The structural and electronic properties of BiCoO$_3$ under high-pressure have been investigated. X-ray and neutron diffraction studies indicate that the structure changes from a polar PbTiO$_3$ to a centrosymmetric GdFeO$_3$ type above 3 GPa with a large volume decrease of 13%. The first order transition is accompanied by a drop in electrical resistivity and a spin-state transition. X-ray emission spectra of Co K$_\beta$ lines measured at ambient-pressure and 4.8 GPa indicated the spin-state change of Co ions.

The perovskite BiCoO$_3$, a candidate lead-free piezoceramics compound, has received a lot of attention not only in the application but also in the basic science. In the basic science field, BiCoO$_3$ is interesting because of the spin state of Co$^{3+}$ ions. BiCoO$_3$ shows C-type antiferromagnetic ordering below the Néel temperature of 420 K. The ordered moment at ambient pressure (AP) is 3.24 $\mu_B$ indicating that Co$^{3+}$ is in the high-spin (HS) $d^6(t_{2g}^4e_g^2)$ state. Recently, we proposed an expectation that the HS $d^6$ electronic configuration of Co$^{3+}$ ions promotes the structural distortion of BiCoO$_3$ and intermediate-spin (IS) or low-spin (LS) state of Co$^{3+}$ appears in the paraelectric phase. This expectation is supported by the theoretical calculations proposed that BiCoO$_3$ in the paraelectric cubic phase is denser than the tetragonal AP phase and the spin state Co ions is LS.$^2$ These predictions suggest the possibility that LS state of Co ions appears under high-pressure, that is to say, pressure-induced spin-state transition occurs. In order to elucidate the spin-state of Co ions, we have carried out the X-ray emission spectroscopy measurements at ambient-pressure and at 4.8 GPa.

The XES measurements were carried out at the Taiwan IXS Beamline BL12XU at SPring-8 in Japan. The sample was put in a DAC with Daphne oil 7373 as a pressure medium. The pressure inside the DAC was determined by measuring the wavelength of ruby fluorescence. A total energy resolution of the measurement system was set to 1.1 eV. The incident beam was monochromatized by Si 111 double crystal monochromator and then focused into a spot of $22 \times 50 \, \mu m^2$ at the sample position by a Kirkpatrick-Baez mirror. The emitted X-rays were analyzed using Ge 444 spherically bent analyzer of 1 m radius. The energy spectra were measured by rotating the analyzer in the Bragg mode, synchronized with the detector motion so as to maintain the Roland condition. The incident X-ray energy was set to 11.0 keV and the emission energy was tuned from 7615 to 7670 eV corresponding to Co K$_{\beta1,3}$ and K$_{\gamma}$ emission lines. The XES spectra were normalized to the spectra area. A polycrystalline BiCoO$_3$ sample was prepared at 6 GPa and 1200 °C with a cubic anvil-type high-pressure apparatus, as reported in Ref. 3.

**Beamline**
SPring-8 BL12XU

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Figure 1 shows the XES spectra of Co Kβ emission lines at room temperature at ambient pressure and at 4.8 GPa. Both spectra show a main peak located at 7650 eV, referred to as the Kβ1,3 line. At ambient pressure, the XES spectra has a satellite peak at 7037 eV denoted Kβ' line. On the other hand, the Kβ' is less pronounced in the spectrum at 4.8 GPa. The Kβ spectra have been interpreted using atomic multiplet calculations. It is widely accepted that the spectral shape of Kβ emission is dominated by the final state interaction between the 3p core hole and the electron of the partially filled 3d shell. The simplified picture does point out the qualitative changes expected for the 3d electrons going from HS to LS or IS states, namely, smaller energy splitting between the main peak and the satellite as well as a reduction in the satellite to main peak intensity ratio. Therefore, experimental results indicated that the spin state of Co3+ ions was changed by applying pressure.

In order to understand semi-quantitatively this result, the analysis, using the relation between DS (difference of spin number) and IAD (the integrals of the absolute values of the difference spectra) found by Vanko, applied to our experimental spectra. According to Vanko, ΔS is proportional to IAD, IAD = 0.049 for ΔS = 1, 0.084 for ΔS = 3/2, and 0.12 for ΔS = 2. We calculated the IAD value using ∑|IAP − IHP| in the range of 7615 - 7670 eV, where IAP and IHP are the normalized intensities of XES spectra for AP and HP (P = 4.78 GPa), respectively. The value of IAD is 0.041 for BiCoO3. This suggests an IS state for the Co3+ ions in HP phase. This result is in contrast to the result of the structural analysis suggesting the LS state for HP phase. The reason for this discrepancy is not clear at the present stage.

In conclusion, we have studied the pressure-induced spin-state transition of BiCoO3 with high-resolution X-ray emission spectroscopy. The pressure induced XES spectral change of Co Kβ indicated that the spin-state of Co3+ ions of BiCoO3 changed from HS in AP phase to IS in HP phase.

References

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