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Application for beam time at ESRF – Experimental Method

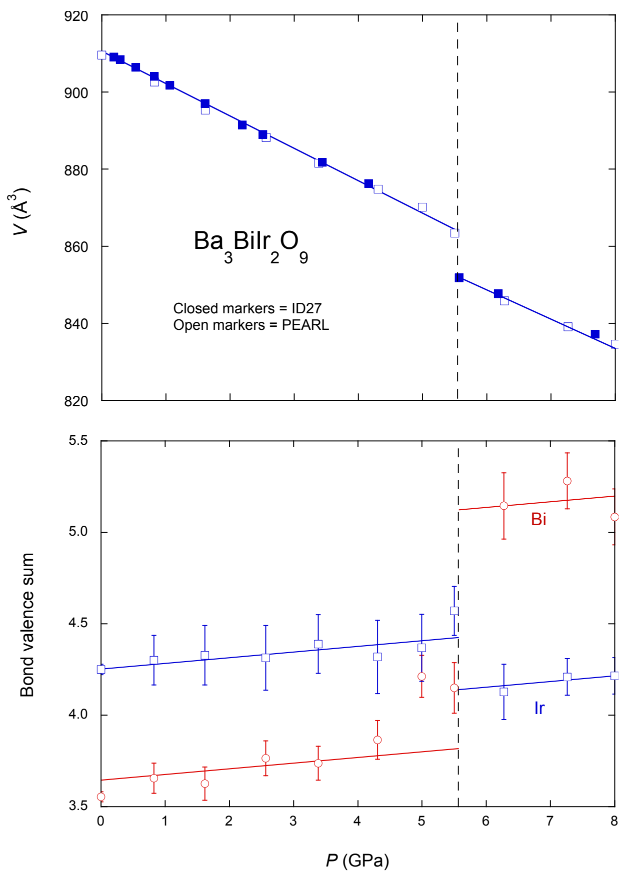
This document should consist of a maximum of two A4 pages with a minimal font size of 12 pt.

Proposal Summary

We wish to use XANES to investigate an unusual pressure-induced transition in a series of hexagonal perovskites. Diffraction experiments (synchrotron and neutron) show that $Ba_3BiIr_2O_9$ and $Ba_3BiRu_2O_9$ undergo first-order volume collapses at 5 and 10 GPa respectively, at which point Bi–O bond lengths decrease and Ir(Ru)–O bonds increase. By collecting XANES data through these transitions, we can verify that they represent the first ever observation of valence transfers between Bi and 4*d* or 5*d* transition metals.

Scientific background :

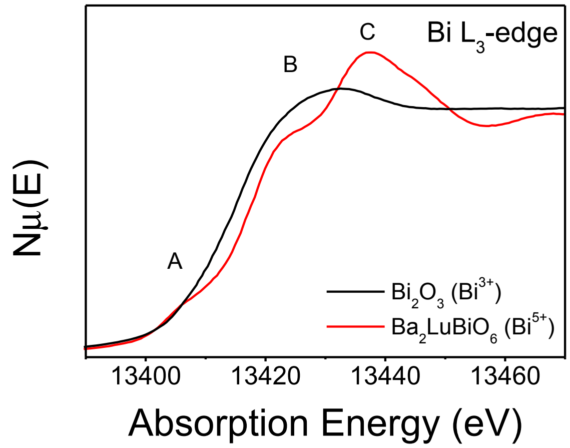
The 6H-type hexagonal perovskites $Ba_3BiIr_2O_9$ and $Ba_3BiRu_2O_9$ first attracted interest due to their unique low-temperature spin-gap transitions, accompanied (in the case of the Ir compound) by a giant 1% negative thermal expansion. [1,2] Bi has a very unusual apparent valence state of 4+ in these compounds, the instability of which appears to play a crucial role. In a diffraction experiment on ID27, we sought to investigate the ability of pressure to suppress the sin-gap transitions. In the process, we discovered that at 5.5 GPa (Ir) and 9 GPa (Ru), the volumes of these compounds collapse again by 1% in an apparently unrelated transition. In a follow-up neutron diffraction experiment on PEARL at ISIS, sufficiently precise metal-oxygen bond lengths could be refined to extract bond valence sums [3] for Bi and Ir, which strongly suggest that this transition is a valence transfer: $Bi^{4+} + 2Ir^{4+} \rightarrow Bi^{5+} + 2Ir^{3.5+}$. (See figures at right).



Experimental methods

We propose to carry out a series of XANES experiments under different external applied pressures. We will focus on the Bi L_3-edge. As shown in the figure at right, the Bi L_3-edge XANES spectrum of Bi^{5+} species has a well-defined low energy feature

(Labelled A) that corresponds to a 2p→6s transition. [4] If valence transfer does occurs in these systems with increasing pressure, we will observe an increase in the intensity of this peak with the formation of Bi^{5+} (increase in the number of unoccupied 6s states). We will also measure the Ir L_3-edge and Ru K-edge XANES spectra. We have previously demonstrated for $Ba_3BiIr_2O_9$ [1] that the Ir L_3-edge absorption edge energy is sensitive to the oxidation state of Ir. The Ru K-edge edge energy shows similar shifts in energy as the oxidation state of Ru changes. [5] We anticipate decrease in the both the L_3-edge and Ru K-edge absorption edge energy at high pressure as the valence state of Ir/Ru changes from 4+ to +3.5+.



Beamline(s) and beam time requested with justification :

ID24 and BM23 are the only beamlines with the necessary energy ranges and ability to accept pressure cells (DAC or PE cell respectively). We will measure Bi L_3-edge and Ir L_3-edge and/or Ru K-edge XANES spectra for 3 samples: $Ba_3BiIr_2O_9$, $Ba_3BiRu_2O_9$ and mixed $Ba_3BiIrRuO_9$. Spectra will be collected from 0–10 GPa in ~1 GPa steps (11 spectra *per* edge). Oxidation state standards (~10 samples) will be measured at ambient pressure. 2x30 min spectra will be collected from ~200 eV below to ~300 eV above the edges. Assuming we can load each sample into its own cell so that pressure changes can be carried out offline, the total time required will be 1 h * 3 samples * 11 pressures * 2.5 edges = 3.5 days, or 4 days in total including oxidation state standards.

Results expected and their significance in the respective field of research :

Comparable pressure-induced valence transitions have only been observed in $LaCu_3Fe_4O_{12}$ [6] (between Cu and Fe) and $BiNiO_3$ (between Bi and Ni). [7] $Ba_3BiIr_2O_9$ and $Ba_3BiRu_2O_9$ appear to be unique cases involving 4*d* (Ru) or 5*d* (Ir) transition metals. Furthermore, $LaCu_3Fe_4O_{12}$ [8] and $BiNiO_3$ [9] both undergo analogous low-temperature and high-pressure transitions; whereas the low-temperature transition in $Ba_3BiIr_2O_9$ and $Ba_3BiRu_2O_9$ causes the opposite volume effect to the high-pressure one, and appears to be entirely unrelated. This is a surprising result, which we need to independently investigate and in greater detail *via* a high-pressure XANES experiment that can directly probe the valence states of Bi and Ir/Ru, prior to publication.

1) Miiller et al., *J Am Chem Soc* **134**, 3265-3270 (2012).
2) Miiller et al., *Phys Rev B* **84**, 220406R (2011).
3) Brese and O'Keeffe, *Acta Cryst B* **47**, 192-197 (1991).
4) Jian et al. *J Phys: Condens Matter* **18**, 8029-8036 (2006).
5) Arčon et al. *X-Ray Spectrom* **36**, 301-304 (2007).
6) Long et al., *Chem Mater* **24**, 2235-2239 (2012).
7) Azuma et al., *J Am Chem Soc* **129**, 14433-14436 (2007).
8) Long et al., *Nature* **458**, 60-64 (2009).
9) Azuma et al., *Nature Commun* **2:347**, 1361 (2011).