Materials Science-Poland, Vol. 22, No. 4, 2004

Optical properties of the one-dimensional organic conductors β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\;{}_{1/6}$I$_2$)$_3$ and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\;{}_x$I$_2$)$_3$, $x = 0.05$

IWONA OLEJNICZAK[1*], BARTŁOMIEJ GROMADZIŃSKI[1,2], ANDRZEJ GRAJA[1],
THOMAS DEVIC[3], PATRICK BATAIL[3]

[1]Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland

[2]Institute of Physics, Poznan University of Technology, Poznań, Poland

[3]Laboratoire de Chimie Inorganique, Matériaux et Interfaces,
CNRS FRE 2447, Université d’Angers, France

We report the room-temperature polarized infrared reflectance spectra of two radical cation salts based on halogenated TTF and two-dimensional polymeric iodoplumbate or Ag-doped iodoplumbate anions. These salts were β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, where $x = 0.05$ and $\square$ is a vacancy. Both materials display a metallic response, characteristic of quasi-one-dimensional organic conductors. The β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$ salt, with $x = 0.05$ is partly transparent along the lowest conductivity direction in the infrared frequency range. The single-crystal polarized absorption spectrum recorded in this direction displays a number of vibrational features related to the intramolecular modes of the EDT-TTF-I$_2$ molecule, which are assigned using available normal mode calculations. In addition, the absorption spectrum of the β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$ material dispersed in a KBr pellet is reported and discussed.

Key words: *EDT-TTF-I$_2$; iodoplumbate anion; organic conductors; reflectance spectrum; absorption spectrum*

1. Introduction

The manipulation of weak noncovalent intermolecular interactions for designing new low-dimensional solids has received increasing attention (see [1, 2] and refer-

---

[*] Corresponding author, e-mail: ywy@ifmpan.poznan.pl.

ences herein). Recently, two metallic radical cation salts based on two-dimensional polymeric iodoplumbate anions and halogenated TTF, namely β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, where $x = 0.05$ and $\square$ is a vacancy, have been synthesized (EDT-TTF-I$_2$ is a shortcut for ethylenedithio-1,2-diiodo-tetrathiafulvalene) [1]. In these materials, organic–halogen$\cdots$inorganic–halogen (I$\cdots$I) van der Waals interactions help stabilise the organic–inorganic interface.

Both β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, have a similar triclinic layered structure with the space group $P\bar{1}$ [1]. A conducting layer parallel to the *ab*-plane is formed by EDT-TTF-I$_2$ molecules, which are arranged in the well-known β-motif with loose stacks of one-electron-oxidized dimers along the *b*-direction. In the charge compensating inorganic Pb$_x$Ag$_y$I$_2$ slab, the edge-sharing octahedra form a polymer of the CdI$_2$-type [1]. Unlike the two-dimensional electronic structure typical of the β-(BEDT-TTF)$_2$X family [3], the intermolecular interactions within a conducting donor layer are characterized by weak interchain interactions, accompanied by significantly stronger uniform interactions along the EDT-TTF-I$_2$ chains. The specific one-dimensional-like electronic band structure [1] is related to the head-to-tail arrangement of asymmetric donor molecules in the stack. In spite of the close similarities between β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, both in their crystal and electronic structures, there is a significant difference between their room temperature d.c. conductivities, which are 2.5 $\Omega^{-1}\cdot$cm^{-1} and 110 $\Omega^{-1}\cdot$cm^{-1}, respectively.

In order to characterize the optical properties of β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, we have measured the room temperature polarized reflectance and absorption spectra of single crystalline samples. Our overall goal is to investigate the structure–property relationships in this class of low-dimensional solids.

2. Experimental

Single crystals of both materials were prepared by the electrochemical method as described elsewhere [1]. Samples of β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ were square-shaped shiny platelets with a typical size of about 0.2 × 0.2 × 0.05 cm^3. On the other hand, β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, crystallizes in very thin, flat, and partly transparent brown needles; the lengths of the largest samples used for measurements were about 1.3 mm. Samples were oriented based on the polarized infrared reflectance spectra and calculated interaction energies [1]. Near-normal incidence polarized reflectance and absorption spectra in the conducting *ab*-plane were measured using a Perkin-Elmer 1725 X Fourier-transform infrared spectrometer, equipped with an infrared microscope (650–7000 cm^{-1}, resolution 2 cm^{-1}) and a gold wire grid polariser. The absorption spectra of the KBr pellets were recorded using a Bruker

Equinox 55 Fourier-transform infrared spectrometer (400–7000 cm^{-1}, resolution 2 cm^{-1}) and a Perkin Elmer Lambda 19 spectrophotometer (5000–40 000 cm^{-1}). Optical conductivity spectra were calculated by the Kramers–Kronig analysis, based on the extrapolation of infrared reflectance to low frequencies with a metallic Hagen–Rubens equation; standard extrapolations were used for higher frequencies.

3. Results and discussion

Figure 1 shows the reflectance (upper panel) and optical conductivity spectra (lower panel) of β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, polarized in the b-direction. Both materials display similar behaviour, characteristic of one-dimensional organic conductor [4, 5]. In the b-direction which is parallel to the stacks of EDT-TTF-I$_2$ molecules, reflectance is high and metallic in

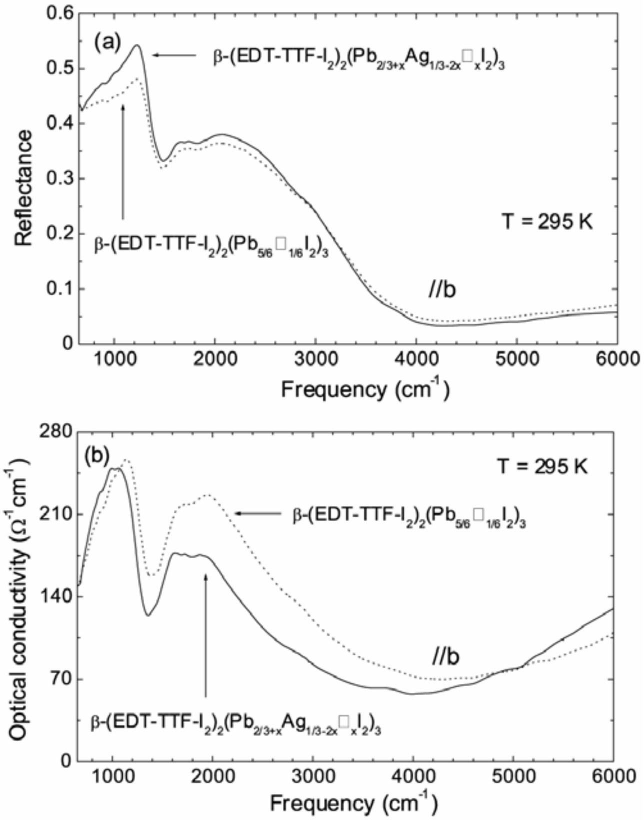

Fig. 1. Infrared reflectance (a) and optical conductivity (b) spectra of β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$ (dotted line) and β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$ (solid line), polarized along the b direction

character, with a plasma edge about 4000 cm^{-1}. The $\perp b$ spectra (not shown) are flat and generally structureless but influenced by interference fringes (weakly in the case of β-(EDT-TTF-I$_2$)$_2$(Pb$_{5/6}\square_{1/6}$I$_2$)$_3$, and very strongly in the case of β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$), which appear because both materials are partially transparent to infrared light. In the $\|b$ optical conductivity spectra (lower panel), two distinct low-energy electronic bands are observed in the frequency range of 1000–2000 cm^{-1}. They are possibly related to charge transfer excitations along the EDT-TTF-I$_2$ stack. The Drude peak, which is expected in a metallic material, does not appear in the two spectra due to the limited frequency range (above 650 cm^{-1}); the Drude feature can be very narrow for organic conductors [4].

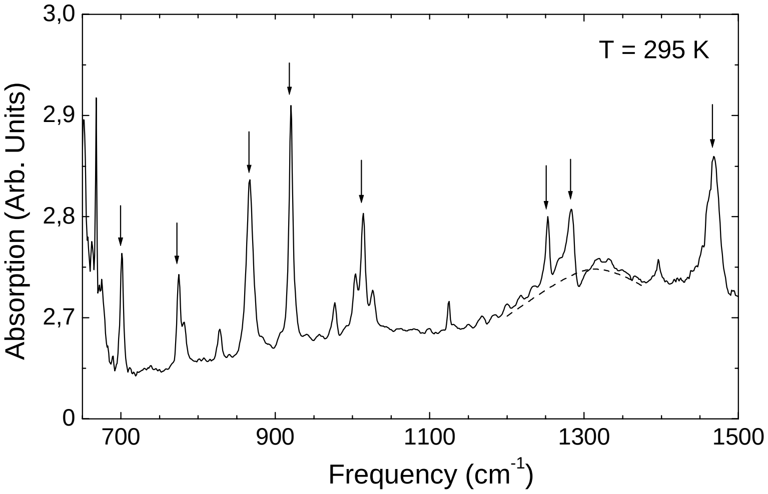

Fig. 2. Absorption spectrum of β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, polarized along the $\perp b$ direction, in the frequency range of intramolecular modes; the bands discussed are shown by arrows

The $\perp b$ absorption of β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, measured in the transmission mode in the frequency range of the vibrational features, is displayed in Fig. 2. The spectrum is polarized approximately parallel to the short EDT-TTF-I$_2$ axis in the crystal structure. Here, a number of vibrational bands are shown, and we assign them as intramolecular modes of the EDT-TTF-I$_2$ molecule. In addition, a weak electronic excitation is observed about 1300 cm^{-1}; another weak and very broad electronic band appears about 3000 cm^{-1} (not shown). Due to the low symmetry of β-(EDT-TTF-I$_2$)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$ with $x = 0.05$, which results from an asymmetric donor molecule, all intramolecular modes can appear both in Raman and infrared spectra. Using normal mode calculations, infrared spectra, and Raman spectra for neutral EDT-TTF-I$_2$ [6], we attribute the 1468 cm^{-1} feature as a stretching C=C mode, whose frequency is downshifted from 1516 cm^{-1} (the Raman mode in neutral molecule) due to oxidation and also possibly to electron-molecular vibration (EMV) coupling with low-lying electronic excitations [7, 8]. In the case of an asymmetric donor molecule, only weak coupling is expected, but basically all intramolecular vibrations are allowed for coupling*. In fact, the C=C stretching vibration is barely seen in the infrared spectra of neutral EDT-TTF-I_2 [6], and it is the strongest band in the infrared spectrum of β-(EDT-TTF-I_2)$_2$(Pb$_{2/3+x}$Ag$_{1/3-2x}\square_x$I$_2$)$_3$ with $x = 0.05$. This can serve as a proof that the band is activated by EMV coupling. Other relatively strong and broad features that are possibly EMV-activated include the mode at 1283 cm^{-1} related to C–H wagging, 1253 cm^{-1} (C–H wagging), 1014 cm^{-1} (C–H rocking, C–C stretching), 920 cm^{-1} (C–S stretching, C–I stretching), 867 cm^{-1} (C–H rocking), 775 cm^{-1} (C–H rocking, C–S stretching), and 701 cm^{-1} (C–S stretching, C–I stretching).

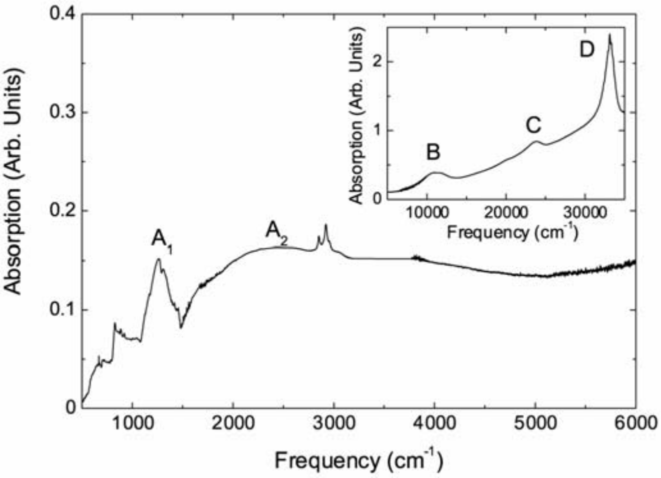

Fig. 3. Infrared and optical (inset) absorption spectra of β-(EDT-TTF-I_2)$_2$(Pb$_{2/3+x}$ Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, dispersed in a KBr pellet (unpolarised)

Figure 3 shows the unpolarised absorption spectrum of β-(EDT-TTF-I_2)$_2$(Pb$_{2/3+x}$ Ag$_{1/3-2x}\square_x$I$_2$)$_3$, with $x = 0.05$, dispersed in a KBr pellet. We relate most of the bands in the spectrum to electronic excitations. In the infrared frequency range, we observe features polarized in both the $\parallel b$- and $\perp b$ directions. The A$_1$ band is probably related to the lowest energy excitation in the b direction (Fig. 1b), and to the $\perp b$ excitation (the dashed line in Fig. 2). A very broad A$_2$ band is probably connected to both the 2000 cm^{-1} excitation polarized in the b direction (Fig. 1b) and the 3000 cm^{-1} excitation in $\perp b$-direction. The sequence of higher energy excitations (the inset in Fig. 3) is somehow reminiscent of the classification developed by Torrance et al. for one-dimensional TCNQ-based compounds (TCNQ – tetracyanoquinodimethane) [9]. In this picture, A and B bands both involve charge transfer between donor molecules (B excitation

---

*In the case of the lowest symmetry (C_1), all intramolecular modes are of the A-type and can be coupled with the electronic states.

leads to a double-charged donor molecule, so its energy can serve as a rough estimation of the electron Coulomb interaction U); C and D bands correspond to intramolecular excitations. On the other hand, EDT-TTF-I_2 is substantially different than TCNQ, and it is well known that iodoplumbate compounds can have excitations in the visible frequency range, which is where C and D bands are located [10].

4. Conclusions

We investigated the room temperature polarized response of the organic conductors β-(EDT-TTF-I_2)$_2$($Pb_{5/6}\square_{1/6}I_2$)$_3$ and β-(EDT-TTF-I_2)$_2$($Pb_{2/3+x}Ag_{1/3-2x}\square_x I_2$)$_3$, with x = 0.05, in the infrared frequency range. These materials exhibit similar one-dimensional metallic behaviour, as expected from electronic band structure calculations [1]. In the vibrational frequency range, signatures of EMV coupling are found. The strongest bands, arising from intramolecular modes, are assigned. Further studies are on the way to give more information on the complicated picture of charge transfer excitations and EMV coupling in both materials.

Acknowledgements

This work was supported by the Polish Committee for Scientific Research as the research project in the years 2004–2007.

References

[1] Devic T., Evain M., Moëlo Y., Canadell E., Auban-Senzier P., Fourmigue M., Batail P., J. Am. Chem. Soc., 125 (2003), 3295.

[2] Devic T., Canadell E., Auban-Senzier P., Batail P., J. Mater. Chem., 14 (2004), 135.

[3] Whangbo M.-H., Williams J.M., Leung W.P.C., Beno M.A., Emge T.J., Wang H.H., Carlson K.D., Crabtree G.W., J. Am. Chem. Soc., 107 (1985), 5815.

[4] Jacobsen C.S., *Infrared Properties of Organic Conductors*, [in:] D. Jérome and L.G. Caron (Eds.), *Low-Dimensional Conductors and Superconductors*, Plenum Press, New York, 1987, p. 253.

[5] Kawamoto T., Ashizawa M., Aragaki M., Mori T., Yamamoto T., Tajima H., Kitagawa H., Mitani T., Misaki Y., Tanaka K., Phys. Rev. B, 60 (1999), 4635.

[6] Łapiński A., Świetlik R., unpublished results.

[7] Rice M.J., Phys. Rev. Lett., 37 (1976), 36.

[8] Yartsev V.M., Graja A., Int. J. Mod. Phys. B, 12 (1998), 1643.

[9] Torrance J.B., Scott B.A., Kaufman F.B., Solid State Commun., 17 (1975), 1369.

[10] Ishihara T., *Optical Properties of Pb-Based Inorganic–Organic Perovskites*, [in:] T. Ogawa and Y. Kanemitsu (Eds.), *Optical Properties of Low-Dimensional Materials*, World Scientific, Singapore, 1995, p. 286.

Received 30 October 2004
Revised 3 November 2004