LS-HS Spin Transition in $BiCoO_3$ Induced by Pressure

Masaichiro Mizumaki[1], Kengo Oka[2], Naoki Ishimatsu[3], Nozomu Hiraoka[4], Wei-Tin Chen[5], and Masaki Azuma[2]

[1]Japan Synchrotron Radiation Research Institute, Sayo, Japan
[2]Institute for Chemical Research, Kyoto University, Uji, Japan
[3]Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Japan
[4]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
[5]Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Edinburgh, UK

Co^{3+} is known to exhibit spin state change. Co^{3+} in perovskite $LaCoO_3$ has nonmagnetic low-spin state as a ground state and intermediate-spin state with S = 1 and high-spin state with S = 2 as thermally excited states. Newly synthesized $BiCoO_3$ has, on the other hand, high-spin Co^{3+} down to the lowest temperature. We recently found that $BiCoO_3$ exhibits a pressure induced structural transition from tetragonal $PbTiO_3$ type structure to orthorhombic $GeFeO_3$ type structure by synchrotron radiation X-ray diffraction study [1]. Surprisingly, the unit cell volume decreases by 10% at this transition. Considering the ionic radii of low-spin and high-spin Co^{3+}, this volume change suggests the pressure induced spin-state transition. The aim of this study is to determine the spin-states of Co^{3+} in the ambient-pressure and the high-pressure phases of $BiCoO_3$. In order to investigate a spin state, we measure Co Kβ emission lines excited by X-rays with E=10 keV. It is well-known that the intensity ratio of Kβ' to $K\beta_{1,3}$ reflect the spin state. When this intensity ratio is high, the spin state is the low-spin state. Therefore, we use this intensity ratio as a probe of the spin state and measure Kβ lines under P = 4.8 GPa and ambient pressure.

$BiCoO_3$ is a quite rare material that preserves the high-spin Co^{3+} down to the lowest temperature. The investigation of the spin state change is quite important. We found that the structural change with volume decrease was thermally induced at 1 GPa. This phenomenon can be called unusually large negative thermal expansion. Unfortunately, this compound decomposes at high temperature before the structural change at the ambient pressure. If it is possible to bring this volume change to the ambient pressure by chemical modification, this material is technologically quite useful. For such materials design, it is quite important to clarify the origin of large volume change which we suppose a spin state change.

Figure 1 shows Co Kβ emission spectra under P = 4.8 GPa and ambient pressure. Both spectra consisits of two peaks. The pek at lower energy corresponds to Kβ' and the one at higher energy corresponds to $K\beta_{1,3}$. The intensity ratio of Kβ' to $K\beta_{1,3}$ decreases with increasing pressure. This result means that the transition from high-spin to low-spin state of Co^{3+} ions induced by pressure.

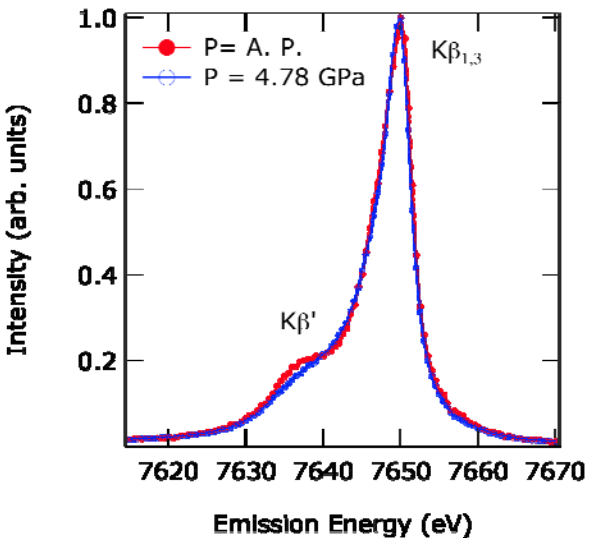

Fig. 1: Co Kβ emission lines of $BiCoO_3$ under under P = 4.8 GPa and ambient pressure.

Reference

[1] A. A. Belik *et al.*, Chemisry of Materials **18,** 798 (2006).