Synthesis and crystal structure of AgYbO_2

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Delafossite-type oxide AgYbO_2 (3R-polytype) was synthesized by a cation-exchange reaction of NaYbO_2 and AgNO_3 in a KNO_3 flux. An almost single phase was obtained at 190°C for 192 h. The structure of AgYbO_2 was refined by Rietveld analysis, giving a trigonal unit cell ($R\bar{3}m$, $a = 337.17$ pm, $c = 1821.4$ pm) with a reasonably small S value of 1.48.

Key-words : Transparent conducting oxide, Delafossite oxide, Cation-exchange reaction, Crystal structure refinement

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1. Introduction

Delafossite (CuFeO_2) is a mineral first reported by Friedel¹⁾ in 1873. Soller and Thompson synthesized CuFeO_2 and analyzed its structure.²⁾ Pabst³⁾ later reported that the synthesized CuFeO_2 was isostructural with delafossite. Numerous delafossite-type compounds with the formula $A^+B^{3+}\text{O}_2$ have been reported. **Figure 1** shows the crystal structure of delafossite-type oxides, which can be described as alternate stacking of two types of layers along the c axis; the layer consisting of A atoms in a twofold linear coordination with oxygen and the one consisting of edge-shared octahedra BO_6 .^{4),5)} The A sites are known to be occupied by Ag, Cu, Pd, and Pt, while the B sites by Al, Co, Cr, Fe, Ga, In, La, Ni, Sc, Y, etc.^{6),7)} Delafossite-type compounds have been of increasing interest due to the discovery of the p-type transparent conductivity of CuAlO_2 .⁸⁾ A series of compounds CuLnO_2 ($\text{Ln} = \text{La, Pr, Nd, Sm, and Eu}$) were then synthesized by Haas and Kordes.⁹⁾ CuLnO_{2+x} with excess oxygen

was reported to have higher conductivity at room temperature than the stoichiometric CuAlO_2 ,¹⁰⁾ however, AgLnO_2 has not been reported. Thus, we tried to explore AgLnO_2 . We noted that among the B site ions of the reported silver delafossites AgBO_2 , Tl has the largest ionic radius, $r(\text{Tl}^{3+}) = 88.5$ pm, which suggests that a trivalent lanthanoid cation smaller than Tl^{3+} may form a delafossite crystal. Therefore, we decided to use Yb^{3+} with $r(\text{Yb}^{3+}) = 86.8$ pm. Herein, we show the preparation of the novel delafossite-type oxide AgYbO_2 by cation-exchange, and structural analysis of the crystal by the Rietveld refinement.

2. Experimental

AgYbO_2 was synthesized by the following cation-exchange reactions using NaYbO_2 and LiYbO_2 as precursors;

The reactions were carried out in a flux of $\text{AgNO}_3\text{--KNO}_3$. NaYbO_2 and LiYbO_2 were prepared by solid-state reactions. Na_2O (Aldrich Chemical Co., Inc., 97%) or Li_2O (Kojundo Chemical Lab. Co., Ltd., 99.00%) and Yb_2O_3 (Kojundo Chemical Lab. Co., Ltd., 99.9%) powder were mixed in a dry process (mixing ratio: $\text{Na} : \text{Yb} = 2.5 : 1.0$, $\text{Li} : \text{Yb} = 1.2 : 1.0$) and shaped into a pellet by cold isostatic pressing (49 MPa, 5 min). Shaped samples were heated at 900°C for 12 h (heating rate: 250°C h^{-1}). The products were washed with distilled water, ethanol and finally with acetonitrile to eliminate the flux and byproducts. The obtained samples were then dried in air at 23°C for 48 h. The NaYbO_2 and LiYbO_2 powder specimens were mixed with AgNO_3 (Kanto Chemical Co., Inc., 99.8%) and KNO_3 (Wako Pure Chemical Industries, Ltd., 99.00%) in a dry process (mixing ratio: $\text{Na} : \text{Ag} : \text{K} = 3.0 : 3.0 : 2.0$, $\text{Li} : \text{Ag} : \text{K} = 1.0 : 1.0 : 1.0$). The molded samples were heated from 150 to 300°C . After heat treatment, the products were washed in the same way as described above.

The cation-exchanged samples were evaluated by electron probe microanalysis (EPMA) with wavelength dispersive spectroscopy (JXA-8900R, JEOL Ltd.) and powder X-ray diffraction (RV-200, Rigaku Co., Ltd.) using $\text{CuK}\alpha$ radiation. The crystallographic data was refined using Rietveld analysis with the computer program RIETAN 2000.¹¹⁾ The

Fig. 1. Crystal structure of delafossite-type ABO_2 (space group: $R\bar{3}m$).

Table 1. Relationship between Reaction Conditions and Products in Ag–Yb–O System

System	Heat treatment conditions	Main product
Cation-exchange reaction of LiYbO ₂ , AgNO ₃ and KNO ₃	200°C, 48 h	Yb ₂ O ₃ , Ag ₂ O
	200°C, 240 h	Yb ₂ O ₃ , Ag
	300°C, 48 h	Yb ₂ O ₃ , Ag
Cation-exchange reaction of NaYbO ₂ , AgNO ₃ and KNO ₃	150°C, 96 h	AgYbO ₂ , NaYbO ₂
	190°C, 192 h	AgYbO ₂ , Ag ₂ O
	200°C, 48 h	AgYbO ₂ , Ag, Ag ₂ O

Fig. 2. Rietveld analysis of the Ag–Yb–O system obtained at 190°C for 192 h with NaYbO₂ used as a precursor. Plus marks indicate observed X-ray diffraction intensities, and the solid line represents calculated intensities. The vertical marks below the patterns indicate the positions calculated for Bragg reflections. The curve at the bottom shows the difference between the observed and calculated intensities. Rietveld refinement was achieved assuming two phases of AgYbO₂ (space group: $R\bar{3}m$) and Ag₂O (space group: $Pn\bar{3}m$).

powder X-ray diffraction measurements were performed in 2θ range from 5° to 140° at room temperature with a scan speed 0.3° min^{−1} and a scan step 0.04°. The Voigt function was used for the diffraction profile, and the O atom occupancy factor was fixed as 1.

3. Results and discussion

The reaction conditions and the products are summarized in **Table 1**. In the case of the LiYbO₂ precursor, the main phases were Yb₂O₃ and Ag. On the contrary, the X-ray diffraction patterns of the sample synthesized using a NaYbO₂ precursor at 190°C for 192 h were, apart from a minor Ag₂O impurity phase, quite similar to those of other silver delafossites. EPMA analysis revealed that the sample consisted of Ag, Yb and O without Na, suggesting that the exchange from Na to Ag in the crystal was sufficient. Therefore, Rietveld analysis was performed assuming two phases, i.e., a delafossite structure with the composition AgYbO₂ (space group: $R\bar{3}m$) and the impurity phase Ag₂O (space group: $Pn\bar{3}m$).

Figure 2 shows the result of the Rietveld refinement. The refined lattice parameters are $a = 337.17(10)$ pm, $c = 1821.4(4)$ pm, and $V = 179.32(8) \times 10^6$ pm³ with R -factors, $R_{wp} = 8.26$, $R_e = 6.07$, $R_B = 1.04$, $R_F = 0.65$ and $S = 1.48$. From these results, we conclude that AgYbO₂ has a delafossite-type structure. The atom positions and isotropic atomic displacement parameters are shown in **Table 2** and the selected interatomic distances and bond angles are shown in **Table 3**.

Table 2. Atom Positions and Isotropic Atomic Displacement Parameters for AgYbO₂ (space group: $R\bar{3}m$)

Atom	x	y	z	B _{iso} ($\times 10^4$ pm ²)
Ag	0	0	0	0.47(10)
Yb	0	0	0.5	0.35(7)
O	0	0	0.1091(7)	1.50

Table 3. Selected Interatomic Distances (pm) and Bond Angles (°) for AgYbO₂ (space group: $R\bar{3}m$)

Ag–O	($\times 2$)	198.7(12)	O–Yb ^(b) –O ^(a)	99.4(4)
Yb ^(b) –O	($\times 6$)	221.1(6)	O–Yb ^(b) –O ^(d)	80.6(4)
O–O ^(a)	($\times 6$)	337.2(1)	Ag–O–Yb ^(b)	118.3(3)
O–O ^(d)	($\times 3$)	286.1(18)	Yb ^(b) –O–Yb ^(c)	99.4(4)
Symmetry code	none	x y z		
a	x	y – 1	z	
b	x + 1/3	y + 2/3	z – 1/3	
c	x + 1/3	y – 1/3	z – 1/3	
d	x + 2/3	y + 1/3	1/3 – z

Fig. 3. Lattice parameters a for AgYbO₂ (○: this work) and various delafossite-type compounds (▲: Ref. 6, 13) as a function of ionic radii of the B site ion.

The obtained values for the Ag–O and Yb–O distances are 198.7 and 221.1 pm, respectively, which are in good agreement with the values calculated from the ionic radii, ^{II}Ag⁺ = 67, ^{VI}Yb³⁺ = 86.8, ^{IV}O^{2−} = 138 pm¹²⁾ (where II, VI, and IV are coordination numbers).

Figure 3 shows the relationship between the lattice parameters (a axis) and the ionic radii of the B site ion in silver delafossite oxides AgBO₂. The a parameter was determined to increase linearly with increasing ionic radius of the B site ion. **Table 4** compares both the a - and c -lattice parameters of AgYbO₂ with those of other silver delafossites reported.^{6),13)} The c axis of AgYbO₂ is the shortest in the series containing an Ag⁺ ion in the A site. Haas and Kordes suggested that the c axis of delafossites containing lanthanoid ions is shorter than that of others.⁹⁾ The same trend is seen in our data.

4. Conclusions

A novel delafossite AgYbO₂ was synthesized by cation-

Table 4. Lattice Parameters for AgYbO₂ and Various Delafossite-Type Compounds

Compounds	<i>a</i> (pm)	<i>c</i> (pm)	Reference
AgAlO ₂	289.0	1827	(6)
AgCoO ₂	287.29	1833.6	(6)
AgNiO ₂	293.6	1835	(13)
AgCrO ₂	298.43	1855.1	(6)
AgGaO ₂	298.89	1853.4	(6)
AgFeO ₂	303.91	1859	(6)
AgRhO ₂	306.84	1857.9	(6)
AgScO ₂	321.12	1853.8	(6)
AgInO ₂	327.72	1888.1	(6)
AgYbO ₂	337.17	1821.4	This work
AgTlO ₂	356.8	1881.8	(6)

exchange. The structure was confirmed by Rietveld refinement, giving the trigonal $R\bar{3}m$ space group with lattice parameters of $a=337.17$ and $c=1821.4$ pm.

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