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Pressure-Induced Valence Change and Semiconductor−Metal Transition in $PbCrO_3$

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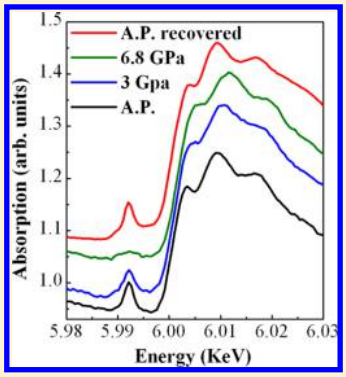
ABSTRACT: Pressure-induced valence change and semiconductor−metal transition were revealed in perovskite compound $PbCrO_3$ by X-ray absorption spectroscopy (XAS) and resistance measurements, respectively. The Cr $L_{2,3}$ edge XAS spectra indicate a charge disproportionation of Cr ($3Cr^{4+} \rightarrow 2Cr^{3+} + Cr^{6+}$) at ambient pressure, suggesting that the ambient-pressure phase of $PbCrO_3$ has complex local structure and cannot be explained using the simple cubic perovskite structure (*Pm*-3*m*). Upon compression up to 4.2 GPa, Cr^{3+} and Cr^{6+} ions were converted to Cr^{4+} via charge transfer, associated with semiconductor−metal transition. The high-pressure metal phase is determined to be cubic perovskite structure (*Pm*-3*m*). Compared with the previous X-ray diffraction experiment, the large volume collapse (∼9.8% at 1.6 GPa) may be related to valence change and semiconductor−metal transition.



■ INTRODUCTION

The chromate perovskites $RCrO_3$ (R = Sr, Ca), which present the Cr^{4+} ion in octahedral coordinations, have been much studied due to their anomalous electronic and magnetic states for the past few years.[1−5] $PbCrO_3$ was first synthesized at high pressures and high temperatures in the late 1960s.[6,7] Previous X-ray and neutron diffraction experiments showed that $PbCrO_3$ has a cubic perovskite structure with anomalously large volume.[6−8] Its lattice parameter (4.00 Å) is much larger than cubic $SrCrO_3$ (3.82 Å) even though the atomic radius of Sr (1.44 Å) is similar to that of Pb (1.49 Å).[1] $PbCrO_3$ was considered as a perovskite compound with the Cr^{4+} ion occupying the octahedral site, coordinated with six oxygen atoms.[6,7,9] However, recent electron diffraction and high-resolution microscopy study revealed that the microstructure of $PbCrO_3$ is a rather complex perovskite with superlattice structure of $a_p \times 3a_p \times (14-18)a_p$, where a_p is the lattice constant of the cubic perovskite structure.[10] On the other hand, Ganesh et al. suggested a tetragonal structure which is more stable than cubic perovskite structure at ambient pressure for $PbCrO_3$ from density functional theory (DFT)+*U* calculations.[11] In the first-principle local density approximation (LDA)+*U*, Wang et al. indicated a mixture of $PbCrO_3$−$CrPbO_3$ at ambient pressure.[12] In the mixture model of $PbCrO_3$−$CrPbO_3$, CrO_6 in $CrPbO_3$ is converted to PbO_6. Cr ions occupy two different sites in the structure. Theoretical calculation shows that the cubic perovksite structure $PbCrO_3$ should be a conductor,[13,14] whereas experimental results demonstrated that $PbCrO_3$ is a semiconductor.[8,15,16] Therefore, the structure of $PbCrO_3$ at ambient conditions is still controversial. Here, we report a charge disproportionation phenomenon in $PbCrO_3$ and bring a new way for understanding this issue.

Recently, it was surprisingly found by Xiao et al. that $PbCrO_3$ underwent an isostructural phase transition with large volume collapse of approximate 9.8% at 1.6 GPa. This is one of the largest volume collapses known for transition-metal oxides.[17] The isostructural phase transitions induced by high pressures were usually considered to be originating from the electronic structural change.[18−20] However, they considered the high-pressure phase transition of $PbCrO_3$ not to be related with any change of electronic state but could be related to the abnormally large volume and compressibility. In contrast, Ganesh et al. attributed the large volume collapse to the first-order transition from a tetragonal structure to a cubic phase in the density functional theory (DFT)+*U* calculation,[11] whereas Wang et al. indicated that the large volume change stems from the R3 phase of $PbCrO_3$−$CrPbO_3$ to the cubic perovskite $PbCrO_3$ transition which is accompanied by an insulator−metal transition.[12] In these studies, the structure of the ambient-pressure (AP) phase remains controversial, while theoretical and experimental results supported that the high-pressure (HP) phase has the cubic perovskite structure. Experiments, especially the X-ray absorption spectroscopy (XAS) and

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resistance measurements which can provide information on valence change and electron transport, are required to study the local structure of the AP phase, relationship of the AP and HP phases, and mechanism of large volume collapse in the phase transition.

In this paper we investigate the change of the electronic state of $PbCrO_3$ at different pressures by XAS. Additionally, resistance measurements were performed to investigate the change of the electron transport property at high pressure. A pressure-induced valence change and a pressure-induced semiconductor−metal transition were observed. We analyzed the unusual properties of AP phase $PbCrO_3$ and attributed the large volume collapse of phase transition to the charge transfer between chromium ions associated with semiconductor−metal transition.

EXPERIMENTAL SECTION

The $PbCrO_3$ samples were synthesized from high purity yellow PbO and black CrO_2 powder with a cubic anvil-type high-pressure apparatus. The mixture was treated at 5.8 GPa and 1200 °C for 30 min and quenched to room temperature prior to the release of pressure. Powder X-ray diffraction experiments (λ = 0.6199 Å) for sample identification were carried out in the 4W2 beamline at Beijing Synchrotron Radiation Facility (BSRF), China. The XRD results are consistent with the cubic perovskite structure and space group *Pm*-3*m*, and the lattice constant (a = 4.005 Å) is in accordance with previous reports.[6−8,16,17] A small number of weak peaks from impurities can also be seen (Figure 1). The Cr $L_{2,3}$ edge XAS

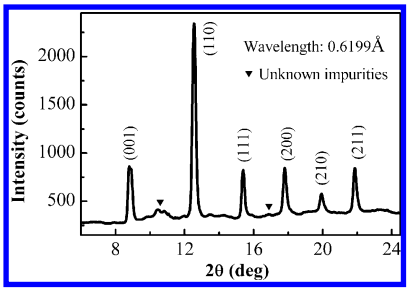

Figure 1. Powder X-ray diffraction pattern of the $PbCrO_3$ sample used for our experiments. These diffraction experiments (λ = 0.6199 Å) were carried out in the 4W2 beamline at Beijing Synchrotron Radiation Facility (BSRF), China.

measurements were performed in total electron yield (TEY) mode at the beamline 4B9B of BSRF. The $PbCrO_3$ and reference samples were measured under an ultrahigh vacuum of ~10^{-10} Torr at room temperature. The XAS measurements at the Cr K edge under various pressures were carried out at the beamline 1W1B of BSRF. The diamond anvil cell (DAC) with a pair of perforated diamond anvils[21] was used to lessen the absorption of diamond and apply the pressure up to 7.6 GPa. The powdered sample and amorphous B powder as a pressure medium were mixed and steeled inside the DAC. A polycapillary X-ray optic was used to focus the X-ray and reduce the disturbance from the diffraction and absorption of diamond.[22] The high-pressure experiments for resistance measurement were carried out using DAC with culets of 500 μm. A small piece of impacted $PbCrO_3$ powder was loaded into the sample hole of ~100 μm in the stainless steel gasket. Four electrodes were attached to the sample and insulated from the gasket. No extra pressure medium was used. The pressures in all experiments were determined by measuring the wavelength of ruby fluorescence[23] and measured at room temperature.

RESULTS AND DISCUSSION

The 3d transition-metal $L_{2,3}$ absorption edges are from the 2p → 3d transition and sensitive to the valence state.[24] The chemical shift (about 0.7 eV toward higher energy for one valence increase) between the different Cr oxidation states is clearly visible at the $L_{2,3}$ edges.[25] Figure 2(a) shows the Cr $L_{2,3}$

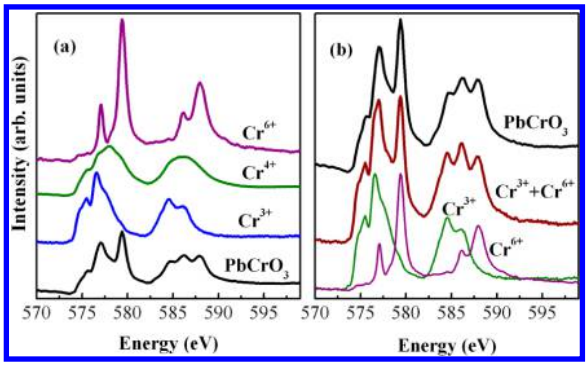

Figure 2. (a) Cr $L_{2,3}$ edge XAS spectra for $PbCrO_3$ and reference samples ($PbCrO_4$, CrO_2, Cr_2O_3). (b) Spectra of $PbCrO_3$ compared to the weighted sum of spectra of Cr^{3+} and Cr^{6+}.

edge XAS spectra of AP phase $PbCrO_3$ (under ultrahigh vacuum actually) and reference samples ($PbCrO_4$, CrO_2, Cr_2O_3). The peaks centered at 575.6 and 579.4 eV in the L_3 edge of $PbCrO_3$ are aligned with the Cr^{3+} (Cr_2O_3) and Cr^{6+} ($PbCrO_4$) reference samples, respectively, and the same as the peaks centered at 584.6 and 588 eV in the L_2 edge. The absence of Cr^{4+} peaks and the "0.7 eV principle" reveal that the Cr ions maybe are Cr^{3+} and Cr^{6+}, rather than Cr^{4+}. The weighted sum of spectra of Cr^{3+} and Cr^{6+}, in a ratio of two to one, agrees with the experimental spectra of $PbCrO_3$ well [Figure 2(b)]. This shows that the Cr ions dissociate into Cr^{3+} and Cr^{6+} via charge transfer in AP phase $PbCrO_3$ ($Pb^{2+}Cr^{3+}{}_{2/3}Cr^{6+}{}_{1/3}O_3$), and AP phase $PbCrO_3$ has a complex structure which cannot be described by a simple cubic perovskite structure.

The valence dissociation is also supported by the bond valence model which can provide information on the valence state of the AP and HP phase $PbCrO_3$. The bond valence sum (BVS) relates the metal valence V to the metal oxygen distance r_i.[26] For each central atom

$$V = \sum s_i, \quad s_i = \exp[(r_0 - r_i)/B]$$

where B is a constant of 0.37 Å and r_0 is the standard parameter for Sr^{2+}, Ca^{2+}, Pb^{2+}, and Cr^{4+}.[26,27] Table 1 shows the calculation results for $SrCrO_3$, $CaCrO_3$, and AP and HP phase $PbCrO_3$. The structure information on $SrCrO_3$, $CaCrO_3$, and HP phase $PbCrO_3$ is from previous research papers.[1,17] The BVSs for the

Table 1. Bond Valence Sums[a] for $SrCrO_3$, $CaCrO_3$, AP Phase $PbCrO_3$, and HP Phase $PbCrO_3$

$SrCrO_3$		$CaCrO_3$		AP phase		HP phase	
Cr	Sr	Cr	Ca	Cr	Pb	Cr	Pb
4.14	2.48	4.19	2.32	3.25	1.73	4.01	2.33

[a] $V = \sum s_i$, $s_i = \exp[(r_0 - r_i)/B]$. Values calculated using r_0 = 2.118 for Sr^{2+}, 1.967 for Ca^{2+}, 2.112 for Pb^{2+}, and 1.773 for Cr^{4+}.

HP phase are similar to that for the Cr^{4+} perovskites $SrCrO_3$ and $CaCrO_3$, which confirm that the HP phase is $Pb^{2+}Cr^{4+}O_3$. In contrast, the BVSs for the AP phase are significantly smaller as the bond distance is enhanced. This deviation implies that the simple cubic structure with Cr^{4+} cannot describe the AP phase exactly, which agrees with the XAS spectra. The two different Cr sites model of $PbCrO_3$−$CrPbO_3$ has been suggested for the AP phase;[12,17] however, the details of local structure in AP phase $PbCrO_3$ are still ambiguous, and more study is needed.

Since Cr atoms may have different valence states in the AP and HP phase, pressure-induced valence change could be directly observed during compression. To identify the valence change of Cr induced by pressure, XAS experiments on the Cr K absorption edge were carried out. Figure 3 shows the Cr K edge XAS spectra of $PbCrO_3$ collected at room temperature and different pressures. There are two obvious differences between the AP and HP (6.8 GPa) phases: the pressure-induced shift of the absorption edge energy (E_0) and the disappearance of the pre-edge peak. E_0 is a good measure of the Cr valence change. E_0 of the Cr K edge has been reported to be linearly dependent on the Cr valence.[28] The pressure-induced valence change is indicated by the shift of the pressure dependence of E_0 in Figure 4, which was determined from the maximum position of the first derivative of the observed XAS spectra. The detected about 0.8 ± 0.2 eV E_0 shift from the AP phase to the HP phase indicates the increase in Cr valence together with structural phase transition. As mentioned above, all the previous studies support the cubic perovskite structure for HP phase $PbCrO_3$ where Cr ions are tetravalent. This means that the application of pressure leads to the transition of Cr^{3+} to Cr^{4+} by charge transfer. Additionally, the Cr^{6+} ions should also change to Cr^{4+} during compression since the AP phase includes Cr^{3+} and Cr^{6+} ions indicated by the Cr $L_{2,3}$ edge spectra. The pre-edge peak has been assigned as the 1s → 3d transition. This transition is strictly dipole forbidden in the HP phase which contains regular octahedral CrO_6 units, and the strong pre-edge peak at ambient pressure indicates that the symmetry of the ligands is lowered.[29] The pre-edge peak for Cr^{3+} with six oxygen coordinations is quite weak, so the strong feature can be considered as the fingerprint of Cr^{6+}. Upon compression, the pre-edge peak decreases in relative intensity and almost disappears at 6.8 GPa, indicating the valence change of Cr^{6+} to Cr^{4+}.

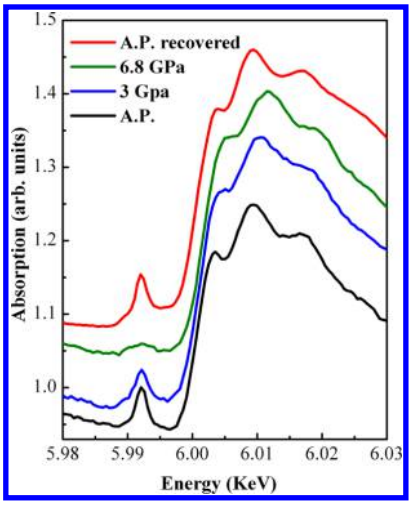

Figure 3. Cr K edge XAS spectra for $PbCrO_3$ at various pressures. The pressure-induced shift of the absorption edge energy and the disappearance of the pre-edge peak can be observed.

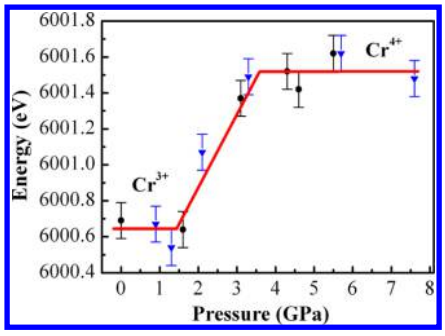

Figure 4. Pressure dependence of absorption edge energy around Cr K XAS spectra for $PbCrO_3$. The circle and triangle indicate separate experiments. The lines are guides to the eyes.

The valence change could be associated with the change of the electron transport properties. Therefore, we further performed the resistance measurement at pressures, as shown in Figure 5. Resistance at room temperature has a steep drop by 3 orders of magnitude in the pressure range of AP to 4.2 GPa. Above 4.2 GPa the resistance of the HP phase changes tinily. The data of temperature-dependent resistance collected at ambient pressure and 8.2 GPa (HP) are also shown in Figure 6. As theory calculations have predicted,[11,12] metallic conductivity of the HP phase $PbCrO_3$ is clearly visible in Figure 6(a). However, then the AP phase $PbCrO_3$ exhibits a semiconducting behavior in the temperature range between 195 and 300 K (see Figure 6(b)), which agrees with the results previously reported.[8,15,16] As plotted in the inset of Figure 6(b), the resistance in this range can be described by the activation law

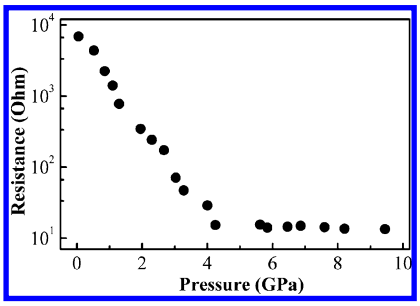

Figure 5. Pressure dependence of resistance of $PbCrO_3$ at room temperature. Resistance has a steep drop by 3 orders of magnitude.

$$R = R_0 \exp[\Delta/(2k_B T)]$$

with different activation energy $\Delta_1 \sim 0.47$ eV and $\Delta_2 \sim 0.24$ eV. R_0 is constant, and k_B is the Boltzmann constant. This abnormal change of activation energy at temperature around 213 K was also observed by Arévalo-López et al. with different values (0.11−0.26 eV at 245 K).[15] The results of activation energy, 0.27 and 0.5 eV, were also reported by different researches.[8,16] These can unambiguously prove that the $PbCrO_3$ causes a pressure-induced semiconductor−metal transition,[30] in agreement with Wang's theoretical calculation.[12] Recently a high-pressure resistance experiment of $PbCrO_3$ was performed in a cubic press apparatus up to 4.1 GPa.[31] The same steep drop of resistance at room temperature was

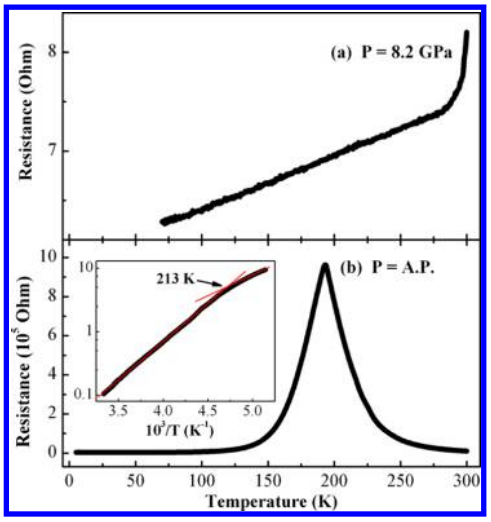

Figure 6. Temperature dependence of resistance of (a) high-pressure phase (8.2 GPa) and (b) ambient-pressure phase $PbCrO_3$. Inset: Arrhenius plot of AP phase $PbCrO_3$, from 300 to 195 K, indicates two activation energies with 0.47 and 0.24 eV.

observed; however, a semiconducting behavior showed at 4.1 GPa at high temperature. Considering the different measured pressure and temperature ranges, this result may also represent the electrical nature of the HP phase $PbCrO_3$. It is noteworthy that below 195 K the AP phase $PbCrO_3$ shows a metallic trend [Figure 6(b)], and it is possible that the HP phase has a similar behavior at high temperature. More studies about this electrical transport are needed.

The valence change should also exist during the releasing sample since $PbCrO_3$ is synthesized via PbO + CrO_2 → $PbCrO_3$ at 5.8 GPa. The compound with Cr^{4+} is rare as Cr^{4+} is relatively unstable.[32] High pressure is a necessary condition to preserve Cr^{4+} and stabilize $PbCrO_3$ at high temperature. Thus, $PbCrO_3$ is a stable phase in the Pb−Cr−O system at high temperature and high pressure and decomposes into Cr_2O_3 with Cr^{3+} and Pb_2CrO_5 with Cr^{6+} when pressure decreases at high temperature.[7] We presume that high pressure (about 4.2 GPa) is still necessary to maintain the Cr^{4+} at room temperature. Then the Cr valence states dissociate as pressure reduces to ambient pressure, leading to the CrO_6 octahedron distortion and abnormal large lattice constant. The previous XRD experiments performed by Xiao et al. showed the AP and HP phase have the same space group,[17] i.e., the same long-range structure, and the AP phase maybe is a metastable state during phase transition or decomposition of the HP phase. In perovskite-type 3d transition metal oxides like $RNiO_3$, the charge disproportionation was reported to induce the metal−insulator transition.[33−36] In this case, the occurrence of valence dissociation is most likely responsible for the phase transition and the charge localization in semiconducting AP phase $PbCrO_3$. If we substitute Pb^{2+} with smaller ions (such as Sr^{2+}), the chemical pressure may suppress the valence dissociation, leading to a marked drop of lattice constant and resistivity ($SrCrO_3$).[1,16]

■ CONCLUSIONS

In summary, we report the valence change and semiconductor−metal transition in $PbCrO_3$ for the first time. The high-pressure-synthesized cubic perovskites $PbCrO_3$ with Cr^{4+} become unstable when the pressure is below 4.2 GPa. Comparing the Cr $L_{2,3}$ edge XAS spectra of $PbCrO_3$ with a reference sample, we infer that the valence states of Cr ions dissociate into Cr^{3+} and Cr^{6+} at ambient pressure, and this valence change is supported by Cr K edge XAS under various pressures. In consequence charge change leads to a pressure-induced semiconductor−metal transition together with the phase transition. The ambient-pressure phase $PbCrO_3$ has ambiguous local structure and maybe is just a metastable state, but more detailed research is needed.

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Notes

The authors declare no competing financial interest.

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