Effect of copper substitution on the electrical transport properties of (Bi,Pb)₂MO₄ (M ≡ Pd, Pt) linear chain compounds

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Abstract

Three extensive new solid solution series were prepared in which M^{2+} (M ≡ Pd, Pt) is replaced by Cu^{2+} in the unoxidized Bi_2PdO_4 and in the partially oxidized $(Bi,Pb)_2MO_4$ phases. For palladium compounds, the tetragonal cell c parameter and therefore the metal–metal distance decreases with increasing copper substitution, while for platinum-based materials, the M–M distance increases with increasing copper concentration. However, for the three series, the resistivity regularly decreases with Cu^{2+} substitution for M^{2+}. Thus, by adjusting both the [Bi]/[Pb] and [M]/[Cu] ratios it is possible to obtain a material with a given room-temperature conductivity ranging from 10 to 10^{-6} S cm^{-1}.

1. Introduction

Although numerous one-dimensional d^8-metal complexes with various kinds of ligands have been extensively studied, the number of one-dimensional oxides investigated is very limited [1]. In the double oxide Bi_2PdO_4 previously synthesized [2], palladium could be partially oxidized by the substitution of Pb^{2+} for Bi^{3+} [3], so new mixed-valence compounds are obtained. Partial oxidation of platinum is necessary to stabilize the analogous platinum compounds [4]. All these oxides are isostructural with Bi_2CuO_4 [5]. Their structures consist of MO_4 groups which are stacked along the c-axis of the tetragonal cell, the metal–metal distance is half the c parameter, and the (MO_4) columns are linked together by Bi^{3+} and Pb^{2+} ions (Fig. 1). Bi_2CuO_4 is an insulator while the unoxidized palladium compound appears to be semiconducting. In the partially oxidized palladium phases, the conductivity increases linearly with the mean oxidation degree (MOD) of the transition metal atom (the MOD increases linearly with decreasing metal–metal distance). Oxidized lead–bismuth platinum phases exhibit relatively high conductivity with small variations with MOD. In this paper, we report the influence of Cu^{2+} substitution in Bi_2PdO_4 and in partially oxidized compounds on metal–metal distances and electrical conductivity properties.

2. Experimental details

The starting materials, synthesis procedure, X-ray powder equipment and the set-up for conductivity mea-
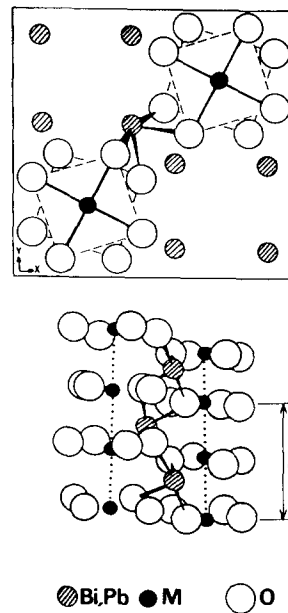

⊘ Bi,Pb ● M ○ O

Fig. 1. Projection along the c axis and perspective view of the $(Bi,Pb)_2MO_4$ structure.

surements have been described previously [3]. Briefly, polycrystalline electrical measurements were obtained by the four-probe method on parallelepipedic samples which had been cold pressed and sintered at 730 °C.

3. Results

3.1. $Bi_2Pd_{1-x}Cu_xO_4 (0 \leqslant x \leqslant 1)$

A complete solid solution exists between the isostructural Bi_2PdO_4 and Bi_2CuO_4. Both a and c parameters

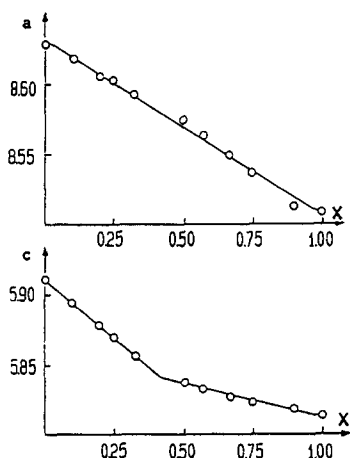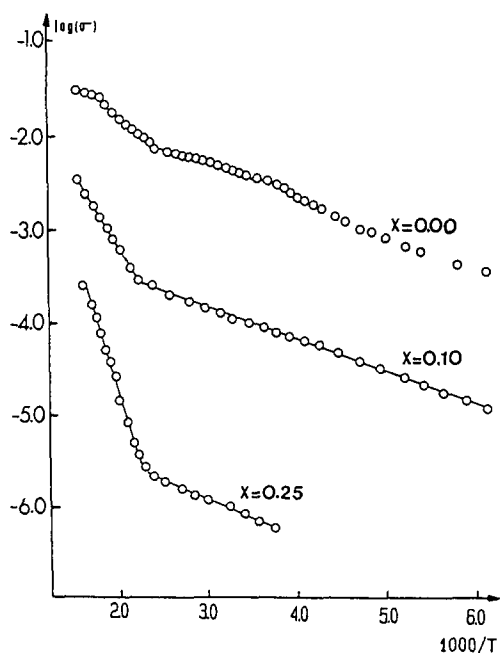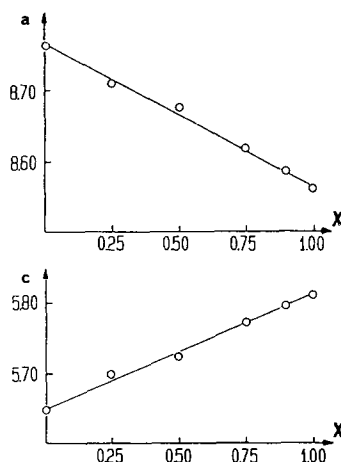Fig. 2. Variation of unit cell parameters (in ångströms) in $Bi_2Pd_{1-x}Cu_xO_4$.

Fig. 4. Variation of unit cell parameters (in ångströms) in the partially oxidized platinum compound as a function of copper substitution.

Fig. 3. Variation of $\log \sigma$ $(S\,cm^{-1}\,cm^{-1})$ vs. $1000/T$ in $Bi_2Pd_{1-x}Cu_xO_4$ compounds.

of the tetragonal unit cell decrease from $x = 0$ to $x = 1$ (Fig. 2). However, while a decreases linearly, the variation of c reveals two different linear parts with an intersection point at $x \approx 0.418$ (approximately 5/12). The variations of $\log \sigma$ vs. the reciprocal temperature for the compositions $x = 0$, $x = 0.10$ and $x = 0.25$ are given in Fig. 3. For higher values of x, the conductivity is too low to be measured by the method used.

3.2. Substitution in partially oxidized platinum compounds

$Bi_{2-y}Pb_yPtO_4$ is stabilized within the range $0.33 \leqslant y \leqslant 0.52$ [3]. To study the influence of copper

substitution, a middle composition $Bi_{1.57}Pb_{0.43}PtO_4$ was chosen. If we assume the presence of divalent and tetravalent platinum with no oxygen vacancies in the oxygen sublattice, the formula of the starting phase can be written:

$$Bi_{1.57}Pb_{0.43}Pt^{II}_{0.785}Pt^{IV}_{0.215}O_4$$
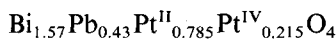
Only 80% of the platinum atoms can be substituted; this result is in good accordance with the presence of tetravalent platinum and with the above formula. The partially substituted phases can be written as

$$Bi_{1.57}Pb_{0.43}Pt^{II}_{0.785(1-x)}Cu^{II}_{0.785x}Pt^{IV}_{0.215}O_4$$
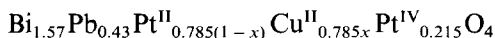
with $0 \leqslant x \leqslant 1$. Figure 4 shows the linear variations of the cell parameters with x. Figure 5 gives the variation of $\log \sigma$ vs. $1000/T$ for the limiting compositions and for three intermediate compositions ($x = 0.25$, 0.50 and 0.75).

3.3. Substitution in partially oxidized palladium compounds

Partial oxidation of palladium in Bi_2PdO_4 is achieved up to $Bi_{1.91}Pb_{0.09}PdO_4$ [3]. Starting from $Bi_{1.925}Pb_{0.075}$-PdO_4, complete copper-substitution for palladium seems to be possible; however, the amount of Pd^{IV} in the starting phase is very low (0.0375) and it is reasonable to assume that the substitution is limited to the Pd^{II} atoms in accordance with the results of the platinum series and with the impossibility of Pb^{2+} substitution for Bi^{3+} in Bi_2CuO_4 (complete substitution of lead leads to $Bi_{1.925}Pb_{0.075}CuO_4$). Furthermore, the cell parameters of the substituted phase are appreciably different from those of Bi_2CuO_4. So, the partially substituted phases can be formulated as

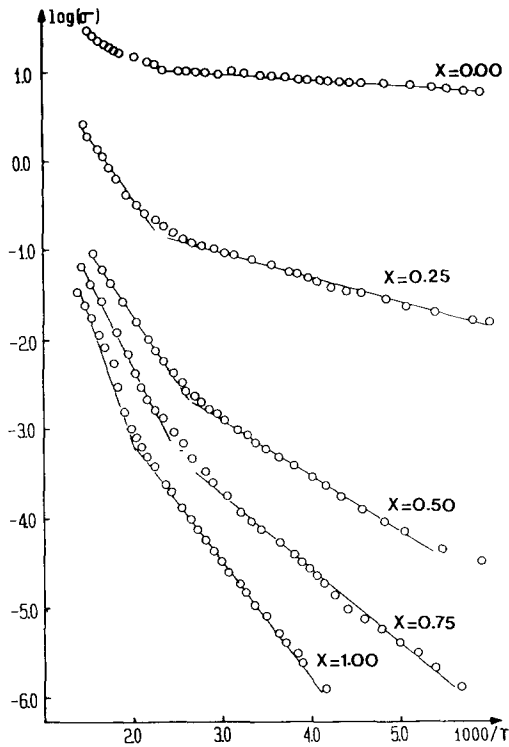$$Bi_{1.925}Pb_{0.075}Pd^{II}_{0.9625(1-x)}Cu_{0.9625x}Pd^{IV}_{0.0375}O_4$$
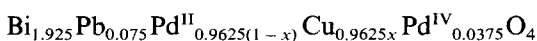
Fig. 5. Variation of $\log \sigma$ ($S\,cm^{-1}\,cm^{-1}$) vs. $1000/T$ in the partially oxidized platinum compound for different copper substitution values.

with $0 \leqslant x \leqslant 1$. Figure 6 gives the cell parameters vs. x while the variation of $\log \sigma$ vs. $1000/T$ for different values of x is shown in Fig. 7.

4. Discussion

In the three series, the parameter a decreases when copper is substituted for palladium or platinum atoms; this decrease is logically correlated with the ionic radii of Pd^{2+}, Pt^{2+} or Cu^{2+} for square planar coordination (0.64, 0.60 and 0.57 Å respectively, from ref. 6). For the palladium oxides, the parameter c also decreases when Pd^{2+} is replaced by Cu^{2+} in accordance with the diminution of the ionic size; in contrast, for the platinum systems, the c parameter (and therefore the metal–metal distance) increases.

Replacing palladium by copper in Bi_2PdO_4 results in a spectacular decrease in the conductivity, as shown in Fig. 3. A change of slope in the $\log \sigma - T^{-1}$ curves occurs at about 450 K. This change would be correlated with extrinsic behaviour of this semiconductor. At high temperature, the activation energy increases with x.

For the two partially oxidized compounds $(Bi,Pb)_2MO_4$ ($M \equiv Pd$, Pt), the conductivity readily decreases when copper takes the place of M^{II}. The variations of the c axis and therefore of the metal–metal
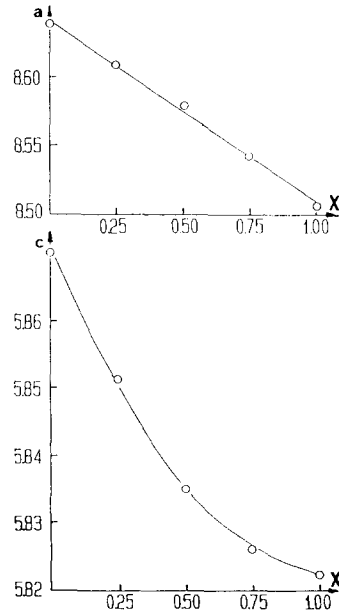

Fig. 6. Variation of tetragonal cell parameters (in ångströms) in the partially oxidized palladium compound as a function of copper substitution.
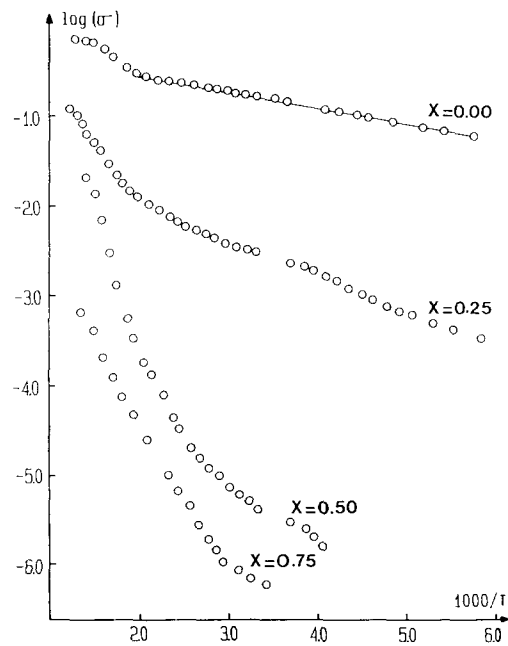

Fig. 7. Variation of $\log \sigma$ ($S\,cm^{-1}\,cm^{-1}$) vs. $1000/T$ in the partially oxidized palladium compound for different ratios of copper substitution.

distance with x are opposite for the two compounds and the variations of the conductivity with metal–metal distance are also opposite: for the palladium compounds it increases with increasing $d_{Pd\,Pd}$, while for the platinum phases it decreases with increasing $d_{Pt\,Pt}$ (Fig. 8).

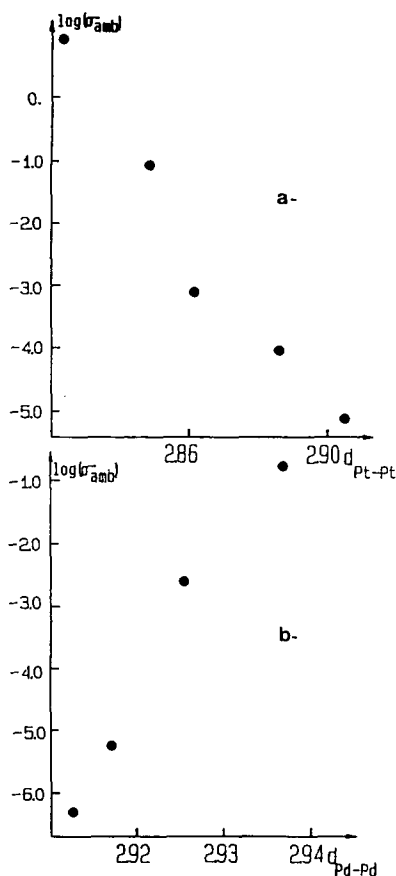We have assumed that (1) there are no oxygen vacancies on the oxygen substructure, (2) copper substituted

Fig. 8. Variation of log σ (300 K) vs. metal–metal distance in the two partially oxidized compounds $(\text{Bi,Pb})_2(\text{M,Cu})\text{O}_4$: (a) $\text{M} \equiv \text{Pt}$, (b) $\text{M} \equiv \text{Pd}$.

non-existence of $\text{Bi}_{2-y}\text{Pb}_y\text{CuO}_4$ also seems to indicate that copper cannot be oxidized past the divalent state in this structure type. Partial oxidation in columnar-stacked compounds involves delocalization of charge-carrying species, so fully oxidized cations do not exist; however, the copper to platinum substitution ratio in $(\text{Bi,Pb})_2\text{PtO}_4$ compounds indicates that only the part of platinum atoms corresponding to Pt^{2+} can be substituted and that the unsubstituted platinum is present as Pt^{4+} at least for $x = 1$; thus, for convenience, notation with Pt^{II} and Pt^{IV} has been used in this paper although the existence of Pt^{4+} (or Pd^{4+}) at square planar sites is questionable. Further investigations, especially neutron diffraction studies and conductivity measurements under different oxygen pressures, are in progress.

5. Conclusion

$(\text{Bi,Pb})_2(\text{M,Cu})\text{O}_4$ (with $\text{M} \equiv \text{Pd}$ or Pt) solid solutions provide a good example of modulation of electrical transport properties which can be achieved in two ways: first, by modification of the mean oxidation degree of a multivalence ion (palladium or platinum) by choosing the [Bi]/[Pb] ratio, and second by substitution of this multivalence ion by a 3d ion such as Cu^{2+}. Thus, it is possible to obtain a material with a given room-temperature conductivity ranging from 10 to $10^{-6} \, \text{S cm}^{-1} \, \text{cm}^{-1}$ by adjusting the different ion concentrations in the same structural framework.

on the square-planar site is rigorously divalent, and (3) tetravalent platinum can exist on a square-planar site.

Assumption (1) is supported by thermogravimetric analysis (TGA) experiments, carried out under a hydrogen stream, which seem to indicate four oxygen atoms by each M atom; unfortunately, TGA experiments lack precision when analysing oxygen in the presence of heavy atoms such as bismuth, lead and platinum. It is also supported by the fact that platinum atoms cannot be totally replaced by copper atoms and that $\text{Bi}_{2-x}\text{Pb}_x\text{CuO}_{4-x/2}$ phases cannot be prepared. The

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