygen atoms in the presence of heavy metals, meant that it was not possible to refine atomic coordinates against S-XRD data. However, Rietveld refinements using the ambient pressure model[8] yielded good agreement with the data, meaning that the structural change at the transition is subtle. Final Rietveld fits to data at 5.52 and 6.77 GPa are given in the Supporting Information, Figure S1.

To investigate the structural nature of the transition, we collected high-pressure neutron powder diffraction (NPD) data for $Ba_3BiIr_2O_9$ with a Paris–Edinburgh (PE) press. Figure 3 a shows the unit cell edge lengths as a function of pressure at room temperature. As for the low-temperature magnetoelastic transition at $T^* = 74$ K, there was no detectable change in space group symmetry from $C2/c$ through the transition. However, unlike the highly anisotropic T^* transition (which occurs almost exclusively along the c axis), the high-pressure transition is essentially isotropic. Structures of the low-pressure form at 5.50 GPa and the high-pressure form at 6.27 GPa, together with the corresponding Rietveld fits to NPD data (Figure S2) are given in the Supporting Information.

Figure 3 b presents the derived BVS data for Bi and Ir as a function of pressure, clearly showing that the origin of the volume contraction is charge transfer between these two ionic species. (Note that the BVS sit on a linear sloping background because the R_0 values are derived from ambient-pressure experimental data.)

Further evidence that the pressure-induced transition is due to a valence state transition involving Bi came from high-pressure S-XRD for isostructural $Ba_3CeIr_2O_9$ and $Ba_3LaIr_2O_9$,[11] where Bi is replaced by Ce^{4+} and La^{3+} respectively, for which no stable higher-valent cation exists. Figure S3 shows that no comparable transition takes place in these compounds over the same pressure range.

To shed further light on these transitions in terms of electronic structure, we carried out ab initio (density functional theory, DFT) geometry optimization (GO) calculations on $Ba_3BiIr_2O_9$. Spin-polarized calculations with a Hubbard correction for the Ir d-electrons were needed to reproduce the experimentally observed[8] semiconducting state with a small band gap. Further calculations with spin–orbit coupling (SOC) and non-collinear magnetic moments resulted in a slightly larger band gap of 0.2 eV.

GO calculations simulating applied pressure showed that the experimentally observed ambient and high-pressure forms are both stable from 5–15 GPa, with the form of the optimized structure depending only on the initial form chosen. The volume difference between them over this range was 10–15 Å^3, consistent with the experimentally observed first-order transition between the two forms (Figure 3). Further validation for our total energy calculations comes from experimentally observed volume difference between $Ba_3BiIr_2O_9$ at 0 and 8 GPa (in the low- and high-pressure forms respectively) is 75.8 Å^3; the enthalpy associated with this change ($P{\cdot}dV$) is 3.79 eV per unit cell (4 formula units), which is remarkably close to the calculated energy difference from the full SOC magnetic calculations (3.78 eV).

The formal charge transfer described thus far is attenuated by covalency. All calculations show a decrease in the Bi s-electron population with increasing pressure. The clearest picture of charge transfer can be obtained from a Mulliken analysis of the charge distribution from CASTEP calculations on the observed 0 and 8 GPa structures. This shows a positive charge increase for Bi with pressure from 2.78 to 3.49 e^-; that is, $+0.71\ e^-$, which can be entirely accounted for by a change in Bi s-electron population corresponding to a one-electron transfer from Bi^{4+} to Bi^{3+}. The corresponding change for Ir is much smaller, from 1.23 to 1.21 e^-. Bi is octahedrally coordinated to the "outer" oxygen atoms of the Ir_2O_9 dimers, and the negative charge on these bridging oxygen atoms increases by 1–5%, while the "inner" three oxygen atoms of the dimers show a 5% negative charge increase. These changes account for the majority of the charge transfer: that is, the loss of almost one s-electron from Bi is distributed over the neighboring Ir_2O_9 dimers.

The question obviously arises as to why these particular compounds undergo such rare pressure-induced charge-transfer reactions. Several unusual features are apparent. First, the BVS of Bi in the low-pressure form is closer to +4 than to +3 (Figure 3b). Bi^{4+} is highly unconventional and implies an unstable $[Xe]5d^{10}6s^1$ configuration, which should disproportionate into Bi^{3+}/Bi^{5+}, as for $BaBiO_3$[12] and $BiNiO_3$.[13] The absence of any evidence for long- or short-range disproportionation in $Ba_3BiIr_2O_9$, $Ba_3BiRu_2O_9$, and $Ba_4BiIr_3O_{12}$ may be related to the triangular disposition of Bi sites in hexagonal perovskites, which geometrically frustrates 1:1 charge-ordering, as discussed previously.[8–10] (Interestingly, the suppression of Bi^{3+}/Bi^{5+} charge ordering by doping K for Ba[14] or Pb for Bi[15] leads to another rare phenomenon, namely superconductivity, in $BaBiO_3$.) Regardless of whether we really have discrete Bi^{4+} cations, or only the average of a disordered Bi^{3+}/Bi^{5+}, mixture, the electronic state of Bi in these compounds is clearly unstable; this instability reduces the activation barrier to charge transfer. Note that charge-disproportionated $BiNiO_3$ ($Bi^{5+}Bi^{3+}Ni_2O_6$) is one of the handful of other compounds known to undergo such a transition.[4]

The change from integer (+4) to non-integer (+3.5 for $Ba_3Bi(Ir,Ru)_2O_9$ or +3.67 for $Ba_4BiIr_3O_{12}$) valence states for M also suggests that the transitions described here might be associated with an insulator–metal transition, as reported for La-doped $BiNiO_3$.[16] This possibility will be investigated in the near future.

Another unusual feature of $Ba_3BiIr_2O_9$, $Ba_3BiRu_2O_9$, and $Ba_4BiIr_3O_{12}$ is very short M–M bonds within face-sharing octahedral units. The fact that ab initio calculations only reproduce pressure-induced charge transfer (in the sense that they yield stable distinct low- and high-pressure forms) when spin polarization is included suggests that exchange interactions through these short bonds, possibly in competition with 90° M-O-M superexchange, plays a role in the finely balanced electronic states of these compounds. The low-temperature magnetoelastic transitions of these compounds[8–10] are another consequence of this electronic instability.

A third unusual feature is the involvement of 4d/5d metal cations. The d-orbitals on such metals are less directional than those on their 3d counterparts, allowing more flexibility in their coordination environments. Changes in IR with oxidation state are also less pronounced for 4d/5d metals.[2] Both these aspects should favor a lowering of the activation barrier to pressure-induced charge transfer; note that the pressure at which the transfer occurs in $Ba_3BiRu_2O_9$ is approximately twice that for $Ba_3BiIr_2O_9$, suggesting that an even higher pressure would be required for a 3d analogue (at present this cannot be tested because no 3d analogue of these phases is known). Recent studies have also demonstrated that the stronger spin–orbit coupling (SOC) in 5d compounds such as Sr_2IrO_4[17] can result in exotic electronic properties The importance of SOC on the observed transitions will be further investigated in the near future.

Despite the unusual and distinct features of these hexagonal perovskites, it is difficult to make a quantitative statement about their uniqueness when so few studies of this type have been done. High-pressure experiments are difficult and time-consuming, especially in the GPa regime, but the results presented herein should provide some motivation by highlighting the interesting phenomena that remain to be discovered and explored. Indeed, in light of this work we believe that a similar reaction $Sr_2Tb^{3+}Ru_{1-x}Ir_xO_6 \rightarrow Sr_2Tb^{4+}Ru_{1-x}Ir_xO_6$ may take place at less than 1 GPa;[18] these, and potentially many other, systems are clearly due for reinvestigation. Our reproduction of the experimental effect using ab initio calculations is particularly significant in this context, because it opens up the possibility of surveying a wide range of candidate systems computationally before committing to experiments.

Experimental Section

Synthesis of $Ba_3BiIr_2O_9$, $Ba_3BiRu_2O_9$, and $Ba_4BiIr_3O_{12}$ was described previously.[8–10] High-pressure S-XRD data were collected using DACs on ID27 at the ESRF ($\lambda = 0.37380$ Å) for $Ba_3BiIr_2O_9$ and the PD beamline at the AS ($\lambda = 0.68862$ Å) for $Ba_3BiIr_2O_9$, $Ba_3BiRu_2O_9$, and $Ba_4BiIr_3O_{12}$; pressures were calibrated against ruby fluorescence line shift. High-pressure time-of-flight NPD data for $Ba_3BiIr_2O_9$ were collected using a PE press on PEARL at ISIS; pressure was calibrated against the unit cell volume of a Pb standard. Structure refinements used the Rietveld method as implemented in the program GSAS[19] with the EXPGUI[20] front-end. Spin-polarized DFT GO calculations used the CASTEP[21] and VASP[22] codes with a Hubbard correction for the Ir d-electrons ($U = 3$ eV and $J = 1$ eV); all calculations used the GGA-PBE functional and were converged with respect to k-point sampling and plane-wave energy cut-off.

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[1] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192–197.
[2] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.
[3] a) E. J. Verwey, P. W. Haayman, F. C. Romeijn, *J. Chem. Phys.* **1947**, *15*, 181–187; b) E. J. W. Verwey, P. W. Haayman, *Physica* **1941**, *8*, 979–987.
[4] M. Azuma, S. Carlsson, J. Rodgers, M. G. Tucker, M. Tsujimoto, S. Ishiwata, S. Isoda, Y. Shimakawa, M. Takano, J. P. Attfield, *J. Am. Chem. Soc.* **2007**, *129*, 14433–14436.
[5] M. Azuma, W. T. Chen, H. Seki, M. Czapski, S. Olga, K. Oka, M. Mizumaki, T. Watanuki, N. Ishimatsu, N. Kawamura, S. Ishiwata, M. G. Tucker, Y. Shimakawa, J. P. Attfield, *Nat. Commun.* **2011**, *2*, 347.
[6] Y. W. Long, N. Hayashi, T. Saito, M. Azuma, S. Muranaka, Y. Shimakawa, *Nature* **2009**, *458*, 60–63.

[7] T. Seda, G. R. Hearne, *J. Phys. Condens. Matter* **2004**, *16*, 2707–2718.

[8] W. Miiller, M. Avdeev, Q. Zhou, B. J. Kennedy, N. Sharma, R. Kutteh, G. J. Kearley, S. Schmid, K. S. Knight, P. E. R. Blanchard, C. D. Ling, *J. Am. Chem. Soc.* **2012**, *134*, 3265–3270.

[9] W. Miiller, M. Avdeev, Q. Zhou, A. J. Studer, B. J. Kennedy, G. J. Kearley, C. D. Ling, *Phys. Rev. B* **2011**, *84*, 220406(R).

[10] W. Miiller, M. T. Dunstan, Z. Huang, Z. Mohamed, B. J. Kennedy, M. Avdeev, C. D. Ling, *Inorg. Chem.* **2013**, *52*, 12461–12467.

[11] a) Y. Doi, Y. Hinatsu, *J. Solid State Chem.* **2004**, *177*, 3239–3244; b) Y. Doi, Y. Hinatsu, *J. Phys. Condens. Matter* **2004**, *16*, 2849–2860.

[12] D. E. Cox, A. W. Sleight, *Solid State Commun.* **1976**, *19*, 969–973.

[13] S. Ishiwata, M. Azuma, M. Takano, E. Nishibori, M. Takata, M. Sakata, K. Kato, *J. Mater. Chem.* **2002**, *12*, 3733–3737.

[14] R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farrow, L. W. Rupp, A. E. White, K. Short, W. F. Peck, T. Kometani, *Nature* **1988**, *332*, 814–816.

[15] A. W. Sleight, J. L. Gillson, P. E. Bierstedt, *Solid State Commun.* **1975**, *17*, 27–28.

[16] S. Ishiwata, M. Azuma, M. Hanawa, Y. Moritomo, Y. Ohishi, K. Kato, M. Takata, E. Nishibori, M. Sakata, I. Terasaki, M. Takano, *Phys. Rev. B* **2005**, *72*, 045104.

[17] a) B. J. Kim, H. Jin, S. J. Moon, J. Y. Kim, B. G. Park, C. S. Leem, J. Yu, T. W. Noh, C. Kim, S. J. Oh, J. H. Park, V. Durairaj, G. Cao, E. Rotenberg, *Phys. Rev. Lett.* **2008**, *101*, 076402; b) B. J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi, T. Arima, *Science* **2009**, *323*, 1329–1332.

[18] Q. D. Zhou, B. J. Kennedy, *J. Solid State Chem.* **2005**, *178*, 3589–3594.

[19] A. C. Larson, R. B. Von Dreele, Los Alamos National Laboratory Report LAUR 86–748, **1994**.

[20] B. H. Toby, *J. Appl. Crystallogr.* **2001**, *34*, 210–213.

[21] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne, *Z. Kristallogr.* **2005**, *220*, 567–570.

[22] G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169–11186.