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SYNTHESIS, STRUCTURE AND ELECTRICAL PROPERTIES OF THE TWO-DIMENSIONAL ORGANIC CONDUCTOR, $(BEDT\text{-}TTF)_2BrI_2$

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Single crystals of α-$(BEDT\text{-}TTF)_2BrI_2$ and β-$(BEDT\text{-}TTF)_2BrI_2$ were prepared using standard electrochemical techniques in nitrogen saturated benzonitrile solution containing $(n\text{-}C_4H_{10})NBrI_2$ as supporting electrolyte. The crystals have nearly identical structure features of α-$(BEDT\text{-}TTF)_2I_3$ and β-$(BEDT\text{-}TTF)_2I_3$, except that the BrI_2^- anions are disordered in α-$(BEDT\text{-}TTF)_2BrI_2$ and β-$(BEDT\text{-}TTF)_2BrI_2$. Their electrical behavior is different from the corresponding α-,β-$(BEDT\text{-}TTF)_2I_3$species.

INTRODUCTION

Recent discoveries of the superconductivity of BEDT-TTF polyhalide systems have attracted a considerable physical and chemical interest[1]. The extraordinaly variety of structures of BEDT-TTF compounds is originated from the mutidimensional molecular arrangements of BEDT-TTFs. Metallic conduction along the transverse molecular array is one of the most striking feature of the BEDT-TTF compounds. In addition,it may be note worthy that a slight structural modification leads to significant changes of the electrical properties. In this paper, synthesis, crystal structure and electrical properties of α-, β-$(BEDT\text{-}TTF)_2BrI_2$ will be described.

EXPEREMENTS

The redish brown needles of $TBABrI_2$ were prepared by a reaction of TBABr with I_2(mol. ration 1:1) in CCl_4 and glacial acetic acid, through 2 times recrystalisation from abs. ethanol, mp. 58 °C . Single crystals of $(BEDT\text{-}TTF)_2BrI_2$ were grown by electrochemical oxidation in a nitrogen saturated benzonitrile solution containing $TBABrI_2$ as supporting electrolyte. We have found at least two phases of $(BEDT\text{-}TTF)_2BrI_2$ crystals in which the α- and β-forms were determined by x-ray diffraction techniques.

The structures of α-,β-$(BEDT\text{-}TTF)_2BrI_2$ were solved via direct and Fourier methods and refined by "blocked cascade" leastsquare for a scale factor, position and anisotropic thermal parameters.

RESULTS AND DISCUSSION

the crystals data of α-$(BEDT\text{-}TTF)_2BrI_2$ and β-$(BEDT\text{-}TTF)_2BrI_2$ are: α-form, triclinic, space group $P\bar{1}$, a=9.142,b=10.818 c=17.370 Å, α=96.977, β=97.967;γ=90.813°

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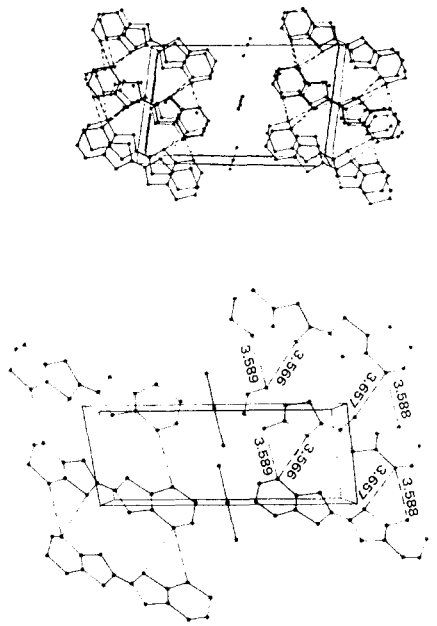

Fig.1,The crystal structure of α-(BEDT-TTF)$_2$BrI$_2$(top) and ß-(BEDT-TTF)$_2$BrI$_2$ (bottom), the intermolecular S-S contacts <3.7Å between the stacks are drawn as broken lines.

v=1687.94,z=2; ß-form,triclinic, space group P$\bar{1}$, a=6.610,b=9.040,c=15.212Å, α=94.257,ß=95.268,γ=110.062°,v=842.40, z=1. The unit cell structures of the α-ß-(BEDT-TTF)$_2$BrI$_2$ crystals are shown in Fig.1. The structural feature of the organic cations in the α-BrI$_2$ salt is almost identical with that of α-(BEDT-TTF)$_2$I$_3$. Significant S···Scontact distances less than the Van der Waals radii of 3.70Å are only observed in the interstack direction , while considerably longer S···S contacts (>3.70Å) appear in the intrastack direction. There is a pronounced difference in the geometry of their anions with respect to the I_3 salt. In I_3-salts it has been found that the anions are linear-centrosymmetric and both bond lengths of I-I are identical being 2.937Å [2], while in the case of BrI_2^- the bond lengths of I-I and I-Br are 2.894(2.890) and 2.933 Å (2.937Å) respectively for the two different chains and the Br-I-I anion is not linear and has interbond angle of 171.7 and 171.8° respectively. Short I···Br contacts (3.933Å and 3.823Å) along the chains smaller than the V.d. Waals distance of 4.05Å are obeserved in α-(BEDT-TTF)$_2$BrI$_2$.

The structure of ß-(BEDT-TTF)$_2$BrI$_2$ has the most uniform 2D-(BEDT-TTF) network and all organic molecules are crystallographically equivalent compared with the ß-form of the I_3-salts[3].There is a significant difference in the structure of the trihalide anions. The geometry $(I-Br-I)^-$ has not been observed, the bond length of I-Br and I-I are 2.833Å and 2.792Å respectively, the shortest I···Br contact along the chain is 4.119Å .

The anisotropic conductivities of the α-phase crystals in the ab-plane were measured using the Montgomery method. Typical observed values for the room temperature conductivities in the ab-plane range from 5-10 $(\Omega,cm)^{-1}$, σ_a/σ_b <2; the conductivity along the direction of the alternating cations and anion sheets,σ_c, is 1000 times smaller, that means the crystals exhibit a pronounced two dimensionnal conductivity. The small conductivity anisoptropy in the ab-plane is kept down to low temperatures. The conductivities in the ab-plane (σ_a, σ_b) increase somewhat with decreasing temperature. Phase transitions in the two different directions occur at about 245K and 265K.Thus

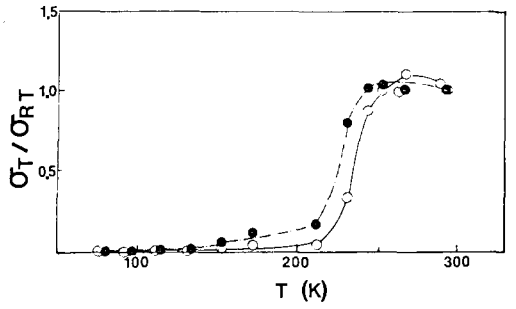

Fig. 2. Temperature dependence of conductivities along ab-plane of α-(BEDT-TTF)$_2$BrI$_2$.

in spite of the similar structural features of I_3^- and $(BrI_2)^{-1}$ salts, which includes the BEDT-TTF molecular packing and the S···S contacts in the BEDT-TTF network, the electrical properties of α-(BEDT-TTF)$_2$BrI$_2$ is different from that of α-(BEDT-TTF)$_2$I$_3$, in which a metal insolator transition occurs at 135K[2].

The conductivity of β-(BEDT-TTF)$_2$BrI$_2$ crystals was measured by the standard four probe method using d.c. and a.c. techniques. The temperature dependence of the resistivity of β-(BEDT-TTF)$_2$BrI$_2$ crystals along the b-direction in the temperature range between 70-300K is shown in Fig.3.A metallic like behaviour is observed between 300 and 160K. Below 160K the resistivity increases suddenly while at 130K it starts to decrease again. This behaviour was observed on several crystals. In the moment it is not clear to us whether the increase in resistivity at around 160K is due to crystal cracks or if their excists some other reasons (at about this temperatue in the β-I$_3$-crystals the incommensurate phase starts to build up).

In the thermopower data which are

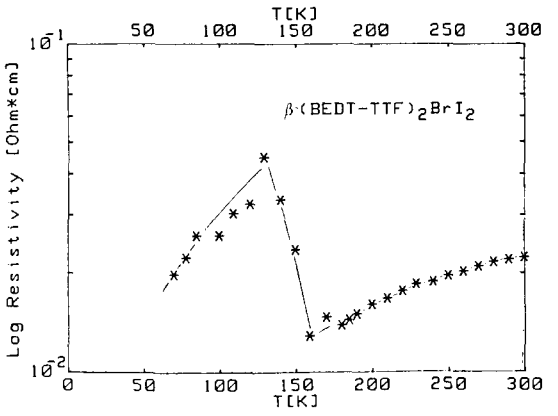

Fig.3. Temperature dependence of resistivity of β-(BEDT-TTF)$_2$BrI$_2$.

shown in Fig. 4 no unusual change is observed in the temperature range between 130 and 160K. The temperature dependence of the thermopower of β-(BEDT-TTF)$_2$BrI$_2$ crystals is very similar to those of the β-I$_3$ crystals[4], which are metallic down to 1.3K and become superconducting there. The only difference is that in the β-I$_3$-crystal at about

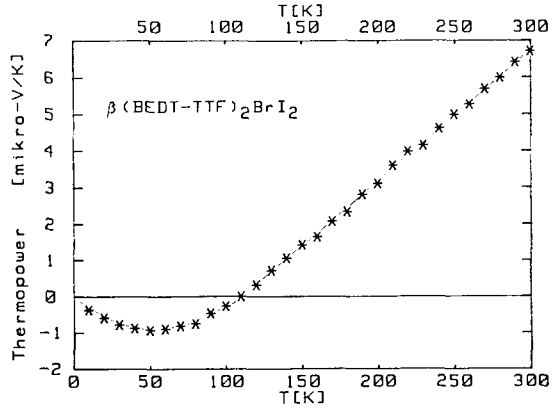

Fig.4. Temperature dependence of thermopower of β-(BEDT-TTF)$_2$BrI$_2$

120K a sharp break in the slope is observed[4], while here the thermopower changes smoothly from a positive to a small negative value. The rather small positive value of about 7 μv/K at room temperature indicates that the conductivity is dominated by holes, and the linear temperature dependence down to about 100K is typical for a metal. Below 100K the thermopower is within the experimental error (±1μv/K) more or less zero.

In principle it is possible to calculate the bandwidth from the thermopower data, but due to the two dimensional character of the material and the dimerization of the BEDT-TTF molecules within the stacks it is not quite clear which band model should be used . In order to get an estimate we used an isotropic 2 dim. tight binding model and obtained a conduction bandwidth of 0.26 ev which is only a rough estimate.

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