Optical investigation of $A_2Ru_2O_7$ (A = Y, Tl, and Bi): temperature dependent self-doping effects

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Abstract

We measured the temperature (T-) dependent optical conductivity spectra $\sigma(\omega)$ of $Y_2Ru_2O_7$ (insulating), $Tl_2Ru_2O_7$ (metal–insulator transition) and $Bi_2Ru_2O_7$ (metallic). $\sigma(\omega)$ of $Y_2Ru_2O_7$ show absorption peaks around 1.7 and 3.2 eV, which are nearly T-independent. $\sigma(\omega)$ of $Bi_2Ru_2O_7$ are also nearly T-independent, but have a Drude-like peak in the far-infrared (IR) region. On the other hand, $\sigma(\omega)$ of $Tl_2Ru_2O_7$ have a very strong mid-IR peak, and its spectral weight is strongly T-dependent. Its T dependence through the metal–insulator transition is quite similar to the doping dependence of doped transition metal oxides, but there is no external dopant in $Tl_2Ru_2O_7$. Therefore, these phenomena of $Tl_2Ru_2O_7$ can be interpreted in terms of T-dependent self-doping effects; namely, the electronic structures near the Fermi level change due to the self-doping for the Ru 4d state in the presence of an easily polarizable Tl ion. © 2001 Elsevier Science B.V. All rights reserved.

For most high-T_c superconductors (HTSCs), their exotic physical properties are achieved by doping carriers, such as by substituting cations or by generating oxygen vacancies. Apart from the usual external-doping cases, some HTSCs with Bi or Tl elements, such as $Bi_2Sr_2CaCu_2O_8$ or Ba_2Tl_2-CuO_6, are known to experience self-doping, where the Bi or Tl ions can act as a charge reservoir [1,2].

Pyrochlore ruthenates, $A_2Ru_2O_7$, show a wide range of electrical properties depending on the A-site ions; $Y_2Ru_2O_7$ is an insulator and $Bi_2Ru_2O_7$ is

a metal. On the other hand, $Tl_2Ru_2O_7$ shows a metal–insulator transition accompanied by a structural change at $T_{MI} \sim 125$ K [3]. Up to now, the roles of the A-site ions on changes of the electrical properties have not been clearly identified. There are two possible scenarios; (1) A-site ions just change the Ru 4d bandwidth to induce a metal–insulator transition [4], and (2) their states will actively contribute to the states near the Fermi level, E_F [5,6], resulting in self-doping effects just like in the Bi- and Tl-related HTSCs. In this paper, we will address this interesting issue by investigating the optical conductivity spectra, $\sigma(\omega)$, of the pyrochlore ruthenates, $A_2Ru_2O_7$ (A = Y, Tl, and Bi).

The polycrystalline samples were synthesized by applying a high oxygen pressure [7]. Near normal

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incident reflectivity spectra, $R(\omega)$, were measured in a wide photon energy range of 5 meV–30 eV. The Kramers–Kronig (K–K) analyses were used to calculate $\sigma(\omega)$ from the measured $R(\omega)$. The calculated $\sigma(\omega)$ were consistent with experimental $\sigma(\omega)$ obtained by spectroscopic ellipsometry in the near-infrared (IR) and the visible ranges, which shows the validity of our K–K analyses [8].

Fig. 1 shows $\sigma(\omega)$ of $A_2Ru_2O_7$ (A = Y, Tl, and Bi). As A-site ions are varied from Y to Bi, $\sigma(\omega)$ show systematic spectral weight changes with an insulator–metal transition. The spectral features of the pyrochlore ruthenates can be divided into three parts: (1) the interband transition and/or the Drude-like responses below 1.5 eV, indexed by α, (2) the interband transition between the Hubbard bands of Ru 4d orbitals around 1.7 eV, indexed by β [9], and (3) the interband transition from O 2p bands to the upper Hubbard bands of Ru 4d orbitals above 2.5 eV, indexed by γ. Since $Y_2Ru_2O_7$ is considered to be a Mott insulator [4], only the peak β and γ can be observed. For me-

tallic $Bi_2Ru_2O_7$, the peak β, corresponding to the d–d transition, cannot be seen. These differences are attributed to variations of the electronic structures near E_F.

Detailed studies on spectral weight changes related to the metal–insulator transition of $Tl_2Ru_2O_7$ can provide further insights. Fig. 2 shows T-dependent $\sigma(\omega)$ of $Tl_2Ru_2O_7$. $\sigma(\omega)$ of other two compounds are nearly T independent. Although $Tl_2Ru_2O_7$ at 10 K is insulating just like $Y_2Ru_2O_7$, the corresponding spectrum shows an additional excitation in the mid-IR region. As T increases, the position of the mid-IR peak shifts to lower frequencies, and its spectral weight increases with the reduction of spectral weights of two peaks at the higher frequencies. In results, $Tl_2Ru_2O_7$ gets into the metallic state. These behaviors are reminiscent of the external doping dependences of the doped metal oxides. In the doped metal oxides, such as $(Y,Ca)VO_3$ and HTSCs [10,11], with increasing doping concentration, the mid-IR peak shifts to the lower frequencies and its spectral weight increases, which are quite similar to the T-dependent behaviors of the mid-IR peak for $Tl_2Ru_2O_7$.

Although $Tl_2Ru_2O_7$ is stoichiometric [7], the doping effects are also possible. The pyrochlore structure of $Tl_2Ru_2O_7$ can be considered to be
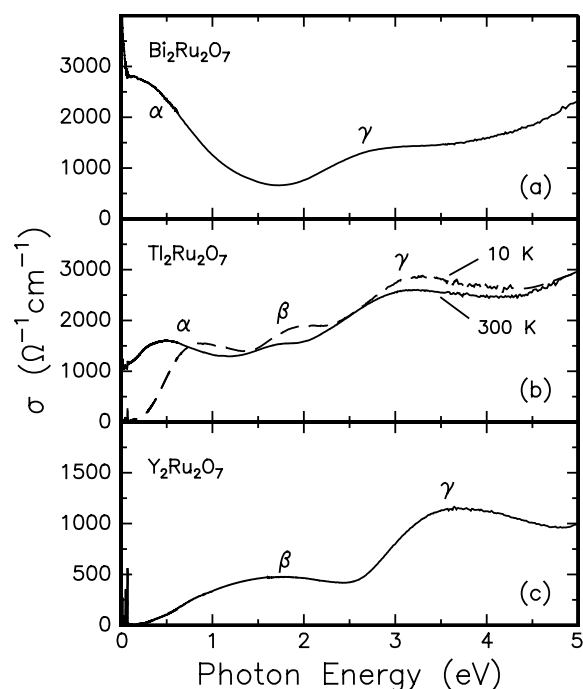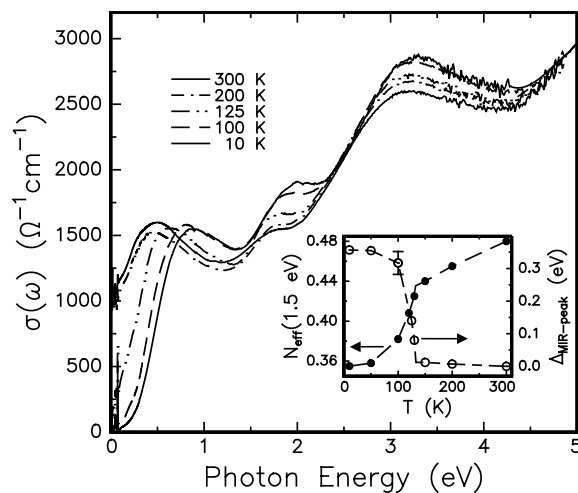

Fig. 1. $\sigma(\omega)$ of $A_2Ru_2O_7$ (A = Y, Tl, and Bi) at 300 K. For $Tl_2Ru_2O_7$, $\sigma(\omega)$ at 10 K is also shown.

Fig. 2. T-dependent $\sigma(\omega)$ of $Tl_2Ru_2O_7$. The inset displays the T-dependent effective carrier numbers at 1.5 eV with arbitrary unit, and the energy shift of mid-IR peak relative to the value at 300 K.

composed of the RuO(1)$_6$ octahedra and the Tl$_2$O(2) zigzag chains, where O(1) and O(2) denote oxygen atoms at two different sites. Then, there could be a charge density transfer (hole doping) from the Tl$_2$O(2) chains to the RuO(1)$_6$ octahedra, similarly to the cases of the Bi- or Tl-related HTSCs [1,2]. Accordingly, mid-gap states induced by the self-hole doping for the Ru ions could be located just above E_F [10,12] with partially filled Tl–O(2) bands [5]. Thus, the mid-IR excitation in $\sigma(\omega)$ can be originated from the transition between these bands and the lower Hubbard bands of Ru 4d orbitals. And, its spectral weight might indicate the degrees of self-doping concentration.

The inset of Fig. 2 shows the T-dependent energy shift of the mid-IR excitation relative to the value at 300 K, $\Delta_{MIR-peak}$, and the effective number of carriers, N_{eff} (1.5 eV), which were obtained by integrating the spectral weights up to 1.5 eV. As was indicated above, with decreasing T, N_{eff} (1.5 eV) decreases and $\Delta_{MIR-peak}$ increases, namely, the mid-IR peak shifts to higher energies. Note that these changes of two parameters occur very abruptly around T_{MI}. With decreasing through T_{MI}, Tl$_2$Ru$_2$O$_7$ experiences a structural symmetry lowering from cubic to orthorhombic, where two unequal Tl–O(2) bonds with different lengths exist [3]. This charge disproportion of the Tl–O(2) network can result in changes of the electronic structures related to the hole reservoir, and induces an abrupt reduction of N_{eff} (1.5 eV) below T_{MI}. Therefore, the metal-insulator transition in Tl$_2$Ru$_2$O$_7$ is closely related to the T-dependent reduction of the self-doping.

T-dependent $\sigma(\omega)$ of Tl$_2$Ru$_2$O$_7$, such as the existence of a mid-IR excitation and its systematic development with T could be well explained in terms of the self-doping effects. Thus, it can be concluded that the electronic structures near E_F change due to the self-doping for the Ru 4d state in the presence of an easily polarizable Tl ion.

The self-doping effects might explain the metallic state of Bi$_2$Ru$_2$O$_7$. Since Bi ions are also easily polarizable and have extended 6p wave functions, they can work as a charge reservoir similar to the Tl case. Fig. 3 shows $\sigma(\omega)$ of A$_2$Ru$_2$O$_7$ (A = Y, Tl, and Bi) in the low frequency region. For Bi$_2$Ru$_2$O$_7$, the mid-IR peak moves to a lower frequency
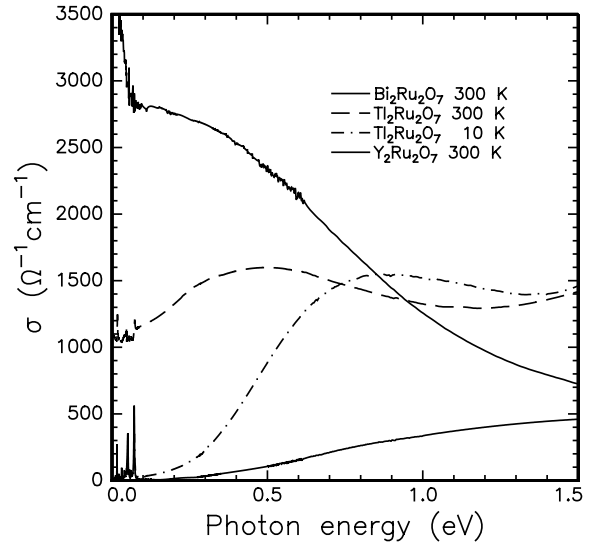
Fig. 3. $\sigma(\omega)$ of A$_2$Ru$_2$O$_7$ (A = Y, Tl, and Bi) in the IR region.

than that of Tl$_2$Ru$_2$O$_7$, and a Drude-like peak appears at the far-IR region. Therefore, the metallic state of Bi$_2$Ru$_2$O$_7$ can be considered as a self-doped state with more doping concentration than that of Tl$_2$Ru$_2$O$_7$. However, this interpretation should be confirmed with more care.

In summary, we investigated the optical conductivity spectra of various pyrochlore ruthenates. There are large spectral weight changes in the IR region through the metal–insulator transition. We suggest that these behaviors could be understood in terms of appearance of a mid-gap state due to the self-doping in the presence of the Tl or Bi ions, of which self-doping mechanism is quite similar to the Bi- or Tl-related high-T_c cuprates.

Acknowledgements

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