In-plane conduction and *c*-axis polarization in the misfit-layered oxide $[Bi_2Ca_2O_4]_qCoO_2$

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We have used low-frequency dielectric measurements to study the evolution of anisotropic charge transport in misfit-layered oxides $[Bi_2Ca_2O_4]_qCoO_2$. Above ~60 K, the in-plane dc conductivity obeys the Arrhenius law and the dielectric polarization occurs along the *c* direction. We point out that this *c*-axis polarization is attributed to the activated carrier which is confined to *ab* plane.

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The different temperature dependences between in-plane and out-of-plane charge transport are observed on a number of layered materials. Especially in the studies of high-T_c cuprates, the discrepancy is called the ''charge confinement'' in connection with the strong electron correlations or the pseudogap phenomena. In order to gain insight into the origin of the anisotropic behavior, it is worthwhile to investigate the evolution of anisotropic charge transport in various types of layered insulators such as band insulators, Mott insulators, and Peierls insulators. The low-frequency dielectric measurement is appropriate for this purpose because it provides relevant information about the electrical conduction, the dielectric polarization, and the effects of disorder. By means of this method, we have already reported the properties of Bi-based cuprates near the insulator-metal transition.[1]

In the present Brief Report, we report on the case of misfit-layered cobaltite $[Bi_2Ca_2O_4]_qCoO_2$, which is an insulating end member of Bi-*M*-Co-O (*M*=Ca, Sr, and Ba) systems.[2–6] Since the valence of Co ion is about 3+ and the paramagnetic (low-spin state) configuration is realized in these materials,[7] the energy gap opens between fully occupied t_{2g} and empty e_g levels. Considering the misfit atomic structure and the chemical nonstoichiometries, the insulating Ca analog is regarded as a disordered band insulator.

Our single crystal is synthesized by a flux method with the starting composition of $2Bi_2O_3$: $2CaCO_3$: $\frac{2}{3}Co_3O_4$ and annealed under 1 bar argon at 600 °C. Figure 1 shows the x-ray (0,0,*l*) diffraction patterns, which are in good agreement with those of previous reports.[2,8] The actual chemical composition determined by inductively-coupled plasma spectrometry is $[Bi_{2+0.52}Ca_{2-0.52}O_4]_qCoO_2$ with the misfit parameter of $q=0.627$. This q value is reasonable for Ca analog.[9] The fact that about 26% Bi replaces Ca may arise due to an excess Bi_2O_3 flux mixing. The dc resistivities are measured using a standard four-probe method. The complex permittivity $\epsilon_c^*=\epsilon_c'-i\epsilon_c''$ is measured between 20 Hz and 2 MHz using an LCR meter (Agilent Technologies E4980A). The electrodes were attached on both sides of cleaved *ab* surfaces, and the ac field was applied along the *c* axis.

The temperature dependence of the in-plane resistivity ρ_{ab} is shown in Fig. 2(a). The insulating behavior ($d\rho_{ab}/dT<0$) is observed at all measured temperatures. In the high-T region, ρ_{ab} obeys the thermal activation formula with an activation energy of ~32 meV, as shown in Fig. 2(b). In the low-T region, the data coincide with Mott variable-range hopping (VRH) formula for a noninteracting Fermi glass,[10] indicating the existence of the localized states due to some disorders [Fig. 2(c)].[11] The crossover temperature T^* is estimated to be 63 K. Out-of-plane resistivity ρ_c is shown in Fig. 2(d). Above T^*, ρ_c remains to obey the Mott VRH mechanism. The ratio of ρ_c/ρ_{ab} has a weak temperature dependence and on the order of 50–150 [Fig. 2(e)].

Out-of-plane dielectric spectra ϵ_c' and ϵ_c'' are shown in Figs. 3(a) and 3(b), respectively. At lower temperatures, ϵ_c' exhibits a steplike change reflecting to a dielectric relaxation phenomenon. In ϵ_c'' spectra, the leak (dc) conductivity contribution $\sigma_{c,\omega=0}/\omega\epsilon_0$ is dominant as shown by a straight line with a slope of −1,[1] and the corresponding loss-peak structures are hidden. We note that the extrinsic component, such as interfacial (contact) polarization, does not substantially contribute to the dielectric constant. The high-frequency ϵ_c' value of ~7 does not contradict with the reported value of ϵ_∞.[3]

With increasing temperature, the rapid ϵ_c' growth is visible in the lower frequencies, reaching 5×10^4 at 20 Hz and 250 K. This polarizability growth, which appears below 10^4 Hz and above 40–70 K, is closely related to an increase in the mobile carrier number. We show the excitation-field dependent ϵ_c' spectra in Figs. 4(a) (20 V_{rms}/mm) and 4(b) (200 V_{rms}/mm) for another sample. As high voltage is applied, ϵ_c' swells on the low-frequency side are completely

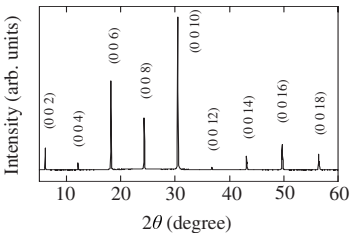

FIG. 1. X-ray (0,0,*l*) diffraction patterns measured using Cu $K\alpha$ radiation.

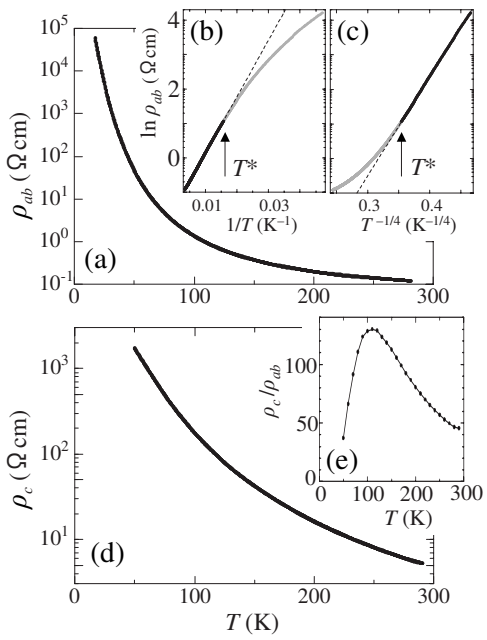

FIG. 2. (a) Temperature dependence of ρ_{ab}. The same data are plotted against $1/T$ in (b) and $T^{-1/4}$ in (c). (d) Temperature dependence of ρ_c. The ratio of ρ_c/ρ_{ab} is plotted in (e).

suppressed and turn to negative values. This result implies that the short-range localized (dielectric) carriers move across potential barriers and have the screening ability under the strong field.

The dielectric and conducting properties in $[Bi_{2+0.52}Ca_{2-0.52}O_4]_{0.627}CoO_2$ are summarized in Fig. 5. The dc conductivity σ_c obtained from ρ_c measurement and the leak conductivity $\sigma_{c,\omega=0}$ estimated from ϵ_c'' spectra exhibit almost the same T dependence that is expected for the hopping between the localized states. On the other hand, ϵ_c' ap-

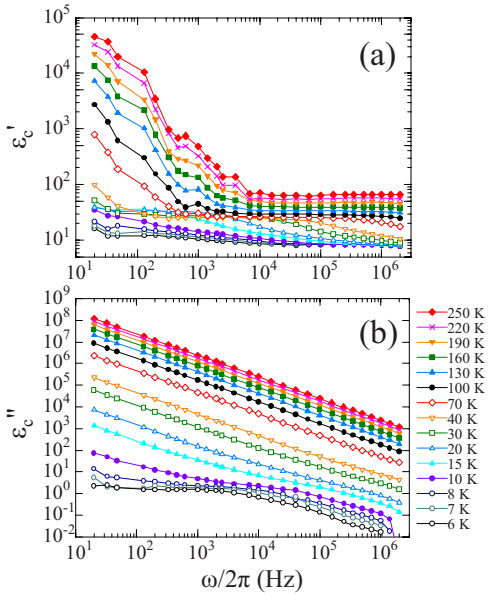

FIG. 3. (Color online) (a) Frequency dependence of the dielectric constant ϵ_c' and (b) the corresponding loss (ϵ_c'') spectra. $\omega = 2\pi f$ is the angular frequency. The applied ac field is 20 V_{rms}/mm.

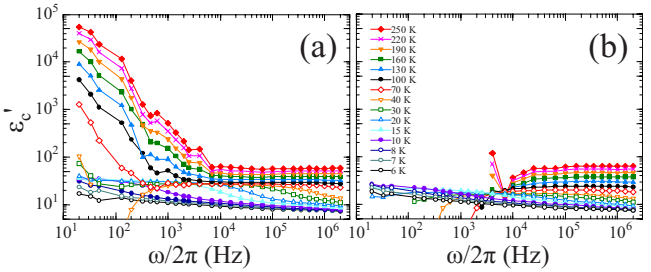

FIG. 4. (Color online) ϵ_c' spectra taken under the voltage gradient of (a) 20 V_{rms}/mm and (b) 200 V_{rms}/mm.

pears to rise from the vicinity of T^*, above which the thermally activated behavior becomes dominant within the *ab* plane, indicating that the delocalized carriers bring about the *c*-axis polarization.

We interpret our data as the direct observation of the anomalous *c*-axis charge dynamics in lightly-doped Bi-*M*-Co-O systems. Naively considering, the carrier can be released from the *ab* plane when the interlayer tunneling time $\tau \sim \hbar/t_c$ (here t_c denotes the *c*-axis hopping integral) is much shorter than the in-plane lifetime τ_{ab}. Contrarily, our observation indicates that the carriers stay within the *ab* plane even if they can excite across the in-plane energy gap. Interestingly, the temperature dependence of ρ_c/ρ_{ab} shown in Fig. 2(e) is qualitatively similar to that of lightly-doped cuprates, in which the in-plane charge localization and the so-called charge confinement within the planes coexist.[12,13] Therefore, we expect that the observed *c*-axis polarization will provide a clue to the understanding of the mechanisms underlying the anisotropic charge localization. In Bi-*M*-Co-O (M=Sr, Ba) systems, the anomalous *c*-axis transport has been discussed in terms of the coherent-incoherent crossover or the resonant tunneling via the interlayer defects.[14,15] It has been also reported that the Co ions are in the Co^{3+}-Co^{4+} mixed-valent states and the holes are located in the out-of-plane a_{1g} state which is split off from the t_{2g} triplet due to the trigonal crystal field;[6,16,17] this is in contrast to the case of cuprates where holes have in-plane character. For our insulating sample, the electronic state of

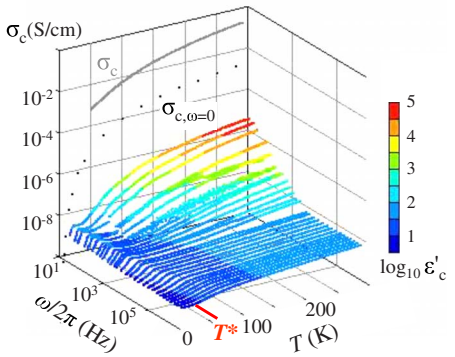

FIG. 5. (Color online) The dielectric and conducting properties in $[Bi_{2+0.52}Ca_{2-0.52}O_4]_{0.627}CoO_2$. T^* is the crossover temperature. σ_c is obtained from ρ_c. $\sigma_{c,\omega=0}$ is estimated by extrapolation of ϵ_c'' spectrum to zero frequency.

Co and its relation to the localization phenomenon are as yet obscure.[18] Further dielectric measurement on Bi-Ca-Co-O with various Bi and/or O concentrations is being undertaken.

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[18] In our sample, the average Co valence expected from the chemical composition is less than 3+ because of the excess amount of bismuth.