

## Optical reflectivity of single-crystal $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$ ( $M = \text{Ca}, \text{Sr}, \text{and Ba}$ ) from the infrared to the vacuum-ultraviolet region

I. Terasaki, T. Nakahashi, A. Maeda, and K. Uchinokura

*Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*

(Received 11 May 1992; revised manuscript received 31 August 1992)

The dielectric functions of single-crystal  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$  ( $M = \text{Ca}, \text{Sr}, \text{and Ba}$ ) were obtained by optical-reflectivity measurements. The Bi-based Co oxides have a characteristic  $\text{Bi}_2\text{O}_2$  layer with two sheets of  $\text{CoO}_2$  plane per primitive cell, and can be a reference material for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ . The obtained spectra are transformed to give the optical conductivity, and the optical properties of the  $\text{CoO}_2$  plane are discussed. Comparison of the electronic states of the Co and Cu oxides reveals two characteristics of high- $T_c$  cuprates. One is that the peak of the midinfrared absorption seen in optical conductivity decreases in energy toward 0 eV upon doping. The other is that the doping-dependent excitation associated with the  $\text{CuO}_2$  plane is confined in the low-energy region and is separated from other excitations such as those in the  $\text{Bi}_2\text{O}_2$  layer.

### I. INTRODUCTION

Since the discovery of the high- $T_c$  cuprates, a number of superconducting oxides have been synthesized. Almost all of them have a characteristic  $\text{CuO}_2$  plane, which is thought to be responsible for high- $T_c$  superconductivity. Although many works have been devoted to understanding the physical properties of the  $\text{CuO}_2$  plane, crucial data have not been obtained up to now. Recently, a set of single-crystal samples of high- $T_c$  cuprates with various amounts of dopant have been prepared, and the carrier-concentration dependence of the optical properties of the  $\text{CuO}_2$  plane has been investigated.<sup>1-5</sup> These studies have revealed that a broad absorption in midinfrared (mid-ir) region is widely seen in the optical conductivity spectra of doped samples, such as  $(\text{La}, \text{Sr})_2\text{CuO}_4$ ,<sup>1</sup>  $(\text{Pr}, \text{Ce})_2\text{CuO}_4$ ,<sup>2</sup>  $\text{YBa}_2\text{Cu}_3\text{O}_y$ ,<sup>3,4</sup> and  $\text{Bi}_2\text{Sr}_2(\text{Ca}, \text{L})\text{Cu}_2\text{O}_{8+\delta}$  ( $L = \text{Y}$  and  $\text{Nd}$ ).<sup>5</sup> This means that the optical spectra of high- $T_c$  cuprates cannot be fitted by a simple Drude term. Many models, including ours, have been proposed to explain the doping mechanism,<sup>5-10</sup> but the best answer cannot be selected at present.

Noncopper metallic oxides have been studied much earlier but much less than the high- $T_c$  cuprates. One may say that the difficulty in the study of high- $T_c$  cuprates is due to insufficient knowledge on physical properties of conducting oxides in general. Thus it would be important to compare superconducting oxides with other metallic oxides and find the property inherent in high- $T_c$  cuprates. We previously reported the optical study of the metallic Co oxide  $(\text{Nd}, \text{Sr})\text{CoO}_3$ , and found a broad mid-ir absorption in the conductivity spectra for doped samples.<sup>11</sup> We concluded that the formation of the mid-ir absorption is common to conducting  $3d$ -transition metal oxides. Taking a closer look at the carrier-concentration dependence of the mid-ir absorption, we found that the peak of the mid-ir absorption in cuprates shifts to lower energy with doping and it cannot be seen at finite energy for sufficiently doped samples.<sup>5</sup> On the other hand, the

energy of the peak of the mid-ir absorption in Co oxides stays at 0.3 eV for all the prepared samples (up to 40 at. % Sr substitution for Nd). We attributed the above difference to the different energy of the charge-transfer (CT) excitation between O  $2p$  and Cu/Co  $3d$ , and reported that a characteristic optical property in high- $T_c$  cuprates is the energy shift of the peak of the mid-ir absorption toward 0 eV.

One would wonder if the different behavior of the mid-ir absorption between high- $T_c$  cuprates and  $(\text{Nd}, \text{Sr})\text{CoO}_3$  comes from the different dimensionality of the two systems, or not. It is thus necessary to study conducting two-dimensional Co oxides. For this purpose, the conducting oxides  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$  ( $M = \text{Ca}, \text{Sr}, \text{and Ba}$ ) are the best materials with the following advantages.<sup>12</sup>

(i) They have a characteristic  $\text{Bi}_2\text{O}_2$  layer and a conducting  $\text{CoO}_2$  plane instead of a  $\text{CuO}_2$  plane in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (their crystal structure is schematically drawn in Fig. 1).

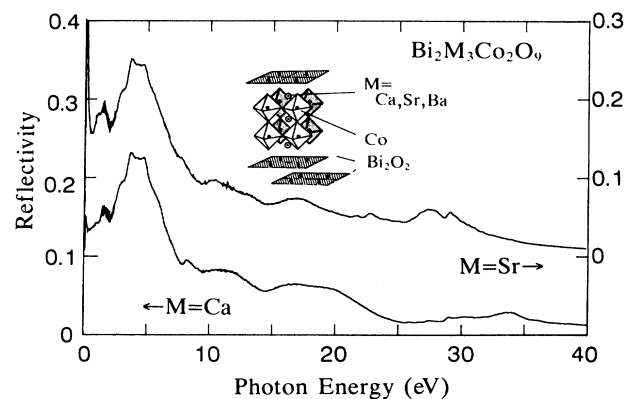


FIG. 1. Optical reflectivity spectra for  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$  ( $M = \text{Ca}$  and  $\text{Sr}$ ). Their crystal structure is schematically drawn in the inset.

(ii) They become more conducting in going from  $M = \text{Ca}$  to  $\text{Ba}$ , which shows that the carrier concentration can be varied by the alkaline earth element  $M$ . (Resistivities at 300 K are 10, 0.04, and 0.005  $\Omega \text{ cm}$  for  $M = \text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ , respectively.)

(iii) Cobalt cations in the crystal are nearly trivalent, and it is possible to compare them with the three-dimensional  $\text{Co}^{3+}$  system,  $(\text{Nd}, \text{Sr})\text{CoO}_3$ .

(iv) They have the perfect cleavability like Bi-based cuprates, and are free from surface contamination.

In this paper, we report the measurements and analyses of the optical reflectivity of single-crystal  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$  ( $M = \text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ) at room temperature in the wide range from 0.03 to 40 eV. The measured spectra were transformed into the optical conductivity through the Kramers-Kronig (KK) relation. The doping effects and the electronic states of Bi-based Co oxides are discussed, and compared with those of high- $T_c$  cuprates.

## II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Single crystals of  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$  ( $M = \text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ) were prepared by the  $\text{Bi}_2\text{O}_3\text{-Co}_3\text{O}_4$  flux method reported by Tarascon *et al.*<sup>12</sup> (We refer to  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$  as  $M$  phase. For example,  $\text{Bi}_2\text{Ca}_3\text{Co}_2\text{O}_{9+\delta}$  is referred to as Ca phase hereafter.) Obtained samples were platelike with typical dimensions of  $3 \times 3 \times 0.05$ ,  $3 \times 3 \times 0.05$ , and  $1 \times 1 \times 0.03 \text{ mm}^3$ , for Ca, Sr, and Ba phases, respectively. We checked the quality of the prepared samples by x-ray diffraction and dc resistivity measurements, and found that our results well reproduce those of Ref. 12.

Optical reflectivity spectra at room temperature were measured by two systems. The Seya-Namioka monochromator with synchrotron radiation as a light source was employed for high-energy region (from 2 to 40 eV), whereas the rapid-scanning Michelson interferometer was used for low-energy region (from 0.03 to 3 eV). The magnitude of reflectivity was determined by using the signal of photomultiplier for direct light as a reference above 3 eV, and by using Ag mirror as a reference below 3 eV. An infrared microscope accessory was attached for the lower-energy measurement, and the spot of incident light was focused within  $0.3 \times 0.3 \text{ mm}^2$ . In the common energy region of both systems (from 2 to 3 eV), no serious differences including the magnitude of reflectivity could be observed. Reflectivity for Ca and Sr phases was measured from 0.03 to 40 eV, while that for Ba phase was measured up to 3 eV because its size was too small for the high-energy measurement. Samples were peeled with adhesive tapes before measurement in order to avoid surface contamination.

## III. RESULTS

The measured reflectivity spectra for Ca and Sr phases are shown in Fig. 1. They roughly resemble each other, and also resemble those of the Bi-based cuprates.<sup>5,13</sup> They have a characteristic band of peaks around 4–7 eV, and their magnitude above 7 eV decreases with increasing energy with weak peaks and edges. Similar spectra were

also obtained for other Bi-based oxides, e.g.,  $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$  and  $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{9+\delta}$ ,<sup>14</sup> and thus we conclude that these features are common to the spectra for all the oxides containing the  $\text{Bi}_2\text{O}_2$  layer. The excitation around 4–7 eV was assigned to the interband transitions between O  $2p$  and Bi  $6p$  in our previous paper<sup>13</sup> and other reports.<sup>15,16</sup> The present study strongly supports the previous assignment. Although qualitative similarity is seen among all the spectra of the oxides with the  $\text{Bi}_2\text{O}_2$  layer, their dielectric functions are quantitatively different. This is directly shown in the magnitude of reflectivity. For instance, the reflectivity at 5 eV for Ca and Sr phases is about 0.22–0.25, whereas the corresponding value for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  is about 0.12–0.13. Such difference in magnitude comes from the difference of the dielectric function, which is most clearly seen in the conductivity spectra discussed in the next section.

There are three remarkable differences between the spectra for Ca and Sr phases. One is seen around 27–35 eV, the second around 20–24 eV, and the last one is below 1 eV. As this paper is the first report on the high-energy excitation of  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_{9+\delta}$ , the energy levels of the core electrons, valence, and conduction bands are unknown now. Thus we assign some peaks and edges by comparing the spectra with those of the Bi-based cuprates. Of course, it is not clear whether the energy levels of the core electrons and conduction bands are unchanged among the Bi-based oxides, but Tajima *et al.* reported that the high-energy excitation for  $(\text{La}, \text{Sr})_2\text{MO}_4$  ( $M = \text{Cu}$ ,  $\text{Ni}$ ,  $\text{Co}$ , and  $\text{Fe}$ ) is similar to one another.<sup>17</sup> Therefore we assume that the Bi-based Co oxides have the core levels and conduction bands at the same energies as the Bi-based Cu oxides.

We start to consider the difference near 27–35 eV at first. The reflectivity for Sr phase has a pair of peaks near 27 and 29.5 eV, which are also seen in the spectra for the Bi-based cuprates. These two peaks have been assigned to the transition from spin-orbit split Bi  $5d$  to Bi  $6p/O 2p$ .<sup>13,15</sup> On the contrary, these are weakened or distorted in the spectrum for Ca phase because of the presence of the excitation near 34 eV. The 34-eV excitation is observed in the oxides containing  $\text{Ca}^{2+}$  such as  $(\text{Ca}, \text{Sr})\text{CuO}_2$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .<sup>13</sup> Thus we assign the 34-eV peak to the excitation from Ca  $3p$  to  $3d$  bands, and this is consistent with the results of photoemission study in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ , where the central energy of Ca  $3p$  and  $3d$  bands are found near 24 eV below  $E_F$  and 10 eV above  $E_F$ , respectively.<sup>18</sup> It should be noted that the 34-eV peak for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  is weaker than that for Ca phase, and the 27-, 29.5-, and 34-eV peaks are observed in the former spectrum. This may come from the fact that the number of  $\text{Ca}^{2+}$  cation per primitive cell is less in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  than in Ca phase.

The second difference is that a clear edge exists near 20–24 eV only in the spectrum of Ca phase. As a similar edge is seen in the spectrum of  $(\text{Ca}, \text{Sr})\text{CuO}_2$ , it can be attributed to excitation associated with  $\text{Ca}^{2+}$ . One possible candidate for this edge is the end of excitation to Ca  $3d$  states which are located at 10 eV above  $E_F$  in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .<sup>18</sup> As for Sr phase or Bi-based cu-

prates, the edge corresponding to the end of excitation to Sr  $4d$  is expected to be higher, since the central energy of Sr  $4d$  band is located at higher energy (13 eV above  $E_F$ ) than that of Ca  $3d$  band.<sup>18</sup> Thus the edge would be smeared or broadened by overlapping the higher excitation.

In order to emphasize the last difference seen below 1 eV, the reflectivity below 1 eV is shown in Fig. 2 with that for Ba phase. Obtained spectra are similar to those of the study of Watanabe *et al.*<sup>19</sup> The reflectivity for Ca phase is almost constant except for sharp peaks of optical phonons. This is consistent with high resistivity of Ca phase (about 10  $\Omega$  cm at 300 K). For Sr phase, the phonons are considerably screened and reflectivity shows a monotonic rise toward 0 eV with the edge near 0.3 eV. The rise of reflectivity becomes steeper for Ba phase, while the energy of reflectivity edge stays almost constant at 0.3 eV. The monotonic rise of reflectivity and the edge at a constant energy are the characteristic features seen in the carrier-concentration dependence of the reflectivity for high- $T_c$  cuprates<sup>1-5</sup> and (Nd,Sr)CoO<sub>3</sub>.<sup>11</sup> In other words, the reflectivity and dc conductivity of Bi-based Co oxides are well understood if it is assumed that the carrier concentration increases by changing  $M^{2+}$  from Ca to Ba. It seems mysterious that the carrier concentration is varied with the valence of  $M^{2+}$  unchanged, but  $M^{2+}$  would control the oxygen content  $\delta$  in the crystal, since the alkaline earth cation with a larger ionic radius tends to attract the neighboring oxygen anion more strongly. A similar case is seen in La<sub>2-x</sub>(Sr,Ca)<sub>1+x</sub>Cu<sub>2</sub>O<sub>6+ $\delta$</sub> , where La<sub>2</sub>SrCu<sub>2</sub>O<sub>6+ $\delta$</sub>  is more conducting than La<sub>2</sub>CaCu<sub>2</sub>O<sub>6+ $\delta$</sub> .<sup>20,21</sup> In the following section, the three spectra will be discussed more quantitatively on the assumption that the carrier concentration increases in going from Ca to Ba phase.

#### IV. DISCUSSION

##### A. Low-energy excitation

The measured reflectivity spectra were transformed into the optical conductivity through the KK relation. Since the KK transformation needs the reflectivity from

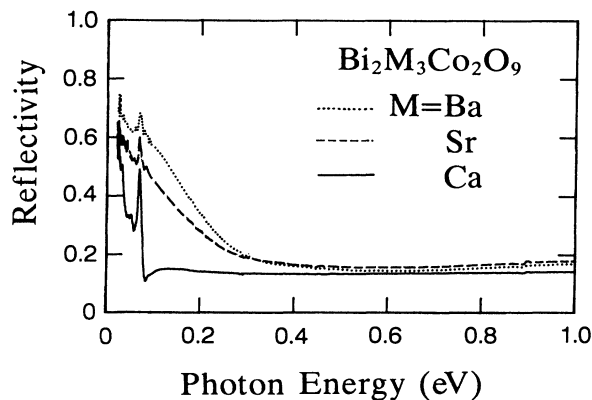


FIG. 2. Low-energy reflectivity spectra for Bi<sub>2</sub>M<sub>3</sub>Co<sub>2</sub>O<sub>9+ $\delta$</sub>  ( $M$  = Ca, Sr, and Ba).

zero to infinite energy, the measured spectra were extrapolated both in lower- and higher-energy regions. We adopted the Hagen-Rubens relation for the lower-energy extrapolation, expressed as follows:

$$R(\omega) = 1 - 2 \left[ \frac{\omega}{2\pi\sigma(0)} \right]^{1/2},$$

where  $\sigma(0)$  is the dc conductivity. We used the relation as  $R(\omega) \propto \omega^{-4}$  for higher-energy extrapolation.

The transformed conductivity in the lower-energy region is shown in Fig. 3(a). The spectrum for Ca phase has no remarkable structures except for phonons, whereas the spectra for Sr and Ba phases have a broad absorption with the maximum near 0.1 eV (almost overlapping the sharp peak of the highest-energy phonon). The 0.1-eV absorption directly shows that the spectra for Bi-based Co oxides cannot be fitted to a simple Drude model, since any conductivity spectra described by a Drude model must have a maximum at 0 eV and make a smooth slope with increasing energy.

As is already described in the Introduction, a broad mid-ir absorption is widely seen in Bi-based cuprates and (Nd,Sr)CoO<sub>3</sub>, whereas its carrier-concentration dependence is different between both systems.<sup>5,11</sup> For comparison, the conductivity spectra of single-crystal Bi<sub>2</sub>Sr<sub>2</sub>(Ca,Nd)Cu<sub>2</sub>O<sub>8+ $\delta$</sub>  with various Nd contents are shown in Fig. 3(b) (from Ref. 5). The mid-ir absorption of the Bi-based Co oxides has a maximum at almost con-

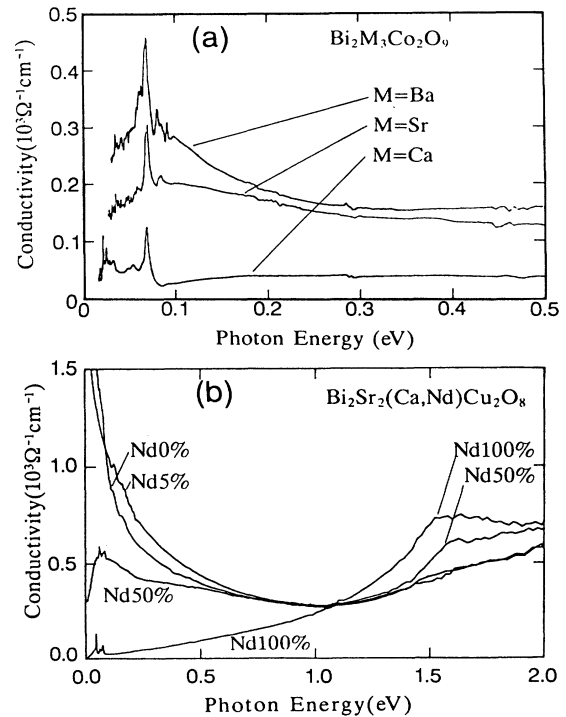


FIG. 3. Optical conductivity spectra transformed from the measured reflectivity through the Kramers-Kronig relation. (a) Bi<sub>2</sub>M<sub>3</sub>Co<sub>2</sub>O<sub>9+ $\delta$</sub>  ( $M$  = Ca, Sr, and Ba); (b) Bi<sub>2</sub>Sr<sub>2</sub>(Ca,Nd)Cu<sub>2</sub>O<sub>8+ $\delta$</sub>  (from Ref. 5).

stant energy (0.1 eV) independent of doping. On the other hand, the mid-ir absorption for Bi-based cuprates has a maximum near 0.1 eV for the 50 at. %-Nd substituted sample, but has no distinguishable peak at finite energy for heavily doped samples (0 and 5 at %-Nd substituted ones).

In the previous paper,<sup>11</sup> a characteristic feature in superconducting cuprates is that the energy of the peak of the mid-ir absorption is lowered toward 0 eV upon doping. It does not mean, however, that the high-temperature superconductivity occurs only when the mid-ir peak cannot be seen at finite energy. In fact, the conductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  with  $T_c = 30$  K has a clear peak near 0.7 eV,<sup>3</sup> and that of  $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$  with  $T_c \sim 20$  K has a shoulder near 0.4 eV.<sup>1</sup> Recent optical study in single-crystal  $\text{Pb}_2\text{Sr}_2\text{DyCu}_3\text{O}_8$  ( $T_c = 80$  K) has also shown that the mid-ir absorption has a clear peak near 0.15 eV.<sup>22</sup> Nevertheless all the above cuprates show the decrease of the energy of the mid-ir peak upon doping, and show a “Drude-like” conductivity for the sufficiently doped samples. (“Drude-like” means that the conductivity has a maximum at 0 eV and smoothly decreases with increasing energy.) Thus the most significant feature of high- $T_c$  cuprates is that the infrared conductivity can be Drude-like in sufficiently doped samples. On the contrary, other doped CT insulators have rarely shown such a Drude-like conductivity for any doping levels.<sup>11,23</sup> For example, the infrared spectrum of  $(\text{Nd,Sr})\text{CoO}_3$  is completely different from a simple Drude excitation even in the most conducting samples. We think that the carrier-concentration dependence of the Bi-based Co oxide resembles that of  $(\text{Nd,Sr})\text{CoO}_3$  rather than cuprates. In other words, the fact that the mid-ir absorption has a maximum at finite energy regardless of the amount of doping is a characteristic nature of conducting Co oxides, and the difference from the high- $T_c$  cuprates. Thus we conclude that the different doping effects between Bi-based cuprates and  $(\text{Nd,Sr})\text{CoO}_3$  do not come from the different dimensionality of the two systems, but from their different electronic states.

It is noteworthy to compare our analyses with the previous study of Bi-based Co oxides by Watanabe *et al.*<sup>19</sup> Although our present result qualitatively agrees with their conclusion that the mid-ir absorption is not a sufficient condition of high- $T_c$  superconductivity, it does not quantitatively agree. Their spectra were measured for narrower energy range than ours, and their analyses were strongly affected by the observed spectra. Actually their proposed model of the electronic states could not predict the lower- and higher-energy excitations observed in the present paper. First they assigned the low-energy spectra ( $\hbar\omega < 0.2$  eV) to a Drude term, which is not consistent with our observation of the 0.1-eV peak in Fig. 3(a). Secondly their high-energy conductivity ( $\hbar\omega > 0.7$  eV) might be distorted by the high-energy extrapolation. Their conductivity for  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$  near  $7000\text{ cm}^{-1}$  is almost  $0\text{ }\Omega^{-1}\text{cm}^{-1}$ , which disagrees with our data. We emphasize that we have succeeded in finding the 0.1-eV peak of the conductivity for  $\text{Bi}_2\text{M}_3\text{Co}_2\text{O}_9$  and assigning the higher-energy excitation (discussed later) by extending the measured energy range.

## B. High-energy excitation

High-energy conductivity spectra of Bi-based Co oxides are shown in Fig. 4, together with those of Bi-based cuprates calculated from the reflectivity of Ref. 13. All the spectra have two peaks at 27 and 29.5 eV (marked with *A* and *B*) corresponding to the transition from Bi  $5d$  to O  $2p$ /Bi  $6p$ , and shapes of the two peaks are similar among them except for the spectrum of Ca phase. Spectra of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  and  $\text{Bi}_2\text{Ca}_3\text{Co}_2\text{O}_{9+\delta}$  have a peak near 34 eV (marked with *C*) corresponding to the transition from Ca  $3p$  to  $3d$ , and its shape for the two spectra is similar. Thus it can be said that the energy levels of core electrons and conduction bands among Bi-based oxides are similar, as was already mentioned in the previous section.

On the contrary, the valence bands or lower-energy excitation below 7 eV are quite different between Bi-based Cu and Co oxides. One can notice that the conductivity around 4–7 eV is larger in Co oxides than in Cu oxides, which is the origin of the different magnitude of 4–7-eV reflectivity between Cu and Co oxides mentioned in the previous section. In Bi-based cuprates, the 4–7-eV conductivity are predominantly due to the transition from O  $2p$  to Bi  $6p$ .<sup>13,15,16</sup> From the assumption that the excitation within the  $\text{Bi}_2\text{O}_2$  layer is similar between Co and Cu oxides, we can infer that additional excitation exists in Co oxides and overlaps the transition between O  $2p$  and Bi  $6p$ . A possible assignment of the additional excitation is the CT excitation from O  $2p$  to Co  $3d$  (and/or the  $d-d$  transition).

Let us estimate the effective electron number associated with the excitation around 4–7 eV. The effective electron number  $N_{\text{eff}}(\omega)$  can be defined as

$$N_{\text{eff}}(\omega) = \frac{m}{2\pi^2 e^2} \int_0^\omega \omega' \text{Im}[\epsilon(\omega')] d\omega' ,$$

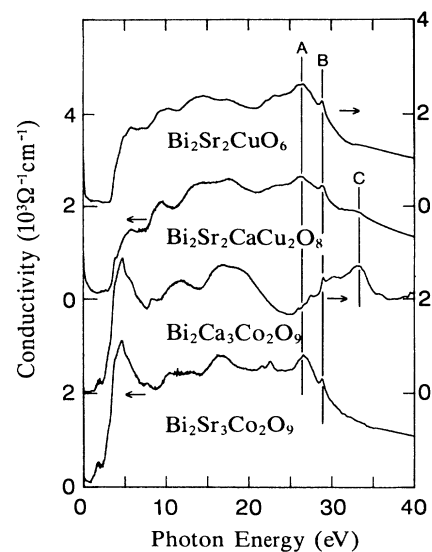


FIG. 4. Optical conductivity spectra for various oxides with  $\text{Bi}_2\text{O}_2$  layer. The conductivity spectra for Bi-based cuprates were calculated from the reflectivity of Ref. 13.

where  $m$  and  $e$  are the mass and charge of electron, respectively. Then the number of electrons that contribute to the excitation around 4–7 eV  $\Delta N_{\text{eff}}$  is estimated as

$$\Delta N_{\text{eff}} = N_{\text{eff}}(7 \text{ eV}) - N_{\text{eff}}(4 \text{ eV}).$$

From the obtained spectra,  $\Delta N_{\text{eff}}$  is calculated as 5.83, 5.16, and 3.08 for  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_{9+\delta}$ ,  $\text{Bi}_2\text{Ca}_3\text{Co}_2\text{O}_{9+\delta}$ , and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ , respectively. These results mean that extra 2.08–2.73 electrons contribute to the additional excitation around 4–7 eV in Co oxides. According to our assignment, the CT excitation is located around 4–7 eV, and the number of electrons involved in it is estimated as 1.04–1.37 per  $\text{CoO}_2$  plane. For cuprates, the CT energy is 1.5–2.0 eV, and the number of electrons is about 0.2–0.5 per  $\text{CuO}_2$  plane.<sup>24</sup> The CT energy tends to increase in going from Cu to Co oxides, reflecting that the central energy of 3d bands relative to that of O 2p bands increases. The electron number involved in the CT excitation also tends to increase in going from Cu to Co oxides, because the number of unoccupied 3d states increases. Therefore the estimated CT energy and electron number for the Bi-based Co oxides are well consistent with those for the high- $T_c$  oxides.

### C. Characteristic features in high- $T_c$ cuprates

By comparing the optical properties of Co oxides with those of Cu oxides, we can point out some characteristic features in high- $T_c$  cuprates. From low-energy spectra, information on the optical properties of doped holes in the  $\text{CoO}_2$  plane can be obtained. The mid-ir absorption in the  $\text{CoO}_2$  plane grows as the system becomes conducting, while its peak remains constant near 0.1 eV. This is similar to the doping effect in three-dimensional Co system (Nd,Sr)CoO<sub>3</sub>, where we have explained the optical spectra by “impurity-state model.”<sup>11</sup> We think that “impurity bands” would be formed when the energy difference between O 2p and transition metal 3d bands is too large to be hybridized. Doped carriers move in the “impurity bands,” and their bandwidth is expected to be narrow on the analogy of doped semiconductors. Carriers in such narrow two-dimensional bands would be localized by the existence of some kind of imperfections. In fact, the dc resistivity of  $\text{Bi}_2M_3\text{Co}_2\text{O}_{9+\delta}$  shows semiconducting behavior at low temperatures.<sup>12</sup> As for the magnetic properties, carriers in the “impurity bands” are expected not to affect the localized 3d electrons on  $\text{Co}^{3+}$ . The susceptibility measurement has revealed that magnetic properties are not drastically changed by changing  $M^{2+}$ .<sup>12</sup>

On the other hand, the mid-ir absorption seen in the spectra of the Bi-based cuprates drastically decreases the energy of its peak toward 0 eV with doping, which we have explained by using “midgap-state model.”<sup>5</sup> From our proposed model, the doped carriers have predominantly O 2p character for lightly doped samples, and begin to transfer from  $\text{O}^{2-}$  to neighboring  $\text{Cu}^{2+}$  for heavily doped ones. The peak of mid-ir absorption corresponds to the energy gap from O 2p to Cu 3d, which is nearly 0 eV in superconducting samples. This means that doped

holes in the  $\text{CuO}_2$  plane drastically modify the physical properties of localized hole on  $\text{Cu}^{2+}$ , which is consistent with the carrier-concentration dependence of magnetic susceptibility.<sup>25</sup>

High-energy spectra have revealed that the CT excitation for the Co oxides is spread above 4 eV, whereas that for high- $T_c$  cuprates is confined below 2 eV. In the high- $T_c$  cuprates, the carrier doping changes the electronic states of the system in the range from 0 eV to the energy of the CT excitation.<sup>1–5</sup> This can be generalized to the doped CT insulators. Since the energy region where the spectra change with doping is from 0 to 5–6 eV for (La,Sr)CoO<sub>3</sub>,<sup>26</sup> it can be said that the spectra for the doped CT insulator change with doping in the energy range from 0 to their CT energy. Thus we point out as a characteristic feature of high- $T_c$  cuprates that the doping-dependent spectra confined in the low-energy region hardly overlap higher excitation such as that in the  $\text{Bi}_2\text{O}_2$  layer. The separation in energy between the low-energy excitation of the  $\text{CuO}_2$  plane and that of the other layers means that the  $\text{CuO}_2$  plane is responsible for the low-energy excitation and the other layers only stabilize the electronic and crystal structures, and also means that the electronic states of the  $\text{CuO}_2$  planes are hardly affected by the species of the other layers. These results agree well with the high flexibility of crystal structures of high- $T_c$  cuprates classified by Tokura and Arima.<sup>27</sup> They proposed that any combinations of the  $\text{CuO}_2$  plane and the block layers can construct a cuprate with the  $\text{CuO}_2$  plane as long as the charge neutrality is conserved. On the other hand, such high flexibility is not reported for Co oxides. The present study reveals one origin of the high flexibility of cuprates by comparing them with Co oxides.

## V. SUMMARY

Single-crystal samples of  $\text{Bi}_2M_3\text{Co}_2\text{O}_9$  ( $M = \text{Ca}, \text{Sr},$  and  $\text{Ba}$ ) were prepared, and their optical reflectivity spectra were measured from 0.03 to 40 eV. A broad absorption with a 0.1-eV peak is observed in the conductivity spectra of the Bi-based Co oxides as well as (Nd,Sr)CoO<sub>3</sub> and high- $T_c$  cuprates, and we find that the broad midinfrared absorption is generally seen in conducting 3d-transition-metal oxides. The energy of the peak of the absorption stays at constant energy upon doping in Bi-based Co oxides as well as in (Nd,Sr)CoO<sub>3</sub>, whereas it drastically decreases toward 0 eV in high- $T_c$  cuprates. Therefore we conclude that a characteristic property inherent in high- $T_c$  cuprates is the energy shift of the midinfrared peak toward 0 eV.

High-energy spectra of Bi-based oxides are investigated, and it is shown that the energy levels and electronic states of Bi 5d, Bi 6p, Ca 3p, and Ca 3d bands are similar among Bi-based oxides. The CT and/or d-d excitation associated with Co is spread above 4 eV, and overlaps the transition in the  $\text{Bi}_2\text{O}_2$  layer. On the contrary, the doping-dependent excitation in high- $T_c$  cuprates is confined in the low-energy region, and is well separated from other interband transitions. This is another characteristic property inherent in high- $T_c$  cuprates.

## ACKNOWLEDGMENTS

The authors would like to thank H. Eisaki, T. Arima, T. Ido, and S. Uchida for collaboration. They also appreciate M. Seki and S. Suga for technical assistance for

the measurement of vacuum-ultraviolet reflectivity at Synchrotron Radiation Laboratory in the Institute for Solid State Physics, The University of Tokyo. This work was partially supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

- 
- <sup>1</sup>S. Tajima *et al.*, in *Advances in Superconductivity III*, Proceedings of the 3rd International Symposium on Superconductivity (ISS '90), edited by K. Kajimura and H. Hayakawa (Springer-Verlag, Tokyo, 1991) p. 185; S. Uchida *et al.*, *Phys. Rev. B* **43**, 7492 (1991).
- <sup>2</sup>S. L. Cooper *et al.*, *Phys. Rev. B* **41**, 11 605 (1990).
- <sup>3</sup>J. Orenstein *et al.*, *Phys. Rev. B* **42**, 6342 (1990).
- <sup>4</sup>L. D. Rotter *et al.*, *Phys. Rev. Lett.* **67**, 2741 (1991).
- <sup>5</sup>I. Terasaki *et al.*, *Physica C* **165**, 152 (1990); I. Terasaki *et al.*, *Physica B* **165&166**, 1251 (1990).
- <sup>6</sup>H. Matsuyama *et al.*, *Physica C* **160**, 567 (1989).
- <sup>7</sup>H. Matsumoto *et al.*, *Solid State Commun.* **71**, 829 (1989).
- <sup>8</sup>J. Inoue and S. Maekawa, *J. Phys. Soc. Jpn.* **59**, 2110 (1990).
- <sup>9</sup>C. M. Varma *et al.*, *Phys. Rev. Lett.* **63**, 1996 (1989).
- <sup>10</sup>H. Jichu *et al.*, *J. Phys. Soc. Jpn.* **58**, 4280 (1989).
- <sup>11</sup>I. Terasaki *et al.*, *Phys. Rev. B* **43**, 551 (1991).
- <sup>12</sup>J. M. Tarascon *et al.*, *Solid State Commun.* **71**, 663 (1989).
- <sup>13</sup>I. Terasaki *et al.*, *Phys. Rev. B* **41**, 865 (1990).
- <sup>14</sup>I. Terasaki (unpublished).
- <sup>15</sup>M. K. Kelly *et al.*, *Phys. Rev. B* **40**, 6797 (1989).
- <sup>16</sup>N. Nücker *et al.*, *Phys. Rev. B* **39**, 12 379 (1989).
- <sup>17</sup>S. Tajima *et al.*, *J. Opt. Soc. Am. B* **6**, 475 (1989).
- <sup>18</sup>A. E. Bocquet *et al.*, *Physica C* **169**, 1 (1990).
- <sup>19</sup>Y. Watanabe *et al.*, in *Physics and Materials Science of High Temperature Superconductors*, Vol. 181 of NATO Advanced Study Institute Series E: Applied Sciences, edited by R. Kossovsky *et al.* (Kluwer Academic, Dordrecht, 1990), p. 429; Y. Watanabe *et al.*, *Phys. Rev. B* **43**, 3026 (1991).
- <sup>20</sup>T. Tamegai and Y. Iye, *Physica C* **159**, 181 (1989).
- <sup>21</sup>M. Hiratani *et al.*, *Solid State Commun.* **72**, 541 (1989).
- <sup>22</sup>M. Reedyk *et al.*, *Phys. Rev. B* **45**, 7406 (1992).
- <sup>23</sup>T. Ido *et al.*, *Phys. Rev. B* **44**, 12 094 (1991).
- <sup>24</sup>Y. Tokura *et al.*, *Phys. Rev. B* **41**, 11 657 (1990).
- <sup>25</sup>H. Takagi *et al.*, *Phys. Rev. B* **40**, 2254 (1989).
- <sup>26</sup>I. Terasaki *et al.*, *Supercond. Sci. Tech.* **4**, S397 (1991).
- <sup>27</sup>Y. Tokura and T. Arima, *Jpn. J. Appl. Phys.* **29**, 2388 (1990).