

An Unusual Charge Disproportionation Transition in a High-Valence Perovskite Ferrite $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$

Using a high-pressure synthesis method, researchers have now succeeded to make a new perovskite oxide $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ with an unusually high valence $\text{Fe}^{3.5+}$, which undergoes a temperature dependent charge disproportionation coupled to an insulator-to-insulator transition.

Charge density wave or charge-ordering transitions occur in a variety of quasi one-dimensional (1D), quasi two-dimensional (2D) and three-dimensional (3D) materials. These transitions are often directly associated with an effective charge disproportionation across the transition, *i.e.* a single integral valence metal atom M^v changes to typical mixed valency in the form of $\text{M}^{v+\delta}$ and $\text{M}^{v-\delta}$, where M is the metal atom, v is the integral valency and δ is the change in valency defining the disproportionation. In typical charge-ordering transitions, one expects a metal-insulator transition to accompany the charge-disproportionation, as in the transition metal dichalcogenide system 1T-TiSe₂.¹ In this highlight, we discuss an unusual charge disproportionation which is linked to an insulator-to-insulator transition and the high valence of Fe in the perovskite oxide $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$.

In a very interesting study carried out by Yuichi Shimakawa (Kyoto University) and his collaborators from Japan, Taiwan and the United Kingdom, it was shown that a three-dimensional perovskite $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ containing an unusually high valence of $\text{Fe}^{3.5+}$ could be synthesized by using a high pressure method.² The authors carried out a combination of synchrotron X-ray diffraction and neutron powder diffraction studies (Fig. 1) to establish the rhombohedral structure of $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$, crystallizing in the space group R3c (No.167).

The occupancy of oxygen sites could be fixed to one in the final refinement, indicative of negligible oxygen vacancies in the material, and this helps to provide an accurate determination of valency. The authors calculated the bond valence sum (BVS) from the measured Fe-O bond lengths and the results indicated a BVS value of 3.4+, consistent with a nominal valence of $\text{Fe}^{3.5+}$. The authors then used Mössbauer spectroscopy to measure the valence state of Fe and confirmed the unusual high valence of $\text{Fe}^{3.5+}$ (Fig. 2). Since Mössbauer spectroscopy can probe charge fluctuations on a time scale of $\sim 10^{-7}$ sec, the authors carried out temperature dependent Mössbauer spectroscopy studies and discovered that $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ undergoes a charge disproportionation which is described by the valence transition given by (Fig. 3): $\text{Fe}^{3.5+} \rightarrow 0.75 \text{Fe}^{3.0+} + 0.25 \text{Fe}^{5+}$.

Surprisingly, although a clear charge disproportionation could be measured, the temperature dependent diffraction measurements showed no apparent structural transition as a function of temperature. The compound $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ can be simply considered to be a Bi^{3+} doped SrFeO_3 in which the doped electrons result in forming $\text{Fe}^{3.5+}$ due to Bi^{3+} substitution on Sr^{2+} sites. The structural analysis showed that the substitution causes a significant rhombohedral distortion with the Fe-O-Fe angle changing to 165.5° compared to 180.0° in the cubic SrFeO_3 . The reduced Fe-O-Fe angle causes a conduction band narrowing. Furthermore, a negative

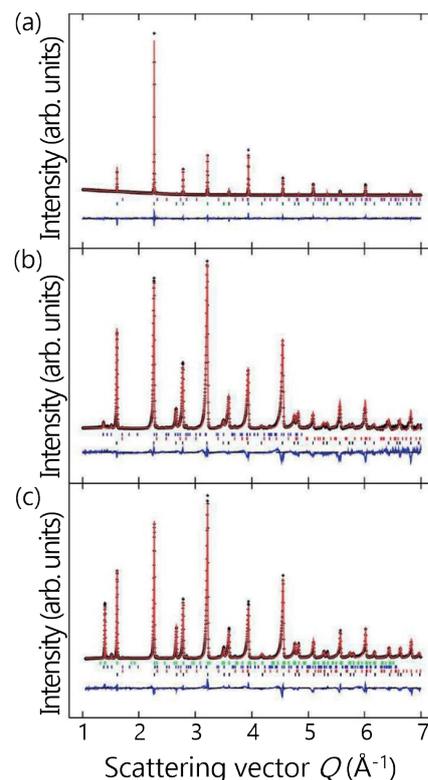


Fig. 1: Rietveld refinement profiles for $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$. (a) Room-temperature synchrotron X-ray diffraction data. The bottom and top vertical bars respectively indicate the diffraction peak positions for $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ and impurity Fe_2O_3 . (b) Room-temperature neutron powder diffraction data. The bottom vertical bars indicate the nuclear diffraction of $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$. The middle and top vertical bars respectively show the nuclear and magnetic reflections of impurity Fe_2O_3 . (c) NPD data collected at 4 K. The bottom and top vertical bars respectively show the nuclear and magnetic reflections of $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$. The third and second vertical bars respectively show the nuclear and magnetic reflections of impurity Fe_2O_3 . [Reproduced from Ref. 2]

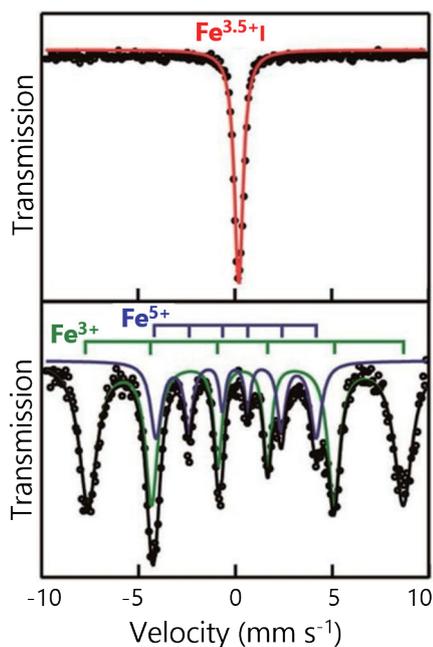


Fig. 2: Mössbauer spectra of $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ at room temperature (top panel) and 4 K (bottom panel). The black circles show experimental data, and the solid lines show the fittings. [Reproduced from Ref. 2]

chemical pressure effect occurs due to Bi^{3+} ions (ionic radius 1.03 Å) occupying the A-site compared to the larger Sr^{2+} ions (ionic radius 1.18 Å) is at play in $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$. This is consistent with the observed low BVS for Bi and is expected to suppress the intermetallic charge transfer transition in $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$. Indeed, this turned out to be the case, because no transition to the metallic phase could be seen in the electrical resistivity as a function of temperature (Fig. 4). The

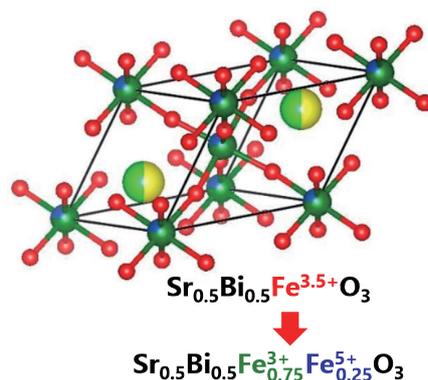


Fig. 3: Rhombohedral unit cell of $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ does not change across the charge disproportionation transition, given by $\text{Fe}^{3.5+} \rightarrow 0.75 \text{Fe}^{3+} + 0.25 \text{Fe}^{5+}$, which occurs at a temperature, $T = 230 \text{ K}$. [Reproduced from Ref. 2]

electrical resistivity only showed a small deviation from a typical activated behavior below 230 K, consistent with a small anomaly seen also in the magnetic susceptibility behavior. The authors thus concluded that the charge disproportionation transition occurs at about 230 K, and it is coupled to an insulator-to-insulator transition, in contrast to a metal-insulator transition seen in typical charge density wave systems.¹ The authors could thus show that $\text{Sr}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ represents a unique case of charge disproportionation coupled to an insulator-to-insulator transition driven by conduct ion band narrowing.² (Reported by Ashish Chainani and Hwo-Shuenn Sheu)

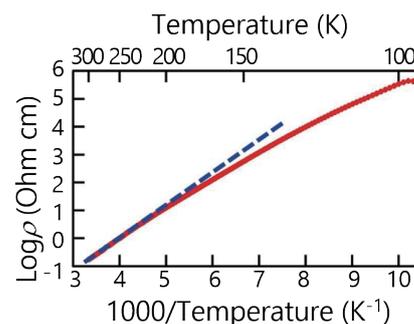


Fig. 4: Temperature dependence of the electrical resistivity as a plot of $\log \rho$ vs. $1000/T$. The blue dashed line represents a typical semiconductor behavior given by an Arrhenius equation. The deviation from Arrhenius behavior was taken as the transition temperature $T = 230 \text{ K}$. [Reproduced from Ref. 2]

This report features the work of Yuichi Shimakawa and his co-workers published in *Inorg. Chem.* **57**, 843 (2018).

TPS 09A Temporally Coherent X-ray Diffraction

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References

1. T. Rohwer, S. Hellmann, M. Wiesenmayer, C. Sohrt, A. Stange, B. Slomski, A. Carr, Y. Liu, L. M. Avila, M. Kalläne, S. Mathias, L. Kipp, K. Rossnagel, M. Bauer, *Nature* **471**, 490 (2011).
2. P. Xiong, F. D. Romero, Y. Hosaka, H. Guo, T. Saito, W.-T. Chen, Y.-C. Chuang, H.-S. Sheu, G. McNally, J. P. Attfield, Y. Shimakawa, *Inorg. Chem.* **57**, 843 (2018).

Highlight from the Cold Neutron Triple Axis Spectrometer SIKA in 2018

The NSRRC neutron group has ran a user program at the cold triple axis spectrometer SIKA since July 2015 at ANSTO in Australia. Here are some results from 2018 in a hope to highlight to NSRRC users, that neutrons and SIKA can be useful to them in the coming years.

The triple axis spectrometer is one of most versatile neutron scattering instrument. With SIKA,¹ scientists have the option to measure elastic scattering and inelastic neutron scattering. Here are three successful projects