JOURNAL OF SOLID STATE CHEMISTRY **103**, 447–450 (1993)

X-Ray and Resistivity Studies on $Ag_5Pb_{2-x}M_xO_6$ ($M = Bi^{3+}, In^{3+}$)

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Received May 26, 1992; in revised form September 23, 1992; accepted September 24, 1992

By reacting Ag_2O and PbO_2 with $AgBiO_3$ and In_2O_3, respectively, at temperatures between 770 and 820 K and oxygen pressures of 100 MPa for 4 days, mixed crystals according to the formula $Ag_5Pb_{2-x}M_xO_6$ ($M = Bi^{3+}$ and In^{3+}) in the stability range from $x = 0$ to $x = 1$ (In $x_{max} = 0.75$) were formed. As characterized by X-ray powder diffractometry the substitution of Bi^{3+} for Pb^{4+} leads to an increase of the cell volume from 196.4 (undoped sample) to 200.4 Å^3 ($x = 1$), while In^{3+} decreases it to 189.9 Å^3. As their metallic behavior is lost, the resistivity of the Bi-doped compounds grows drastically with increasing Bi-content, while In-doping shows only a small increase in resistivity.

Introduction

Based on crystal chemical arguments we consider $Ag_5Pb_2O_6$, containing monovalent silver and tetravalent lead, to show a surplus of one delocalized electron per formula unit (*1*). This feature, which may be expressed by the formula $Ag_5Pb_2O_6(e^-)$, reflects itself in the electrical conductivity. According to four-probe dc measurements the resistivity is about 0.35 mΩ · cm at room temperature and exhibits a metallic type of temperature coefficient. In order to get further evidence for our interpretation we have substituted suitable trivalent cations, In^{3+} or Bi^{3+}, for one of the lead atoms per formula unit successively. This should reduce the charge carrier concentration and consequently the conductivity, too.

Experimental

Powder samples were prepared by reacting stoichiometric mixtures of Ag_2O (p.a. Merck), PbO_2 (p.a. Merck), and $AgBiO_3$ (*2*) or In_2O_3 (Unterharzer Berg- und Hüttenwerke) using corundum crucibles in stainless steel autoclaves at oxygen pressures of 100 MPa for 4 days (cooling rate 50 K/h). The Bi-doped samples were prepared in a temperature range from 770 to 790 K while temperatures of 820–840 K were necessary for reacting In_2O_3.

Powder X-ray diffraction patterns were recorded with a Stoe Stadi-P diffractometer (position sensitive detector) using monochromatized Cu$K\alpha$ radiation. Electrical resistivity measurements on pellets (∅ = 9 mm, $h \approx 1$ mm) were made by a standard

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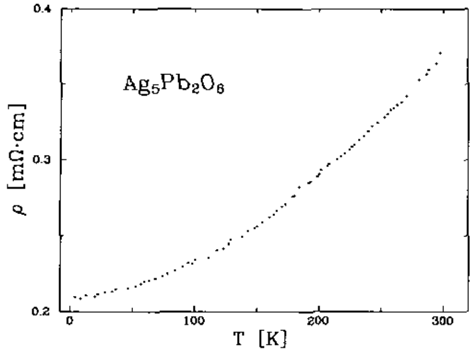

FIG. 1. Temperature dependence of the resistivity for $Ag_5Pb_2O_6$.

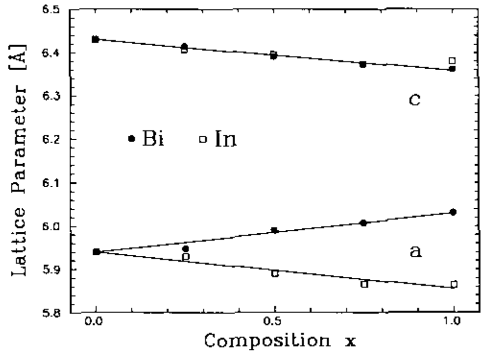

FIG. 3. Lattice parameters of $Ag_5Pb_{2-x}M_xO_6$ as a function of M = Bi and M = In content x. Linear fits to the data are shown.

four-probe technique in the temperature range of 1.5 to 300 K. Silver epoxy was used to attach contacts to the samples. The magnetic susceptibility data were taken using a magnetic balance in an applied field of 8000 Oe from 10 to 300 K.

Results and Discussion

Figure 1 shows the resistivity vs temperature of the undoped sample $Ag_5Pb_2O_6$, which exhibits metallic conductivity with a room temperature resistivity of 0.35 mΩ · cm and a linear temperature coefficient of $\alpha = 6.9 \times 10^{-7}$ Ω · cm/K. The X-ray diffraction pattern of this compound, shown in Fig. 2, was indexed assuming a hexagonal unit cell (*1*).

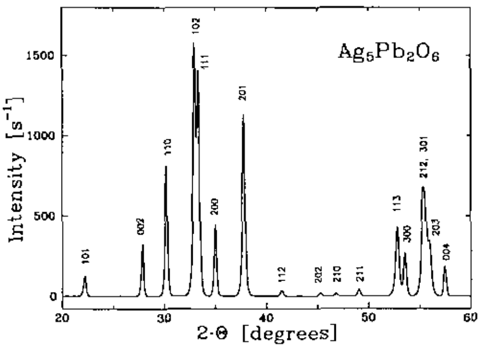

FIG. 2. X-ray diffraction pattern of $Ag_5Pb_2O_6$ using Cu$K\alpha$ radiation.

Reacting appropriate mixtures of the binary components in the solid state, solid solutions $Ag_5Pb_{2-x}Bi_xO_6$ and $Ag_5Pb_{2-x}In_xO_6$ ($0 \leq x \leq 1$) form readily. The lattice parameters of the solid solution vary continuously with composition, which is shown in Fig. 3 and Table I. Doping with bismuth increases the molar volume by 2.7% ($x = 1$), while substituting the smaller indium for lead decreases it by 2.8% ($x = 1$).

For $x > 1$ (In $x > 0.75$) the reaction products are inhomogeneous. In this case one component is Ag_5PbBiO_6 or $Ag_5Pb_{1.25}In_{0.75}O_6$,

TABLE I

LATTICE PARAMETERS OF THE Bi^{3+} AND In^{3+} DOPED SAMPLES

COMPOSITION	a/Å	c/Å	V/Å^3
$Ag_5Pb_2O_6$	5.9393(6)	6.4302(8)	196.4
$Ag_5Pb_{1.75}Bi_{0.25}O_6$	5.9470(13)	6.4148(11)	196.5
$Ag_5Pb_{1.5}Bi_{0.5}O_6$	5.9893(18)	6.3906(15)	198.5
$Ag_5Pb_{1.25}Bi_{0.75}O_6$	6.0073(8)	6.3737(5)	199.2
Ag_5PbBiO_6	6.0314(6)	6.3612(4)	200.4
$Ag_5Pb_{1.75}In_{0.25}O_6$	5.9291(9)	6.4080(7)	195.1
$Ag_5Pb_{1.5}In_{0.5}O_6$	5.8892(7)	6.3957(5)	192.1
$Ag_5Pb_{1.25}In_{0.75}O_6$	5.8654(8)	6.3733(7)	189.9
Ag_5PbInO_6[a]	5.8641(18)	6.3804(16)	190.0

[a] Beginning formation of $AgInO_2$.

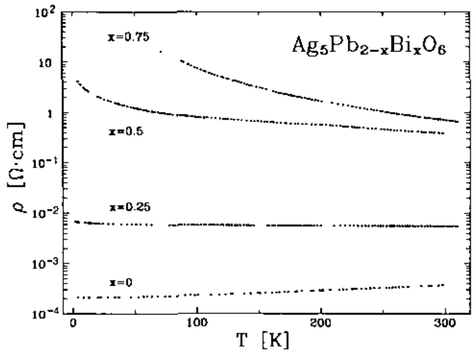

FIG. 4. Resistivity vs temperature for the bismuth doped samples on a logarithmic scale. The $x = 1$ sample was insulating.

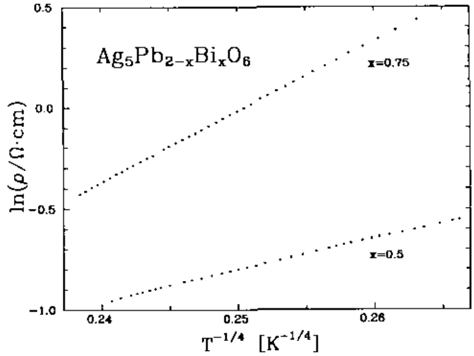

FIG. 5. Plot of $\ln \rho$ vs $T^{-1/4}$ for $x = 0.5$ and $x = 0.75$ bismuth doped samples in the temperature range from 200 to 300 K.

the other Ag_3BiO_3 (*3*) or $AgInO_2$ (*4*), respectively.

The effect of bismuth doping on the electrical resistivity of the samples is shown in Fig. 4. Replacement of even a small portion of lead atoms by bismuth drastically increases the resistivity of the samples and leads to semiconducting behavior. The $x = 0.50$ and $x = 0.75$ bismuth doped samples were found to exhibit a VRH (variable range hopping) regime in the temperature range from 200 K to 300 K. In this temperature range, the resistivity of the samples is given by Mott's law (*5*),

$$\rho(T) = \rho_0 \cdot \exp(T_0/T)^p,$$

with an almost temperature-indepedent prefactor ρ_0 and an exponent $p = 1/(1 + D)$ which is determined by the dimensionality D of the VRH. Figure 5 represents plots of $\ln \rho$ vs $T^{-1/4}$ for these two samples, which appear linear and hence indicate VRH conductivity with a dimensionality of 3. The data might be fitted almost as well with a dimensionality of 2, as it is very difficult to discriminate between the two exponents $p = \frac{1}{4}$ and $p = \frac{1}{3}$ experimentally (*6*).

Ag_5PbBiO_6, the end of the solid solution series, was found to be insulating, which proves that the number of free charge carriers tends toward zero for the $x = 1$ compound.

Contrary to this finding, doping with indium causes only a small effect on the electrical conductivity. Retaining metallic behavior, the temperature dependence is very small and the conductivity decreases only slighly with increasing indium content (Fig. 6). The reason for this unexpected behavior is not clear yet, but possibly it may be found in the different response of the unit cell volume on doping with bismuth and indium.

All samples of the prepared solid solution were found to be diamagnetic with a molar susceptibility of $\chi_{mol} \approx -0.21 \times 10^{-6}$ cm^3/

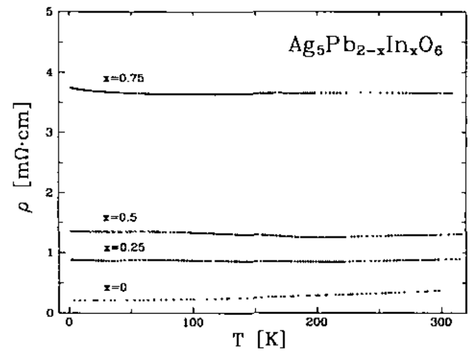

FIG. 6. Resistivity vs temperature for the indium doped samples.

mol (cgs units), in good agreement with values calculated by the method of Klemm (*7*).

Acknowledgment

We thank the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie for financial and material support.

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