Synthesis of Delafossite-Type Ag\textsubscript{0.9}MnO\textsubscript{2} by the Precipitation Method at Room Temperature

Sumio Kato,* Naoto Takagi, Kanji Saito, and Masataka Ogasawara

Graduate School of Engineering Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan

ABSTRACT: A delafossite-type Ag–Mn oxide was successfully synthesized using the precipitation method at room temperature. The delafossite is Ag'-deficient and has a chemical composition of Ag\textsubscript{0.9}MnO\textsubscript{2}. Thermogravimetry of the Ag\textsubscript{0.9}MnO\textsubscript{2} delafossite revealed that on heating to 900 °C, it decomposed to Ag and MnO\textsubscript{2} in air and to Ag and MnO\textsubscript{4} under N\textsubscript{2}. While cooling to room temperature in air, the delafossite phase reformed from Ag and MnO\textsubscript{4}. The reversibility of the decomposition/reformation process is related to the similarity between the delafossite and spinel-type structures, both of which contain an octahedral layer. The reformation process could be used as a new synthetic route to Ag'-containing delafossite-type oxides.

1. INTRODUCTION

Delafossite-type AgMO\textsubscript{2} (M: trivalent cation) has been reported, which can be considered Ag'-containing oxides, consisting of layers of edge-sharing MO\textsubscript{6} octahedra with two-coordinated Ag' cations occupying the interlayer sites\textsuperscript{1−3}. The Ag-containing delafossites have attracted attention as functional materials for electrodes,\textsuperscript{4,5} photocatalysts,\textsuperscript{6−10} transparent semiconductors,\textsuperscript{11−13} solar cells,\textsuperscript{14,15} and gas sensors.\textsuperscript{16} Solid-state reactions of Ag\textsubscript{2}O and M\textsubscript{2}O\textsubscript{3} oxides are not suitable for the synthesis of AgMO\textsubscript{2} delafossites, as Ag\textsubscript{2}O decomposes to metallic Ag at a low temperature.\textsuperscript{17} Several AgMO\textsubscript{2} delafossites have been synthesized by the ion exchange method using AMO\textsubscript{2} (A: alkali metal) and a molten salt containing AgNO\textsubscript{3}. For example, AgCoO\textsubscript{2} was synthesized by exchange of the Li\textsuperscript{+} in LiCoO\textsubscript{2} with Ag\textsuperscript{+} from molten AgNO\textsubscript{3}\cdot 4H\textsubscript{2}O, and the resultant mixture was stirred at room temperature for 24 h. The resulting precipitate was washed with distilled water and dried at 60 °C for 12 h.Phase identification was performed by powder X-ray diffraction (XRD) using Ni-filtered Cu Kα radiation (Rigaku Ultima IV diffractometer). Rietveld analysis was carried out using the RIETAN-FP software.\textsuperscript{23} The elemental composition of the sample was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPSS500, SII NanoTechnology). The average oxidation state of Mn in the sample was evaluated by iodometric titration. The sample (0.06 g) was dissolved in a solution of 5 mL KI (1 mol/L) and 5 mL HCl (6 mol/L), and 40 mL of distilled water was added. During the dissolution process, Mn\textsuperscript{3+} and Mn\textsuperscript{4+} in the sample were reduced to Mn\textsuperscript{2+} by I\textsuperscript{-} as per the following reaction\textsuperscript{1}

\[
\text{MnP}^+ + (p - 2)\text{I}^- \rightarrow \text{Mn}^{2+} + (p - 2)/2\text{I}_2
\]

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3. RESULTS AND DISCUSSION

3.1. Synthesis. The XRD patterns for the samples with an Ag/Mn molar ratio of 1:1, prepared by varying the OH⁻ concentration in the NaOH solution, are shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of samples produced by varying the quantities of aqueous NaOH.

The delafossite phase was formed under acidic conditions (NaOH 14–15 mL, pH = 5.1–6.3) without H₂O₂ addition. In addition, Ag (ICDD-PDF# 4-0783) and a smaller quantity of Mn₃O₄ (ICDD-PDF# 71-6262) were observed at pH = 6.3. At higher pH, no delafossite phase formed, and instead Ag and Mn₃O₄ were observed. In order to suppress formation of the Ag metal, H₂O₂ was added in the NaOH solution and the Ag/Mn ratio was varied. The XRD patterns for the samples prepared by varying the Ag/Mn ratio in the starting solution (H₂O₂ 12 mL + NaOH 15 mL) are shown in Figure 2. In the re

![Figure 2](image2.png)

**Figure 2.** XRD patterns of samples produced by varying the Ag/Mn molar ratio, x:1 (x = 0.7–1.0, NaOH 15 mL + H₂O₂ 12 mL).

The thermal stability of the sample was evaluated by thermogravimetry (TG) and differential thermal analysis (DTA) using Rigaku TG–DTA 8120 and Shimadzu TGA-50H. The measurements were performed in air or under an N₂ flow, first heating to 900 or 1000 °C, and then cooling to 100 °C, at a rate of 10 K/min. The morphology of the particles was investigated using a field-emission scanning electron microscope (FE-SEM, Hitachi SU-70).

The Ag⁺ in the sample was precipitated as AgI, which is insoluble in water. The quantity of I₂ formed by reaction 1 was measured by titration using an aqueous solution of 0.1 mol/L Na₂S₂O₃, and the average oxidation number of Mn was calculated from the quantity of I₂.

The average oxidation number of Mn was calculated from the titration using an aqueous solution of 0.1 mol/L Na₂S₂O₃, and the additional peaks, attributed to the Ag metal and Mn₃O₄, were observed. In the single-phase delafossite obtained for x = 0.8, the Ag/Mn ratio deviated from the stoichiometric ratio. The pH value of the solution for x = 0.8 was 6.5. From the results of the ICP-AES measurement, the Ag/Mn ratio in the single-phase sample was 0.90:1 and the Ag/Na ratio was 0.9:0.01. These results suggest that the lattice is Ag⁺-deficient and that the Na⁺ concentration is low. The average oxidation state of the sample, determined by the iodometric titration, was +3.14, which is close to +3.1, the value estimated for a charge neutral lattice with an Ag/Mn ratio of 0.90:1. Structure refinement using XRD data was performed for the x = 0.8 sample. The initial structural model was based on CuMnO₂ including cation vacancies at the Cu sites. As the Na content was low, distribution of Na⁺ into the two prismatic sites was not considered. The observed, calculated, and difference curves are shown in Figure 3. The refined structural parameters are listed in Table 1. The average composition is +3.14, which is identical to that determined by iodometric titration. The value of a is affected by the ionic radii of the Mn cations in the MnO₆ octahedral layer. As described above, the average pattern for x = 0.8, all the peaks were indexed on the basis of a monoclinic unit cell similar to that of AgMnO₂ reported by Koriche et al.²¹ In the patterns for x = 0.7, 0.9, and 1.0, additional peaks, attributed to the Ag metal and Mn₃O₄, were observed. In the single-phase delafossite obtained for x = 0.8, the Ag/Mn ratio deviated from the stoichiometric ratio. The pH value of the solution for x = 0.8 was 6.5. From the results of the ICP-AES measurement, the Ag/Mn ratio in the single-phase sample was 0.90:1 and the Ag/Na ratio was 0.9:0.01. These results suggest that the lattice is Ag⁺-deficient and that the Na⁺ concentration is low. The average oxidation state of the sample, determined by the iodometric titration, was +3.1, the value estimated for a charge neutral lattice with an Ag/Mn ratio of 0.90:1. Structure refinement using XRD data was performed for the x = 0.8 sample. The initial structural model was based on CuMnO₂ including cation vacancies at the Cu sites. As the Na content was low, distribution of Na⁺ into the two prismatic sites was not considered. The observed, calculated, and difference curves are shown in Figure 3. The refined structural parameters are listed in Table 1. The average composition is +3.14, which is identical to that determined by iodometric titration. The value of a is affected by the ionic radii of the Mn cations in the MnO₆ octahedral layer. As described above, the average

![Figure 3](image3.png)

**Figure 3.** XRD patterns of the sample for x = 0.8. Observed (crosses), calculated (solid line), and difference (solid line below) curves of the Rietveld analysis. The positions of the reflections are shown as bars.

| Atom | Site | g | x | y | z | 100U/(nm²) |
|------|------|---|---|---|---|-------------|
| O    | 4i   | 1 | 0.408(1) | 0 | 0.171(1) | 0.010(2) |
| Ag   | 2d   | 0.863(5) | 0 | 1/2 | 1/2 | 0.001(1) |
| Mn   | 2a   | 1 | 0 | 0 | 0 | 0.019(2) |

²¹“Space group: C2/m (no. 12) a = 0.55647(5) nm, b = 0.28923(2) nm, c = 0.63001(6) nm β = 100.837(6)° Rwp = 3.417% Rf = 0.889%.”

in Table 1. The lattice parameters of the delafossite sample were a = 0.55647(5) nm, b = 0.28923(2) nm, c = 0.63001(6) nm, and β = 100.837(6)°. The value of a is shorter and that of c is longer than those of the stoichiometric AgMnO₂ (a = 0.5583 nm, b = 0.2894 nm, c = 0.6293 nm, and β = 100.6°) synthesized by the ion exchange method,²¹ suggesting compositional deviation of the delafossite phase. The Ag/Mn ratio estimated from the refined occupation factor g of the Ag(2d) site was 0.86:1, which is close to the value obtained by ICP-AES measurement. In addition, the average chemical state of Mn estimated from the refined composition is +3.14, which is identical to that determined by iodometric titration. The value of a is affected by the ionic radii of the Mn cations in the MnO₆ octahedral layer. As described above, the average..
oxidation state of Mn was higher than +3, indicating the presence of Mn$^{4+}$, which has an ionic radius (0.053 nm) smaller than that of Mn$^{3+}$ (0.0645 nm for the high spin state). Oxidation of Mn$^{3+}$ occurred to satisfy the demand for charge compensation related to the Ag$^{+}$ deficiency. Ag-deficient delafossite Ag$_{1-x}$CoO$_2$ has been reported by Shin et al. The structure of the Ag-deficient phase, Ag$_{0.95}$CoO$_2$, is 2H-type, while that of stoichiometric AgCoO$_2$ is 3R-type. Because their lattice parameters ($a$) were similar, it was concluded that the oxidation state of Co was +3 in both delafossites. These results indicate that the Ag$^{+}$-deficient delafossite phase, Ag$_{0.9}$MnO$_2$, was obtained by the precipitation method at room temperature in the present study.

3.2. Thermal Stability of Ag$_{0.9}$MnO$_2$. The thermal stability of the Ag$_{0.9}$MnO$_2$ delafossite was investigated by TG–DTA measurements in air, up to 1000 °C. In the TG curve shown in Figure 4, four mass losses were observed in the temperature ranges 30–200, 350–500, 700–800, and 900–950 °C. In the DTA curve, four apparent endothermic peaks were observed at 628, 748, 937, and 954 °C. The peaks at 748 and 937 °C were accompanied by large mass losses. To clarify the thermal behavior, a high-temperature XRD measurement was performed on Ag$_{0.9}$MnO$_2$, while heating up to 950 °C, in air, as shown in Figure 5. The heating rate was 10 K/min, and the temperature was maintained at 300, 500, 700, and 800 °C while diffraction scans took place. The delafossite phase was observed up to 500 °C. However, it disappeared in the temperature range 700–800 °C. In the XRD pattern recorded at 800 °C, peaks for metallic Ag and Mn$_2$O$_3$ were observed, indicating that reductive decomposition had occurred. The endothermic DTA peak at approximately 954 °C, without an accompanying mass change, was attributed to Ag melting ($T_m$ = 961 °C). The diffraction peaks observed at 700 °C were not assigned to well-known compounds. The endothermic peak at 628 °C, accompanied by a slight mass loss, suggested that the transformation or decomposition of Ag$_{0.9}$MnO$_2$ to an unknown phase occurred. In the XRD pattern of Ag$_{0.9}$MnO$_2$ after heating at 700 °C and quenching to room temperature (not shown here), the Ag metal and Mn$_2$O$_3$ were observed in addition to the unknown phase. Further investigation is necessary to clarify the composition and structure of this unknown phase.

In order to determine the cause of the mass losses below 500 °C, desorption gas analysis was performed. The TG curve of Ag$_{0.9}$MnO$_2$, measured under an N$_2$ flow, is shown in Figure 6. Three mass loss steps were observed in the temperature ranges 30–300, 300–500, and 500–700 °C. A temperature-programmed desorption (TPD) measurement was performed in order to investigate the gas species which caused the mass loss in each temperature range. The TPD curves for the species produced (mass to charge ratios, $m/z$ = 18, 32, and 44) are shown in Figure 7. Large peaks were observed at 450 and 650 °C for $m/z$ = 44 and 32, respectively, indicating that the mass losses at 300–500 and 500–650 °C were caused by CO$_2$ elimination and O$_2$ generation, respectively. The curve for $m/z$ = 18 indicates that the mass loss below 200 °C was due to desorption of water. The O$_2$ generation above 600 °C suggests
the reduction of the Ag$_{0.9}$MnO$_2$ delafossite. The reductive reaction of the delafossite to metallic silver and manganese oxides are represented by reactions 2 and 3.

$$3\text{Ag}_{0.9}\text{MnO}_2 \rightarrow 2.7\text{Ag} + \text{Mn}_3\text{O}_4 + \text{O}_2$$  \hspace{1cm} (2)

$$4\text{Ag}_{0.9}\text{MnO}_2 \rightarrow 3.6\text{Ag} + 2\text{Mn}_2\text{O}_3 + \text{O}_2$$  \hspace{1cm} (3)

The theoretical mass losses during the reactions are 5.80 and 4.35% for reactions 2 and 3, respectively. The observed mass loss in the temperature range 500°C−750°C was 5.77%, suggesting that Ag$_{0.9}$MnO$_2$ decomposed to Ag and Mn$_3$O$_4$ under N$_2$.

The thermal decomposition behavior of Ag$_{0.9}$MnO$_2$ was investigated in detail by TG measurements during both the heating and cooling processes, in air, and under N$_2$ flows, at temperatures up to 900°C. The samples were heated at 500°C for 1 h in air to eliminate CO$_2$ and water before measurement. In the TG curve under air flow, shown in Figure 8, a large mass loss, corresponding to 4.58%, was observed in the temperature range 700−800°C during the heating process, and no mass change occurred during the cooling process. These mass losses in air and N$_2$ flows are comparable to those calculated for the Ag$_{0.9}$MnO$_2$ decomposition reactions represented by reactions 2 and 3, respectively.

Figure 10 shows the XRD patterns of the samples after the TG measurements under (a) air, and (b) N$_2$. These results confirmed the formation of $\alpha$-Mn$_2$O$_3$ (ICDD-PDF# 73-1826) and Mn$_3$O$_4$ under air and N$_2$, respectively. Figure 11 shows the TG curve for the process of heating under an N$_2$ flow and cooling under an air flow. A mass loss was observed in the temperature range 500−700°C in the heating process, and a recovery of mass occurred below 670°C in the cooling process. After the measurement, the single-phase delafossite was obtained, as shown in Figure 10c. These results suggest the reformation of the delafossite from the mixture of Ag and Mn$_3$O$_4$, which formed in N$_2$, during the cooling process in air.

SEM images of the freshly prepared Ag$_{0.9}$MnO$_2$, and the samples after the TG measurements are shown in Figure 12. The particle size of the unheated delafossite was smaller than 500 nm, and thin plate-like particles were observed. After the TG measurements at temperatures of up to 900°C in air, and
under N₂, granular particles with sizes of less than 500 nm were observed, in both cases. After the TG measurement performed with heating up to 900 °C under N₂ and subsequently cooling to room temperature in air, granular particles were observed. The particles appeared larger than those observed after the measurement in N₂. The XRD pattern of the sample shown in Figure 10c indicated that it was the single-phase delafossite, similar to the original Ag₀.₉MnO₂, however, plate-like particles were not observed. These results suggest that the shape of the reformed delafossite phase was influenced by that of the Ag or Mn₃O₄ particles.

The back-scattered images of the sample after the TG measurement with heating of up to 900 °C under N₂ are shown in Figure 13. Large bright particles surrounded by smaller particles were observed. This indicates that coarsening of Ag particles formed by reduction of the Ag₀.₉MnO₂ delafossite occurred upon heating to 900 °C. As described above, the delafossite phase was regenerated during cooling in air and its particle size was larger than that of the Mn₃O₄ in the sample after TG measurement in N₂ at 900 °C. Therefore, it is believed that Ag species diffuse toward the Mn₃O₄ particles, resulting in reformation the delafossite phase.

The above results indicate that Ag₀.₉MnO₂ reformed from metallic Ag and Mn₃O₄, but not from Ag and Mn₂O₃, implying that the crystal structure of the Mn oxide affects the reformation process. The α-Mn₂O₃ and Mn₃O₄ have an orthorhombic distorted bixbite structure and a tetragonal hausmanite-type structure, respectively, the latter of which is a spinel-like structure. We have previously reported the reversible reformation of Cu(Fe₁₋ₓAlₓ)O₂ and Cu(Cr₁₋ₓAlₓ)O₂ delafossites from spinel-type oxides under oxidative/reductive cycles. In these processes, the delafossites decomposed to metallic Cu and spinel-type oxides by H₂ reduction at 300–800 °C and reformed by O₂ oxidation. The reformation of the Cu delafossite is similar to the formation of Ag₀.₉MnO₂ from Ag and Mn₃O₄. However, the reformation of the Ag₀.₉MnO₂ delafossite from Ag and Mn₂O₃ occurred during cooling in air at 670 °C, where metallic Ag is more stable than Ag₂O. We have also reported that metallic Cu formation by H₂-pulse treatment of CuMnO₂ and disappearance of Cu by 50%O₂/He-pulse treatment at 300–500 °C. In this temperature range, Cu₂O is more stable than metallic Cu. This implies that the delafossite regeneration process for Ag₁₋ₓMnO₂ and CuMnO₂ is different. However, further investigation is necessary to clarify the above process in detail. The delafossite reformation process involving oxidation of the Ag metal by O₂ at 670 °C in air is interesting and may help to reveal details about the formation process of Ag delafossites. Sturzenegger et al. reported that the AgNi₀.₅Ti₀.₅O₂ delafossite decomposed to Ag and ilmenite-type NiTiO₃ in O₂ above 650 °C. However, no reformation of the delafossite from either NiTiO₃ was reported. In contrast, Lalanne et al. reported that Cu(Fe₁₋ₓCrₓ)O₂ decomposed to CuO and spinel-structured Cu(Fe₁₋ₓCrₓ)₃O₄ in air, above 400 °C and that the delafossite phase reformed above 800 °C. This delafossite formation includes reduction of the Cu-spinel structure. Reductive reformation processes from spinel-type intermediates have been reported for the formation of CuMnO₂ (M = Al, Cr, Fe, Mn). Transformation processes between Cu delafossites and spinel-type oxides, with Cu incorporation/deposition, have been proposed. During these processes, the octahedral MO₆ layer in both structures is maintained. From the above results, we can extend the transformations between delafossite and spinel-type structures to include Ag-containing compounds.

4. CONCLUSIONS

In the present study, we report the synthesis of a delafossite-type Ag–Mn oxide by the precipitation method at room temperature. The delafossite is Ag⁺-deficient and has a chemical composition of Ag₀.₉MnO₂. The Ag₀.₉MnO₂ delafossite decomposed to Ag and Mn₃O₄ in air, or Ag and Mn₂O₃ under N₂, at temperatures of 700–800 and 500–700 °C, respectively. The reformation of the delafossite from metallic Ag and Mn₂O₃ occurred at approximately 670 °C in air. This reversible decomposition/reformation process is explained by the similarity between delafossite and spinel-type structures, both of which include an octahedral MO₆ layer. The reformation process from Ag and the Mn₂O₃ spinel phase could provide a valuable new synthetic route to Ag⁺-containing delafossite-type oxides.

AUTHOR INFORMATION

Corresponding Author
E-mail: katos@gipc.akita-u.ac.jp
ORCID
Sumio Kato: 0000-0001-9659-9916
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Notes
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