

## Melting of Pb charge glass and simultaneous Pb-Cr charge transfer in $\text{PbCrO}_3$ as the origin of volume collapse

Charge degrees of freedom of transition metal ions gives rise to various fascinating properties of transition-metal compounds, such as superconductivity or magnetoresistance. The ordering or disproportionation of charges in systems with integer or half-integer charge number per atom, such as  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  or  $\text{CaFeO}_3$ , causes metal-insulator transitions. These can be regarded as the crystallization of charges. The insulating state tends to have a glassy nature when randomly located dopants are introduced. A charge cluster glass state owing to geometric frustration arising from a triangular arrangement without randomness was recently observed in an organic, compound  $\theta$ -(BEDT-TTF) $_2$ RbZn(SCN) $_4$ , and is attracting significant attention.

Bi and Pb are the main group elements, but they have a charge degree of freedom depending on  $6s^0$  and  $6s^2$  electronic configurations. These are so-called valence skippers because the  $6s^1$  state is prohibited and charge disproportionation of Bi is found in perovskites  $\text{Ba}^{2+}\text{Bi}^{3+}_{0.5}\text{Bi}^{5+}_{0.5}\text{O}_3$  and  $\text{Bi}^{3+}_{0.5}\text{Bi}^{5+}_{0.5}\text{Ni}^{2+}\text{O}_3$ .  $\text{PbCrO}_3$  has long been regarded as a perovskite compound with a  $\text{Pb}^{2+}\text{Cr}^{4+}\text{O}_3$  oxidation state, like metallic  $\text{SrCrO}_3$  [1]. However, despite the fact that  $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$  have similar ionic radii and that  $\text{PbCrO}_3$  and  $\text{SrCrO}_3$  have the same cubic structure with  $Pm\bar{3}m$  symmetry,  $\text{PbCrO}_3$  is an antiferromagnetic insulator with an enhanced lattice constant of 4.01 Å, which is 4.8% larger than that of  $\text{SrCrO}_3$ . Using synchrotron X-ray scattering and electronic microscopes, we have unraveled a mystery that has eluded researchers for 50 years.  $\text{PbCrO}_3$  was found to be  $\text{Pb}^{2+}_{0.5}\text{Pb}^{4+}_{0.5}\text{Cr}^{3+}\text{O}_3$  where  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  ions forms a distorted “charge glass” state [2].

The Pb-4f hard X-ray photoemission (HAXPES) spectrum for  $\text{PbCrO}_3$  collected at beamline BL47XU is shown in Fig. 1. Both the  $4f_{5/2}$  and  $4f_{7/2}$  peaks, which are split by the spin-orbit interaction, are doubles and asymmetric with shoulders at higher binding energies, indicating the coexistence of two valence states, namely,  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$ . The valence state of  $\text{PbCrO}_3$  is thus determined to be  $\text{Pb}^{2+}_{0.5}\text{Pb}^{4+}_{0.5}\text{Cr}^{3+}\text{O}_3$ .  $\text{Cr}^{3+}$  with the  $t_{2g}^3$  electronic configuration, which accounts for explaining the large lattice constant and insulating nature of  $\text{PbCrO}_3$ .

Next the local structure of  $\text{PbCrO}_3$  was investigated. We performed the pair distribution function (PDF) analysis of synchrotron X-ray total scattering data collected at BL22XU, as shown

in Fig. 2(a), assuming an ordered model with the  $3a_0 \times 3a_0 \times 3a_0$  superstructure suggested by the diffuse scattering in electron diffraction and synchrotron X-ray powder diffraction data collected at BL02B2. The 27 Pb sites are divided into 2 groups, A and B with the rock-salt-type arrangement, as shown in Fig. 2(b), corresponding to  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  or vice versa, as clarified by HAXPES. Then, longitudinal wave-type shift of the Pb positions was applied to both sublattices. The Pb positions were constrained so that these form sine waves in  $a$ ,  $b$ , and  $c$  directions. Large shifts of the Pb positions were indeed observed in the high-angle annular dark-field (HAADF) STEM image (Fig. 2(c)). The distribution of the Pb-Pb lengths, 3.4–4.2 Å, agrees quite well with each other. It should be noted that the numbers of  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  are different in this model, 14:13 or vice versa. Furthermore, there are A-A or B-B arrangements at the interface between  $3a_0 \times 3a_0 \times 3a_0$  cells. The long-range ordering of  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  is therefore prohibited. Taking into account the above results, one can conclude that  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  form a glassy structure, namely, charge glass.

Finally, we investigated the pressure effect on the structure and resistivity of  $\text{PbCrO}_3$ . The unit cell volume calculated from the peak positions of energy-dispersive SXRD (collected at BL14B1) is plotted in Fig. 3 as a function of pressure. It decreases by 2.7%, corresponding to a volume collapse of 7.8% at 2.5 GPa, as reported earlier [3]. The electrical resistivity suddenly drops at the corresponding pressure.

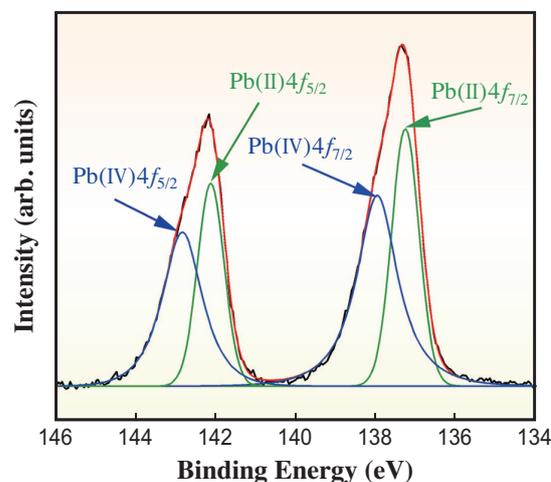


Fig. 1. Pb-4f core-level XPS spectrum of  $\text{PbCrO}_3$  with the fitted results. The black and red lines are observed spectra and total fitted spectrum, respectively.

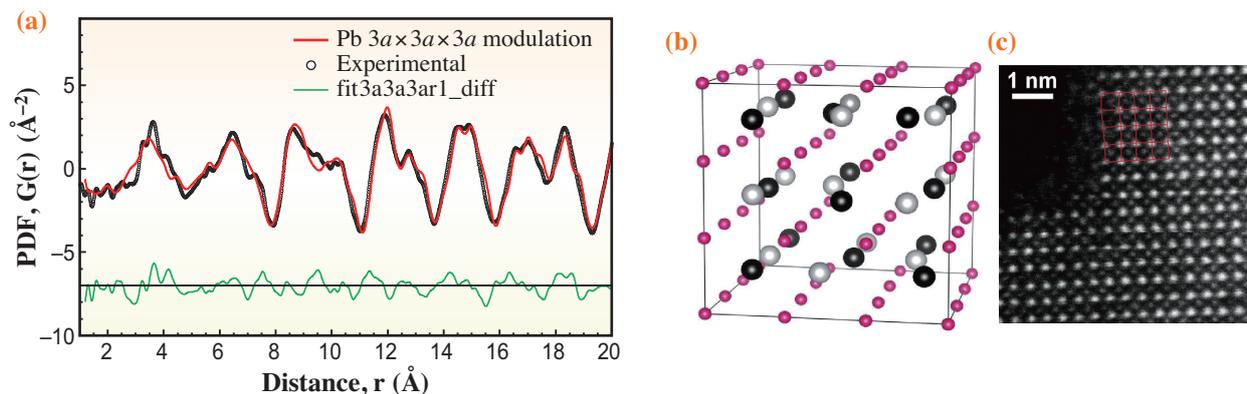


Fig. 2. (a) Observed and calculated PDF of an ordered model with  $3a_0 \times 3a_0 \times 3a_0$  superstructure. (b) The refined crystal structure of the ordered model with  $3a_0 \times 3a_0 \times 3a_0$  superstructure. The pink atoms are Cr and the other atoms are Pb. (c) HAADF STEM image viewed along the perovskite [001] zone axis. The lateral shift of Pb positions is evident.

The observed volume collapse and simultaneous insulator-to-metal transition can be explained by assuming a pressure-induced intermetallic charge transfer between  $Pb^{4+}$  and  $Cr^{3+}$  ions and a  $Pb^{2+}Cr^{4+}O_3$  valence state for the high-pressure phase (see insets of Fig. 3).

In conclusion, we showed that  $PbCrO_3$  has a  $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$  valence state with a glassy distribution of  $Pb^{2+}$  and  $Pb^{4+}$  ions and that intermetallic charge transfer between  $Pb^{4+}$  and  $Cr^{3+}$  induced by the application of pressure leads to the volume collapse and the insulator-to-metal transition.

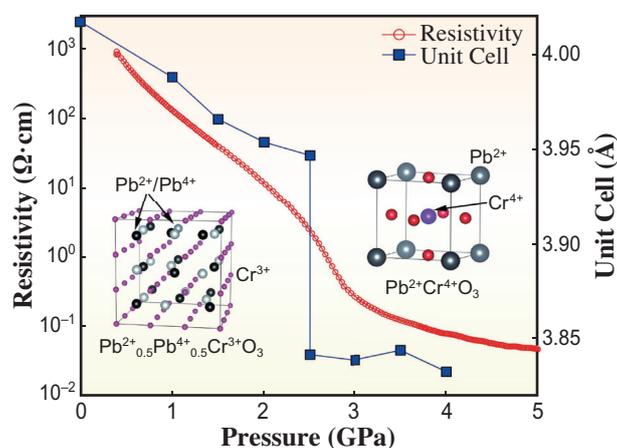


Fig. 3. Pressure evolutions of crystal structure, electrical resistivity and lattice constant of  $PbCrO_3$ . Abrupt decreases in the lattice constant and resistivity owing to the transition from  $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$  to  $Pb^{2+}Cr^{4+}O_3$  are evident.

Runze Yu\* and Masaki Azuma

Materials and Structures Laboratory,  
Tokyo Institute of Technology

\*E-mail: physyu@hotmail.com

### References

- [1] W.L. Roth *et al.*: J. Appl. Phys. **38** (1967) 951.
- [2] R. Yu, H. Hojo, T. Watanuki, M. Mizumaki, T. Mizokawa, K. Oka, H.J. Kim, A. Machida, K. Sakaki, Y. Nakamura, A. Agui, D. Mori, Y. Inaguma, M. Schlipf, K. Rushchanskii, M. Ležaić, M. Matsuda, J. Ma, S. Calder, M. Isobe, Y. Ikuhara and M. Azuma: J. Am. Chem. Soc. **137** (2015) 12719.
- [3] W.S. Xiao *et al.*: Proc. Natl. Acad. Sci. **107** (2010) 14026.