Anomalous metallic state with strong charge fluctuations in $Ba_xTi_8O_{16+\delta}$ revealed by hard x-ray photoemission spectroscopy

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We have studied a charge-orbital driven metal-insulator transition (MIT) in hollandite-type $Ba_xTi_8O_{16+\delta}$ by means of hard x-ray photoemission spectroscopy (HAXPES). The Ti $2p$ HAXPES indicates strong Ti^{3+}/Ti^{4+} charge fluctuation in the metallic phase above the MIT temperature. The metallic phase is characterized by a power-law spectral function near the Fermi level which would be a signature of bad metal with non-Drude polaronic behavior. The power-law spectral shape is associated with the large Seebeck coefficient of the metallic phase in $Ba_xTi_8O_{16+\delta}$.

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I. INTRODUCTION

Transition-metal oxides exhibit various fascinating physical properties such as metal-insulator transition (MIT), colossal magnetoresistance, and spin-charge-orbital ordering [1,2]. Among them, conducting transition-metal oxides with a quasi-one-dimensional (q1D) network of metal sites are characterized by strong charge fluctuation due to electron-electron and electron-lattice interactions. In the case of q1D early transition-metal oxides, MITs are driven by charge ordering or charge density wave (CDW) formation of transition-metal d electrons. In β-$Na_{0.33}V_2O_5$ with V^{4+}/V^{5+} [3,4], spectral weight at the Fermi level is completely suppressed even above the MIT temperature [5] due to the strong electron-lattice interaction. Small polarons associated with CDW are similarly observed as above in the photoemission spectra of q1D $(TaSe_4)_2I$ [6–8].

In $K_2Cr_8O_{16}$ (Cr^{3+}/Cr^{4+}) with q1D hollandite structure [9–11], since the number of d electrons per site is larger than unity, Hund coupling is expected to enhance electronic correlation and suppress the spectral weight at the Fermi level. However, a recent photoemission study of $K_2Cr_8O_{16}$ by Bhobe *et al.* has shown finite spectral weight at the Fermi level above the MIT temperature and BCS-like gap opening below it [12]. In $Sr_{14-x}Ca_xCu_{24}O_{41}$ [13–15] with Cu-O ladder and $PrBa_2Cu_4O_8$ [16,17] with Cu-O double chain, the q1D Cu-O networks exhibit finite spectral weight at the Fermi level although it is reduced due to possible charge fluctuations of Cu^{2+}/Cu^{3+} [18,19]. These q1D transition-metal oxides can be viewed as doped Mott insulators, and conducting d electrons in the metallic phases would form large or small polarons coupled with lattice distortions associated with the charge ordering or CDW [20–22]. The polaronic effect is weak or moderate in the Cu^{2+}/Cu^{3+} and Cr^{3+}/Cr^{4+} oxides probably because charge transfer energy is relatively small and the oxygen $2p$ holes are involved in the polarons [1,2]. On the other hand, small polarons would be formed in the Ti or V oxides with large charge transfer energy. The difference in charge fluctuations may give different polaronic effects between various transitional metal oxides.

Besides the q1D systems, two-dimensional (2D) systems tend to exhibit large or intermediate polarons. A recent photoemission study has shown polaronic peak-dip-hump features indicating large polarons in a $LaAlO_3/SrTiO_3$ metallic system [23]. Large polarons are tuned in anatase TiO_2 with doping [24,25]. An intermediate electron lattice coupling is reported with the isotope effect described with kink feature in ARPES in the doped cuprates [26]. Although the crossover from large to small polarons is highly interesting, conducting a small polaron system is rather rare. Also, the large or small polarons have been studied in various q1D and 2D systems using surface sensitive photoemission spectroscopy. In this context, small polaron systems should be studied using bulk sensitive spectroscopy techniques in a systematic manner.

Transition-metal compounds with CDW or polaronic behavior tend to exhibit large thermoelectric properties [27–29]. Very recently, Murata *et al.* have reported a negative Seebeck coefficient at the metallic phase in hollandite-type $Ba_xTi_8O_{16+\delta}$ which further goes to negatively higher values with decreasing temperature and gives rise to higher resistance [30]. $Ba_xTi_8O_{16+\delta}$ is characterized by double chains consisting of edge-sharing TiO_6 octahedra [Figs. 1(a) and 1(b)] [31–33]. The nominal number of d electrons per Ti(n) is approximately 0.25 in the tetragonal $Ba_xTi_8O_{16+\delta}$ system with $x = 1.13$, $\delta = 0.14$. The MIT is accompanied by a structural transition from metallic tetragonal phase to monoclinic at around 220 K, whereas the resistivity ρ increases at low temperature with anomalies along the c and a axis [30]. Superlattice with the ordering of Ba ions [35] above the T_c and modulation of the d electrons in Ti chain below T_c are reported. Other transport and optical properties of $Ba_xTi_8O_{16+\delta}$ have also shown the anomalies across the transition. Thermal conductivity shows the behavior of a strongly correlated electron system with

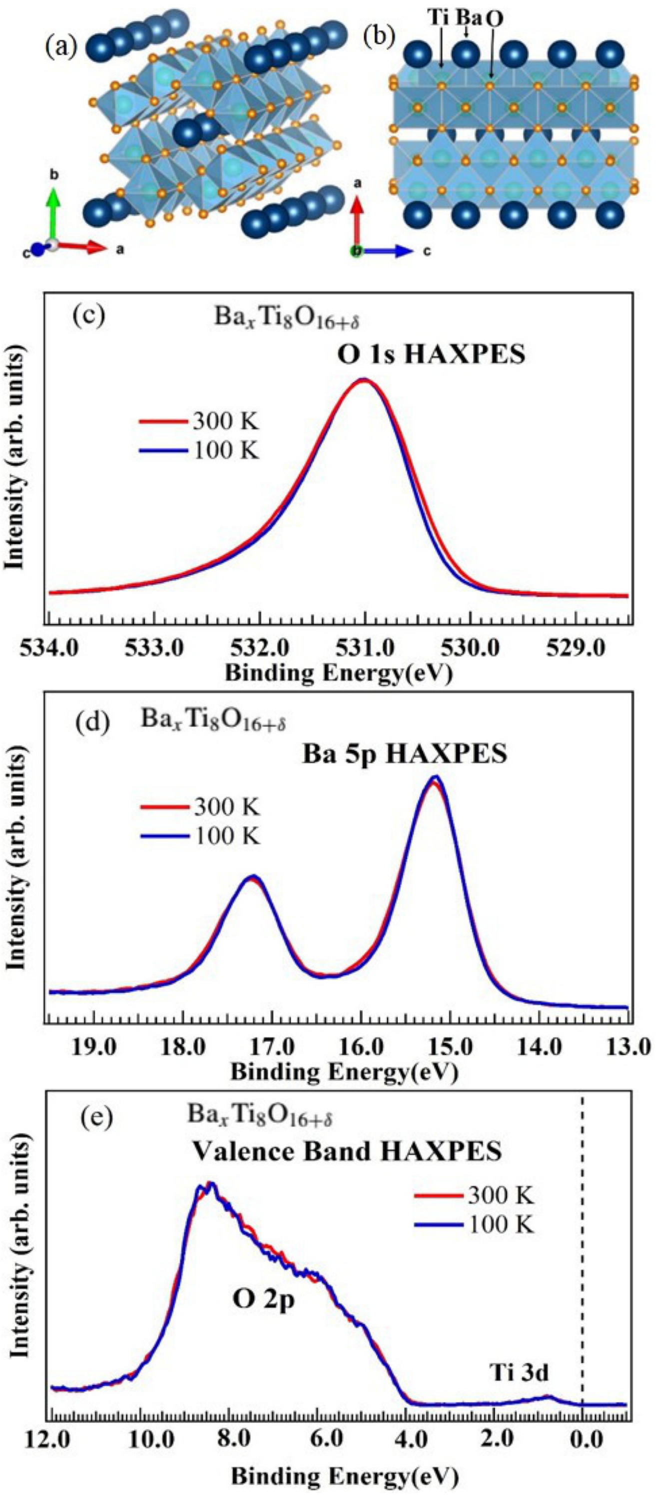

FIG. 1. (a) Crystal structure of $BaTi_8O_{16+\delta}$ [30] using VESTA [34] from the tilted *c* axis, (b) along the *ab* plane. Ba, Ti, and O atoms are shown by filled circles with different colors. (c) HAXPES spectra of $Ba_xTi_8O_{16+\delta}$ at 300 and 100 K for O 1*s*, (d) Ba 5*p*, and (e) valence band.

orbital ordering below T_c [30]. Optical conductivity $\sigma_c(\omega)$ shows 0.9 eV structure compared to $\sigma_a(\omega)$ as the signature of q1D character of the Ti 3*d* electrons [30], which is coupled with lattice distortions. Furthermore, in the optical conductivity $\sigma_c(\omega)$, the higher photon energy peak at 4 eV is ascribed to the presence of charge transfer excitation from the oxygen 2*p* level to the Ti 3*d* level, and the low temperature spectral weight transfer at 2 eV is presumably caused by charge and orbital ordering [36]. A photoinduced dynamics study has shown the presence of the polaron-excitation peak at ∼0.86 eV and the charge gap-excitation peak at ∼2.1 eV, the latter appears only at low temperature [37]. Therefore, $BaTi_8O_{16+\delta}$ provides a unique opportunity to elucidate a novel electronic state with small polarons and strong charge fluctuation.

In the present study we observe small polarons in hollandite-type $Ba_xTi_8O_{16+\delta}$ with the q1D polaronic conductivity as a broad 3*d* peak and completely suppressed weight at Fermi edge using the bulk sensitive photoemission spectroscopy. Compared to the large polaron systems, physics of small polarons is not yet well established although it is highly important for the understanding of MITs in q1D materials. In order to establish the electronic structural change across the MIT associated with the Ti^{3+} and Ti^{4+} charge fluctuation/order, we have performed HAXPES on $Ba_xTi_8O_{16+\delta}$ as a powerful tool to study bulk electronic properties [38,39]. The HAXPES results indicate strong Ti^{3+}/Ti^{4+} charge fluctuation and strong polaronic effect above the MIT temperature associated with the large Seebeck coefficient in $Ba_xTi_8O_{16+\delta}$.

II. EXPERIMENT

The single crystals of $Ba_xTi_8O_{16+\delta}$ are grown by a floating zone method as reported in the literature [30]. HAXPES measurements were performed at BL09XU of SPring-8 [40] with 7930 eV of photon energy that has a probing depth of 10 nm [41–44]. The incidence and detection angles are set to 10 and 90 deg, respectively in order to increase the photoelectron yield. The single crystals were fractured under an ultrahigh vacuum of 10^{-6} Pa at 300 K to avoid surface contamination. Emitted photoelectrons were collected by the OMICRON-SCIENTA R4000 analyzer. The pass energy was set to 200 eV and the total energy resolution was about 270 meV. The binding energy of all the spectra was calibrated using the Fermi edge of Au.

III. RESULTS AND DISCUSSION

Figures 1(c) and 1(d) show the HAXPES spectra of O 1*s* and Ba 5*p* of $Ba_xTi_8O_{16+\delta}$, respectively, collected at 300 and 100 K. Ba 5*p* and O 1*s* spectral features appear to remain unchanged across the MIT. The O 1*s* peak is more asymmetric than the Ba $5p_{3/2}$ and $5p_{1/2}$ peaks due to the screening effect of the valence electrons. In going from 100 to 300 K, the tail of the O 1*s* peak shows a tiny shift towards the lower binding energy indicating that the screening effect increases slightly above T_c. Figure 1(e) shows the valence-band HAXPES spectra of $Ba_xTi_8O_{16+\delta}$ collected at 300 and 100 K across the MIT. Each spectrum is normalized with the total area. The O 2*p* bands are ranging from 4 to 10 eV, and the Ti 3*d* band is located at ∼1 eV below the Fermi level. Ti 3*d* spectral weight at the Fermi level tends to be depleted both below and above the MIT temperature. In general, the metallic phase is expected to show some spectral weight at the Fermi level as commonly observed in the high temperature metallic phases of V_2O_3 [45], $BaV_{10}O_{15}$ [39], and Fe_3O_4 [46]. In this sense, the metallic phase of $Ba_xTi_8O_{16+\delta}$ is very unique among the various transition-metal oxides with MIT and is characterized by the anomalous spectral weight depletion at the Fermi level.

Figure 2 shows the Ti 2p HAXPES spectra taken at 300, 180, and 100 K (indicated by the thick solid curves). Each of the Ti 2p spectra is subtracted with a Shirley type background and fitted to four Voigts (mixture of Gaussian and Lorentzian). The Ti $2p_{3/2}$ peak can be decomposed with Ti^{3+} and Ti^{4+} components which are included in the fit considering the fact that the average Ti valence of $Ba_xTi_8O_{16+\delta}$ is $\sim +3.75$. The energy positions of Ti^{3+} and Ti^{4+} components at different temperatures across the MIT are found at ~457.7 and 459.8 eV, respectively. The peak positions are shifted towards higher binding energy than the typical values in Ti_2O_3 and TiO_2 [47–49] because of the different crystal environment. The intensity ratio between Ti^{3+} and Ti^{4+} fluctuates around 0.29 across the MIT. The Ti^{3+} and Ti^{4+} components are observed separately even above T_c indicating that strong charge fluctuation exists in the metallic phase. The charge fluctuation remains almost unchanged across the MIT, unlike $BaV_{10}O_{15}$ where the charge fluctuation between V^{2+} and V^{3+} is significantly varied across the transition [39]. In $Ba_xTi_8O_{16+\delta}$, the temperature dependence of inverse magnetic susceptibility χ shows a Curie-Weiss law below and above T_c with different Curie constants [30]. Since the Ti^{3+} and Ti^{4+} components are well separated in the Ti 2p HAXPES, the Ti^{3+} sites have localized spins which are surrounded by nonmagnetic Ti^{4+}. Most probably, the localized spins survive even in the metallic phase. Therefore, the nature of two different Curie constants below and above T_c could be related to the charge ordering below T_c and charge fluctuation above T_c, respectively. The Ti^{3+}/Ti^{4+} ordering undergoes a dynamic process where the charge fluctuates in the metallic phase.

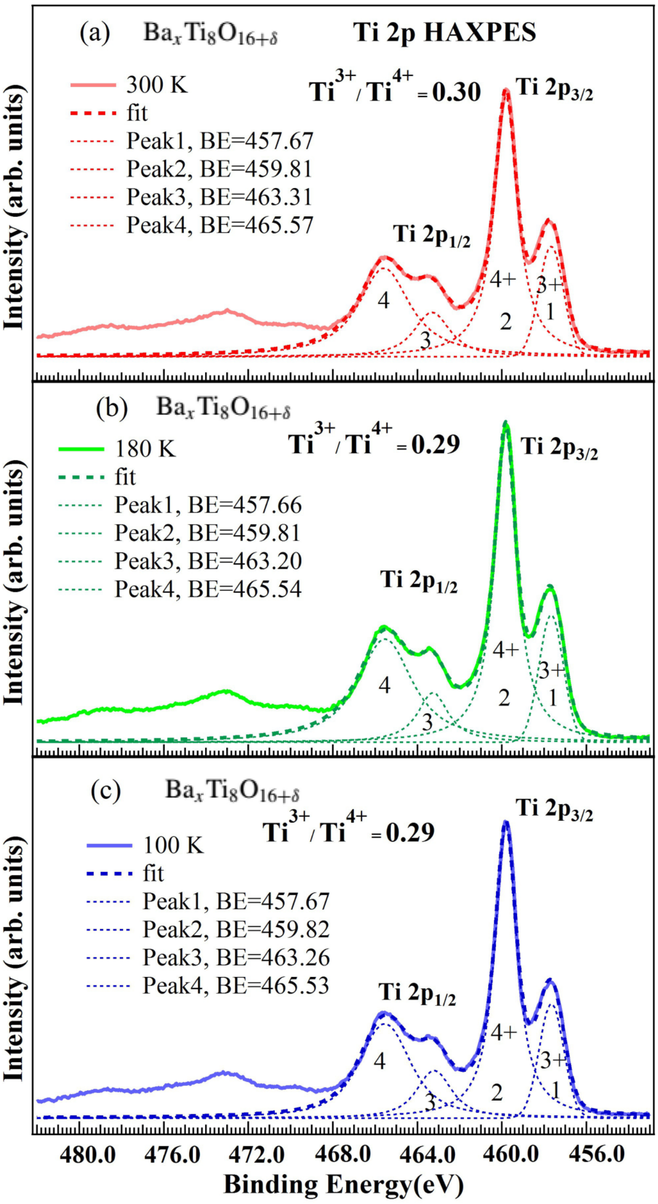

FIG. 2. Ti 2p HAXPES spectra fitted with four Voigt functions for (a) 300, (b) 180, and (c) 100 K. Peaks 1 and 2 represent Ti^{3+} and Ti^{4+} components in the Ti $2p_{3/2}$. Peaks 3 and 4 are fitted for the Ti $2p_{1/2}$ region.

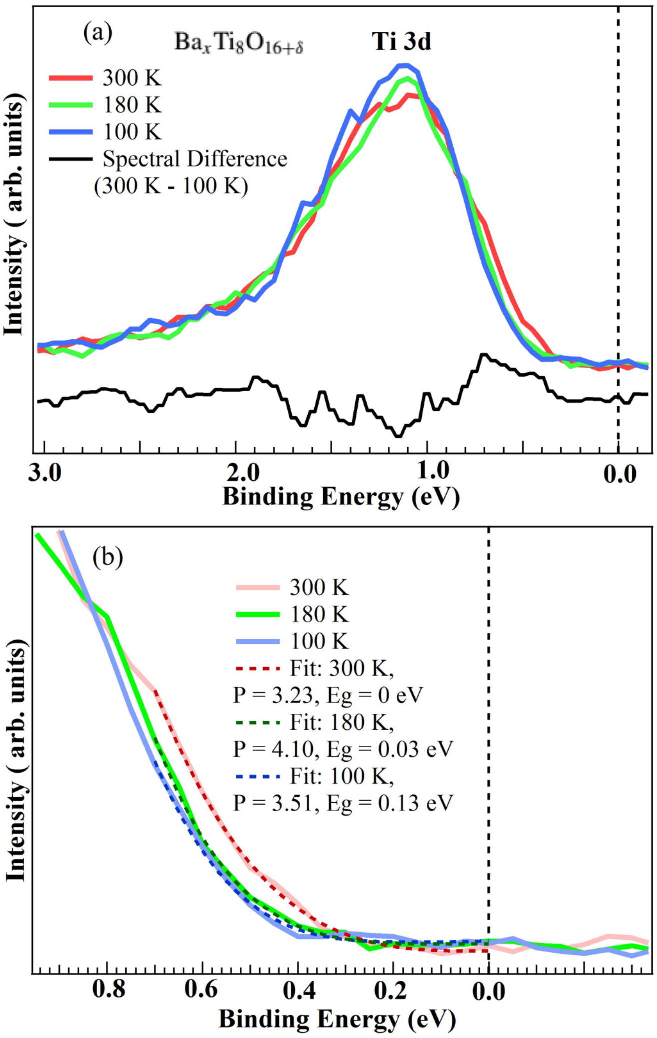

FIG. 3. HAXPES spectra of $Ba_xTi_8O_{16+\delta}$ at 300, 180, and 100 K (a) for Ti 3d area and (b) near the Fermi level.

Figures 3(a) and 3(b) show the valence band spectra of the Ti $3d$ region near the Fermi level for 300, 180, and 100 K, respectively. The spectral weight at the Fermi level is strongly suppressed at the high temperature metallic state and indicates the depletion of the itinerant electron. The behavior is consistent with a polaronic state with charge fluctuations seen from the Ti $2p$ HAXPES. This could be regarded as a bad metallic state with relatively small resistivity and high negative Seebeck coefficient. The spectral weight appears to be quenched more for 180 and 100 K, respectively, than 300 K. The relative spectral difference across MIT from 100 to 300 K is shown in Fig. 3(a). There is a slight enhancement of the spectral feature for the metallic $Ba_xTi_8O_{16+\delta}$ at 300 K compared to the cases of 180 and 100 K. The quasiparticle peak is suppressed around the Fermi level and the foot of the incoherent part is seen around 0.3 eV, which is similar to the case of small polarons in β-$Na_{0.33}V_2O_5$ [5]. Although this argument is not conclusive due to the lack of momentum-resolved experiment, the large energy scale of spectral suppression (up to 600 meV) may indicate an interesting possibility of small polarons [5] due to strong electron phonon coupling observed in the polaronic conductivity from the bulk. The small polarons have been earlier seen in β-$Na_{0.33}V_2O_5$ [5], and in Fe_3O_4 above the Verwey transition [50,51] probed by surface sensitive photoemission spectroscopy. In $Ba_xTi_8O_{16+\delta}$, the spectral weight at the Fermi level at low temperature is quenched further due to a decrease in carrier concentration in the insulating regime as resistivity increases at the order of six in magnitude and the Seebeck coefficient goes to a higher negative value. By using power-law function $(E - E_g)^P$ on the spectral shape near the Fermi level as shown in Fig. 3(b), we obtained the exponent P value as 3.23, 4.10, and 3.51 at 300, 180, and 100 K, respectively. E_g is found at 0.0, 0.03, and 0.13 eV below the Fermi level for 300, 180, and 100 K, respectively. The power-law spectral function in the metallic phase is confirmed in bulk sensitive HAXPES. This behavior indicates that the Ti $3d$ electrons form small polarons in the metallic phase and that the polaronic conductance is responsible for the anomalous transport. The Seebeck coefficient S can be evaluated using the Mott formula as $S = -k_B/e[E_g/k_BT + P + 1]$. Using the corresponding P and E_g obtained from the spectra, S is estimated to be ≈ -361 and -603 μV/K: at 300 and 180 K, respectively using the above formula. The values tend to be overestimated compared to the experimental values reported by Murata *et al.* However, the S value goes to higher negative value at the low temperature as a number of carriers decreases consistently with the experimental results [30].

IV. CONCLUSION

The Ti $2p$ HAXPES results indicate that the strong Ti^{3+}/Ti^{4+} charge fluctuations exist even above the MIT temperature. The ratio Ti^{3+}/Ti^{4+} is close to 0.3. The spectral weight at the Fermi level is highly suppressed in the metallic phase above the MIT temperature, and the spectral shape can be fitted to a power-law function consistent with the presence of non-Drude polaronic conductance. The Ti^{3+}/Ti^{4+} charge ordering of $Ba_xTi_8O_{16+\delta}$ can be viewed as a formation of Wigner lattice of the small polarons. The metallic phase of $Ba_xTi_8O_{16+\delta}$ may provide an interesting opportunity to study enhancement of thermopower due to polaronic effect. In addition, if $Ba_xTi_8O_{16+\delta}$ is associated with the small polaron as suggested from the present work, it would provide a platform to study crossover from small to large polarons.

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