Neutron diffraction and X-ray absorption study of $Ag_5Pb_2O_6$

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Abstract

Neutron diffraction and X-ray absorption measurements were carried out for a silver–lead oxide $Ag_5Pb_2O_6$. The powder neutron diffraction patterns could be fitted to the trigonal $P\bar{3}1m$ structure, as was found by X-ray diffraction. From the bond-valence-sum (BVS) analysis, the valences of the Ag and Pb ions were estimated to be about $1+$ and $3.7+$, respectively. The X-ray absorption measurements indicated that the ionic state of Ag is close to $1+$, while that of Pb stands between $3+$ and $4+$. The deviation of the valence of the Pb ion from $4+$ suggests a contribution of Pb orbitals to the metallic conduction as well as the possible superconductivity of this material, consistently with a recent band-structure calculation.
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1. Introduction

A silver–lead oxide $Ag_5Pb_2O_6$ has a trigonal crystal structure with the space group of $P\bar{3}1m$ (No. 162) [1–6]. The structure has quasi-two-dimensionality, which consists of a characteristic Ag–Ag bonded substructure with three Ag atoms per unit cell in a Kagome lattice as well as two Ag atoms per unit cell in a liner chain perpendicular to the Kagome net. The substructure of Ag interpenetrates the hexagonal layers of a PbO_6 network, inside which each Pb atom is octahedrally coordinated by six O atoms.

This compound shows metallic conductivity below room temperature [1,2]. A few different origins of the conduction mechanism have been proposed so far. One proposed explanation is that a free excess electron per formula unit is spread over the molecule, for which the valence formula can be expressed as $Ag_5^+Pb_2^{4+}O_6^{2-}(e-)$ (e−: excessive electron) [1,2]. Another description was given by a tight-binding calculation assuming the $4+$ valence of the Pb ion:

the valence formula can be expressed as $[Ag_5]^{4+}Pb_2^{4+}O_6^{2-}$ [3] where the Fermi energy lies in a half-filled band consisting mostly of Ag-s orbitals.

It is interesting that the recent low-temperature resistivity measurement suggested that this oxide becomes a superconductor below about 48 mK [5]. The phenomenon was assumed to be due to the Ag conduction electrons. A first-principle calculation of the band structure of this oxide showed that a half-filled conduction band has a single, nearly free-electron-like Fermi surface consisting of an antibonding state of Pb-$6s$ and O$2p$ orbitals mixing with Ag $4d$ and $5s$ [6]. This result provides a considerable different description of the electronic state of this system from those noted just earlier. The presence of the nearly free conduction electrons at the Fermi surface was found by the de Haas–van Alphen effect measurements; the result is in accord with the band calculation and also shows that this oxide is the first example of a monovalent superconductor at ambient pressure [7].

In the course of this study, we have performed neutron diffraction and X-ray absorption measurements of this oxide. Although the crystal structure of $Ag_5Pb_2O_6$ was

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confirmed by X-ray diffraction for our samples prepared from a mixture of nitrates [8], neutron diffraction measurements provide more precise information on the position of oxygen; for the present material, the neutron scattering cross sections of O, Ag and Pb are ~4, ~5 and ~11 (barn), respectively [9]. With the position of each atom, the valence states of the Ag and Pb ions are obtained. X-ray absorption measurements were also performed using synchrotron radiation around the Ag and Pb absorption edges for the same purpose. From these results, a possible origin of conduction electrons in this system is proposed.

2. Experimental

The samples were synthesized from the fused mixture of nitrates [8]. The content of each element was measured by the inductively coupled plasma (ICP) method as well as thermogravimetry in air (Rigaku TAS200) [1,4]. The two-step weight loss accompanied by the two peaks in a differential thermal analysis (DTA) was observed at around 500–600 °C [1,4]. The actual formula of the sample was estimated to be $Ag_5Pb_{2.01(6)}O_{5.96(6)}$, in which the content of Ag was fixed to be 5. Neutron diffraction measurements were carried out at room temperature and 4 K using a high-resolution powder diffractometer (HRPD) at the JRR-3 nuclear reactor of JAEA. The neutron wavelength was 1.82310 Å. The patterns were taken between $2\theta = 5°$ and 140° with an angle step of 0.05° and were fitted by the Rietveld method using the program RIETAN-2000 [10]. X-ray absorption measurements were conducted using synchrotron radiation at the beamline BL01B1 of SPring-8. Photoabsorption by the powered samples fixed between pieces of Scotch tape was measured by sweeping the photon energy at the Ag-K and Pb-L_3 absorption edges at room temperature. The spectra of some reference materials, such as Ag_2O and PbO_2, were measured as well.

3. Results and discussion

Fig. 1 shows the powder neutron diffraction patterns at room temperature for $Ag_5Pb_2O_6$. The experimental pattern could be well fitted assuming the trigonal $P\bar{3}1m$ structure, as was previously determined by X-ray diffraction [1]. The fitting parameters listed in Table 1 are sufficiently close to those in this Ref. [1]. Although the refinement was done with changing the occupation of each atom, it was found that the occupancies of Ag1 and Ag2 were very slightly larger than 1 (typically ~1.003). As this result is not physically meaningful, their occupancies were fixed to be 1. On this assumption, the present result gives a similar content of each atom to that noted in the experimental section and confirms the previous crystallographic parameters [1]. The pattern taken at 4 K (not shown) was also fitted to the $P\bar{3}1m$ structure. The same structure as that at room temperature is consistent with the metallic behavior
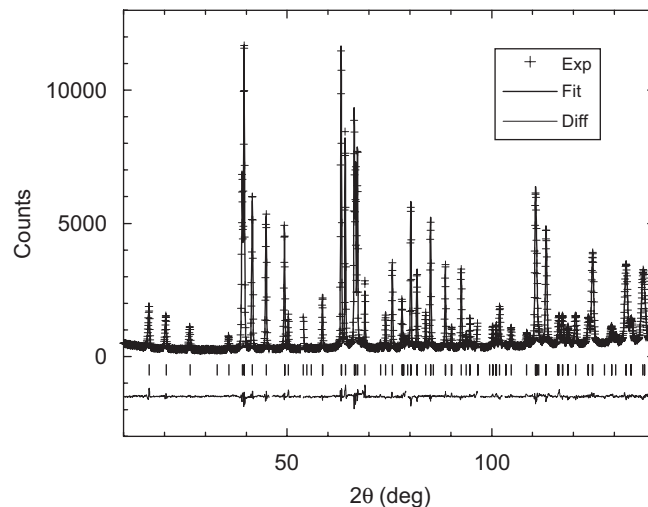

Fig. 1. Powder neutron diffraction patterns of $Ag_5Pb_2O_6$ at room temperature. The upper cross markers (exp) and the solid line (fit) stand for the experimental and calculated patterns, respectively. The vertical markers mean the calculated Bragg angles. The lower solid line (diff) denotes the difference between the experimental and calculated intensities.

without any anomaly down to this temperature [5]. The fitting parameters were also listed in Table 1. The unit-cell volume and the thermal parameters (U) naturally decrease by cooling.

The representative bond lengths around Ag and Pb are shown in Table 2. Ag1 and Ag2 stand for the silver atoms in the one-dimensional chain and in the Kagome layer, respectively [1,3]. As the position of the oxygen ion is assumed to be considerably accurate in this measurement, a bond-valence-sum (BVS) analysis [11] by use of these bond lengths was carried out to estimate the valences of the Ag and Pb ions. The valence of the i ion (V_i) is given by the empirical equation:

$$V_i = \Sigma\exp((l_0 - l_{ij})/B).$$

Here, l_0 and B are the so-called bond valence parameters, and l_{ij} is the distance between the central atom i and the neighboring atom j [11].

The result is also shown in Table 2. Each valence value at room temperature is very close to that at 4 K, as may be estimated from Table 1. The valence of the Ag1 is slightly lower than that of Ag2 due to the smaller number of Ag–O bonds around Ag1 [1,3]. The proposed formulas of $Ag_5^{1+}Pb_2^{4+}O_6^{2-}(e-)$ [1], $[Ag_5]^{4+}Pb_2^{4+}O_6^{2-}$ [3] and $Ag_5^+ \square_2^{4+} O_6^{2-}(e-)$ ($\square$: vacancy, [6]) mean that the averaged ionic state of Ag stands between $0.8+$ and $1.0+$. A similar value of ~0.9–1.0+ is obtained by taking the average of Ag1 and Ag2 in Table 2.

The table also shows the valence state of Pb as approximately $3.7+$, which is comparably close to the value of $4+$ shown in the Refs. [1,3]. However, the slight difference from $4+$ indicates the possible existence of conduction electrons arising from the Pb atomic orbitals. Considering the electronic structure of an elemental Pb atom ([Xe] $4f^{14}5d^{10}6s^26p^2$), the obtained ionic state

Table 1
Crystallographic parameters obtained by the Rietveld analysis

	Position	Occupation	x	y	z	U (Å^2)
Ag(1)	2e	1	0	0	0.2412(2)	0.0201(5)
Ag(2)	3f	1	0.5	0	0	0.0178(4)
Pb	2d	0.995(4)	0.6667	0.3333	0.5	0.0084(4)
O	6k	0.995(4)	0.6208(1)	0	0.6892(2)	0.0114(4)

Trigonal $Ag_5Pb_2O_6$ (room temperature), space group $P\bar{3}1m$ (No. 162)
$a = 5.9405(5)$, $c = 6.4350(4)$ Å, $V = 196.661(28)$ Å^3
$R_{wp} = 5.34\%$, $R_I = 2.48\%$, $R_F = 1.74\%$, $S = 1.53$

	Position	Occupation	x	y	z	U (Å^2)
Ag(1)	2e	1	0	0	0.2348(2)	0.0035(4)
Ag(2)	3f	1	0.5	0	0	0.0045(4)
Pb	2d	0.997(5)	0.6667	0.3333	0.5	0.0030(4)
O	6k	0.998(5)	0.6211(1)	0	0.6892(2)	0.0049(4)

Trigonal $Ag_5Pb_2O_6$ (4 K), space group $P\bar{3}1m$ (No. 162)
$a = 5.9194(1)$, $c = 6.4385(1)$ Å, $V = 195.376(5)$ Å^3
$R_{wp} = 6.55\%$, $R_I = 1.53\%$, $R_F = 1.15\%$, $S = 1.38$

The occupancies of Ag1 and Ag2 were fixed to 1 because they were found to be slightly larger than 1 (typically, 1.003).

Table 2
Representative valence parameters estimated by the bond valence sum (BVS) analysis

Bond	Length (Å)	n	Valence
Trigonal $Ag_5Pb_2O_6$ (room temperature)			
Ag1–O	2.297(1)	3	0.88+
Ag2–O	2.125(1)	2	1.00+
	3.348(1)	4	
Pb–O	2.222(1)	6	3.69+
Trigonal $Ag_5Pb_2O_6$ (4 K)			
Ag1–O	2.296(1)	3	0.88+
Ag2–O	2.125(1)	2	1.00+
	3.340(1)	4	
Pb–O	2.217(1)	6	3.73+

The number of each chemical bond is shown as n. The estimated standard deviation of the valence of each ion is less than 0.01–0.02 on the assumption that n is proportional to the oxygen nonstoichiometry estimated by the Rietveld analysis.

Fig. 2. XANES spectra at the Ag-K edge for $Ag_5Pb_2O_6$ and Ag_2O.

indicates that the charge carriers are ascribed to the Pb-6s electrons. It is interesting that this origin of carriers is in accord with that of the band-structure calculation, i.e., the Fermi level consists of an antibonding state of Pb-6s and O2p orbitals [6]. Although explicit valence states of the Ag and Pb ions were not given in this reference, the assumption of a substructure of $(\square^+)_5Pb_2^{4+}O_6^{2-}(e-)$ ($\square$: vacancy, Ref. [6]) means that the average valence of Pb stands between $3.5+$ and $4+$. An analogous result was also obtained from the X-ray absorption, as noted later. It is also evident that each valence at 4 K in Table 2 is almost the same to that at room temperature.

Fig. 2 shows the X-ray absorption near-edge structure (XANES) spectra at the Ag-K edge. It is well known that the XANES measurement provides information of chemical bonds around the photo-excited atom, such as the valence of Ag in the present case. From the dipole selection rule, the photoabsorption around 25540 eV mainly corre-
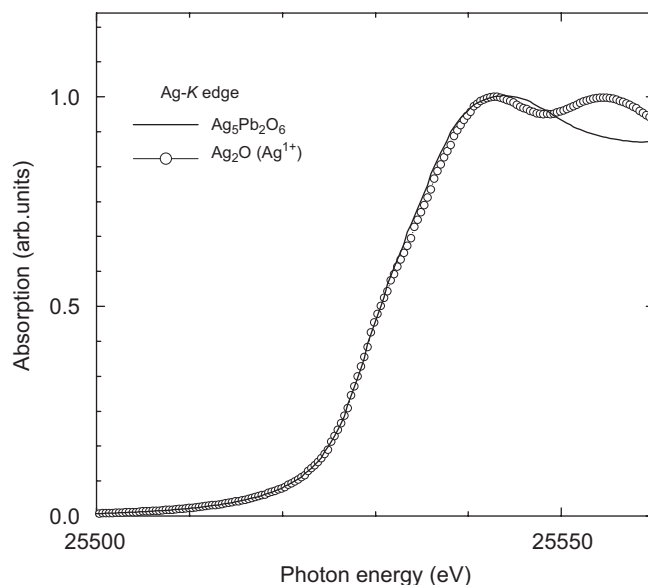
sponds the electron excitation from Ag-K (1s) to Ag-6p unoccupied states. At a glance, the experimental spectrum of $Ag_5Pb_2O_6$ almost traces that of Ag_2O at the absorption edge (below about 25,540 eV). Thus, the valence of Ag in this oxide is nearly identical to $1+$, which is roughly in accord with both of those obtained by the BVS analysis (Table 2) and the proposed ionic states [1,3,6].

Fig. 3a shows the XANES spectra at the Pb-L_3 edge, in which the photoabsorption is attributed to a transition from Pb $2p_{3/2}$ to either 6s or 6d orbitals in unoccupied states. The small peak 1 is brought about by a Pb-6s transition, while peaks 2 and 3 are assigned to the transitions to the Pb-6d t_{2g} and e_g states, respectively [12]. Although the largest absorption peak 3 of $Ag_5Pb_2O_6$ is located near that of PbO$_2$, it is slightly shifted by 1.5 eV to a lower, energy side. This result indicates that the effective
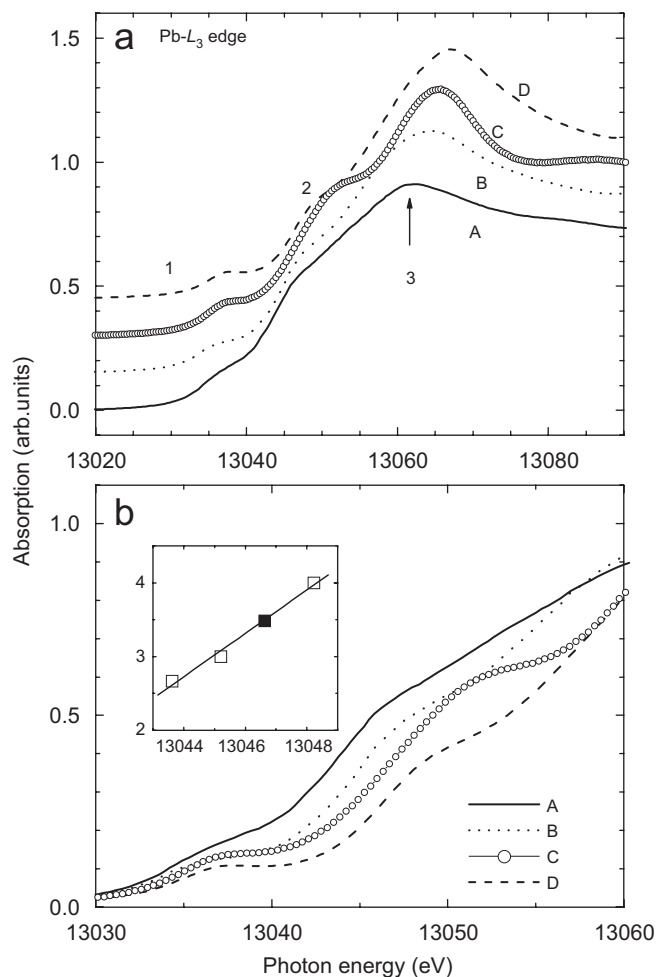
Fig. 3. (a) XANES spectra at the Pb-L_3 edge for (A) Pb_3O_4 ($Pb^{2.67+}$), (B) Pb_2O_3 (Pb^{3+}), (C) $Ag_5Pb_2O_6$ and (D) PbO_2 (Pb^{4+}). The assignments of peaks 1–3 are noted in the text. (b) Expended spectra in the edge-jump region below about 13060 eV. The inset shows an estimation of the valence of Pb in $Ag_5Pb_2O_6$. The abscissa represents the photon energy of the absorption edge (eV), which corresponds to the edge shift against a change of valence. The ordinate scale stands for the valence of Pb in each material. The open squares show the experimental data of Pb_3O_4, Pb_2O_3 and PbO_2. The solid line indicates the linear relationship between the edge shift and the valence, obtained from the data for Pb_3O_4, Pb_2O_3 and (D) PbO_2. The Pb valence of $Ag_5Pb_2O_6$ was estimated as 3.5+ (filled square).

valence of Pb is lower than 4+. Fig. 3b shows that the spectrum in the edge-jump region shifts slightly to higher photon energies with increasing a formal valence of the PbO_x series from 2.67+ to 4+, a result known as a general trend in XANES measurements [13]. It is qualitatively evident that the absorption edge of $Ag_5Pb_2O_6$ stands between those of Pb_2O_3 and PbO_2. These results strongly suggest that the effective valence of Pb stands between 3+ and 4+. The inset shows an estimation of the Pb valence in $Ag_5Pb_2O_6$ obtained from the edge shift (abscissa) against the valence (ordinate) for Pb_3O_4, Pb_2O_3 and PbO_2. Assuming a linear relationship between the edge shift and the valence, the valence state of Pb is about 3.5+. Although the origin of the deviation from the valence obtained from the BVS analysis (Table 2) is unclear at

present, the existence of electrons in the Pb-6s states is assumed for $Ag_5Pb_2O_6$ [6].

These results obtained from the diffraction and absorption measurements indicate that the valence of the Ag ion in $Ag_5Pb_2O_6$ is close to 1+, while that of the Pb ion stands between 3+ and 4+. As noted earlier, the description of these valence formulas is consistent with the band calculation; the Fermi level consists of Pb-6s and O2p orbitals [6]. The presence of charge carriers in the Pb orbitals was also suggested in a resistivity study of a Cu-substituted system $Ag_5Pb_{2-x}Cu_xO_6$ [14]. The superconductivity below 48 mK in $Ag_5Pb_2O_6$ could not be explained in terms of either an electron-electron interaction or an electron–phonon interaction in an optical phonon mode [5]. From the similar metallic behavior of TTF–TCNQ to that of $Ag_5Pb_2O_6$, the so-called librational phonon mode would be another origin of the superconductivity [5,15]. However, this mechanism is not applicable because of the rigidity of the Ag chain against a twisting motion, if the conduction electrons are provided only by the Ag-s orbitals [5]. On the other hand, the present results suggest that the conductivity is possibly ascribable to the Pb ion as well. It is noteworthy that superconductivity is observed below 13 K in $BiPb_{1-x}Bi_xO_3$ [16], which contains the PbO_6 octahedron, such as $Ag_5Pb_2O_6$. In this oxide, a valence exchange between Pb and Bi assisted by a displacement of the O ions may play an important role [16,17], leading to an analogous situation to that of $Ag_5Pb_2O_6$; i.e., the average valence of the Pb ion $BiPb_{1-x}Bi_xO_3$ stands between 2+ and 4+ [16,17]. The potential importance of electron-phonon interactions was also proposed in Ref. [6]. Thus, an investigation of phonon modes in the connected PbO_6 octahedra and their coupling with the conduction electron seem to be necessary to elucidate more details of the superconductivity in this material.

4. Summary

Neutron diffraction and X-ray absorption measurements were carried out for a silver–lead oxide $Ag_5Pb_2O_6$. The powder neutron diffraction patterns could be fitted to the trigonal $P\bar{3}1m$ structure, as was found by X-ray diffraction. From the BVS analysis, the valences of the Ag and Pb ions were estimated to be about 1+ and 3.7+, respectively. The X-ray absorption measurements indicated that the ionic state of Ag is close to 1+, while that of Pb stands between 3+ and 4+. The deviation of the valence of the Pb ion from 4+ suggests a contribution of Pb orbitals to the metallic conduction as well as the possible superconductivity of this material, consistently with a recent band-structure calculation.

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