Direct synthesis of AgInO$_2$

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Abstract

Potential applications as transparent conducting oxides have made the study of ternary metal oxides based on the delafossite structure very attractive. The well known and understood thermal instability of noble metal oxides, and therefore the associated problems with high-temperature solid-state techniques to yield pure complex oxides based on noble metals, clearly illustrates the need for low-temperature alternatives. For the first time, synthesis of 3R-AgInO$_2$ at low temperature (175 °C) and pressure (<10 atm) was achieved by a single-step hydrothermal technique. Particle size of the orange crystallites ranged from 3 to 7 μm.
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1. Introduction

Owing to their potential application as transparent conducting oxides (TCOs) [1–5], investigations of ternary metal oxides that adopt the delafossite (CuFeO$_2$) structure have increased dramatically over the last five years. Delafossites have the general chemical formula ABO$_2$ and can crystallize in either the rhombohedral 3R-($R\bar{3}$m) or hexagonal 2H-($P6_3$/mmc) polytype based on the stacking of the alternating layers of edge-shared BO$_6$ octahedra and two-coordinate noble metal A-site cations. This structure type can accommodate various monovalent A-site cations (Cu^I, Pd^I, Pt^I and Ag^I) and trivalent B-site cations (0.53 < $r(B^{3+}_{VI})$ < 1.09 Å). The synthesis of a particular delafossite material is dictated by the choice of A-site cation, of which Cu^I and Ag^I (d^{10} ions) are more appropriate for enhanced optical transparency [1], while Pd^I and Pt^I (d^9 ions) are better choices for improved electrical conductivity [6]. Although ternary and more complex oxides incorporating copper can easily be synthesized by high-temperature solid-state techniques, such oxides containing Ag, Pd or Pt are difficult to prepare in one step by solid-state reactions. Reagents containing noble metal cations have low free energies of formation, which result in decomposition or dissociation at temperatures that are too low to permit mass diffusion to occur. Consequently, most oxide phases that contain Ag, Pd or Pt are prepared by direct reactions in closed solid state systems [7–10] or by exchange reactions [2,7,11–14].

Recently, we reported a general hydrothermal synthesis method whereby various polycrystalline Cu-based delafossite-like materials (CuMO$_2$, where M = Al, Ga, Fe, La and Al$_{1-x}$Ga$_x$) were synthesized in a single-step, at low temperature (<215 °C) and low pressure (<10 atm) [15,16]. In the present work, we further illustrate the universality of this technique [17] in its application to the synthesis of AgInO$_2$, and we present a possible explanation for the obstacles encountered in previous low-temperature and pressure attempts to synthesize phase-pure samples of Ag-based materials. This work provides more desirable and practical conditions than the early pioneering hydrothermal work on AgInO$_2$ reported by Shannon et al. (500 °C and 3000 atm externally applied) [7] and the improved conditions reported later by Jansen et al. (580 °C and 2000 atm O$_2$) [18]. Furthermore, this work represents the first single-step, low temperature and low pressure example of Ag-containing delafossite synthesis.

2. Experimental procedure

Bulk AgInO$_2$ was synthesized by adding 0.1357 g (3.4 × 10^{-3} mol) of NaOH(s) (Alfa Aesar), 0.3932 g (1.7 × 10^{-3} mol) of Ag$_2$O (D.F. Goldsmith) and

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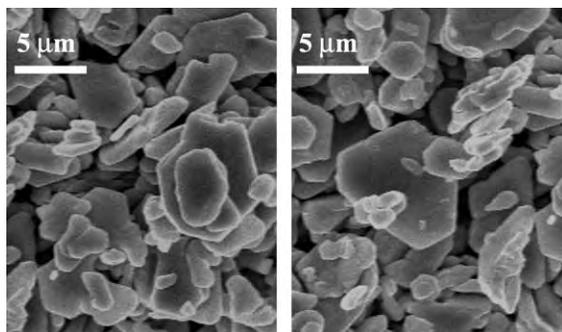
Fig. 1. SEM images of large, highly crystalline grains of AgInO$_2$ grown hydrothermally.

0.4711 g (1.7×10^{-3} mol) of In$_2$O$_3$ (Alfa Aesar) to a FEP (fluoro(ethylene–propylene)) Teflon pouch [19]. The pouch was sealed and placed in a 125 ml Teflon-lined autoclave (Parr) filled with 80 ml of deionized water. The total contents of each pouch were held constant to 1.0 g. Up to 6 additional pouches were inserted into the autoclave. The autoclave was first heated to 150 °C for 5 h to allow water to enter the permeable membrane of the pouch and dissolve the NaOH(s). This was followed by 48 h step at 175 °C, with subsequent cooling to room temperature at 6 °C/h. The pouch was opened and polycrystalline AgInO$_2$ was recovered by filtration.

Powder X-ray diffraction (PXRD) data for all samples, to confirm phase formation and extent of purity, were collected every 0.02° for $10° < 2\theta < 80°$ on a Rigaku XDS 2000 diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). Patterns were indexed with the Jade$^{©}$ software suite, and known phases were identified by comparing them with powder diffraction files (PDF) from within Jade$^{©}$ [20]. Electron microscopy studies were carried out using Hitachi H-8100 transmission electron microscope (TEM) and S-4500 scanning electron microscope (SEM).

3. Results and discussion

After investigating the effects of, and optimizing, important experimental parameters including reaction time, temperature, [NaOH]/[Ag], [NaOH]/[In] and [Ag]/[In], nearly phase pure 3R-AgInO$_2$ was isolated in >90% mass yield. The SEM images in Fig. 1 shows that particle size for the orange crystallites ranged from 3 to 7 μm. The PXRD pattern of the final product mixture is shown in Fig. 2. With the exception of peaks corresponding to unfiltered Kβ transitions and the (111) reflection of metallic Ag, all peak positions correspond to reflections of the rhombohedral phase $R\bar{3}m$ (No. 166), with cell constants $a = 3.272$ Å, $c = 18.858$ Å. These values match those of JCPDS #21-1077 ($a = 3.277$ Å, $c = 18.877$ Å). Significant intensity anomalies suggest a microstructure with a preferred c-axis orientation of grains, which is consistent with other delafossites prepared by this method [16]. Differential thermal analysis revealed that the compound is stable up to 675 °C, at which point it decomposes to In$_2$O$_3$ and Ag. This is consistent with what has been reported previously [7].

The presence of trace amounts of metallic silver in the product mixture is not surprising, as it has been evidenced in previous attempts at Ag-based delafossite synthesis [2,11, 12,21–23]. Phase pure products have been reported for either high oxygen pressure hydrothermal systems [18] or for ion exchange reactions, with KNO$_3$ as an oxidizing flux, in addition to up to 50% excess AgNO$_3$, followed by a post-synthesis removal of excess nitrates by water [2,12]. Reproduction of the latter results by other laboratories has not yet been successful as trace amounts of metallic Ag are observed [14]. Previous hydrothermal work by Croft et al. [24] and Shannon et al. [7] reported that the addition of up to 50% excess Ag$_2$O and increased basic conditions, followed by post-synthesis leaching with nitric acid enable phase pure materials to be obtained [7,24]. In contrast to this result,
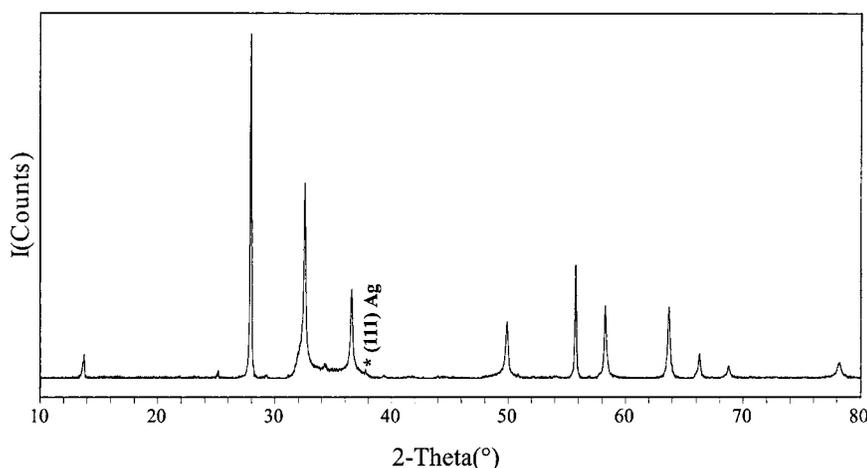
Fig. 2. Powder X-ray diffraction pattern of 3R-AgInO$_2$.
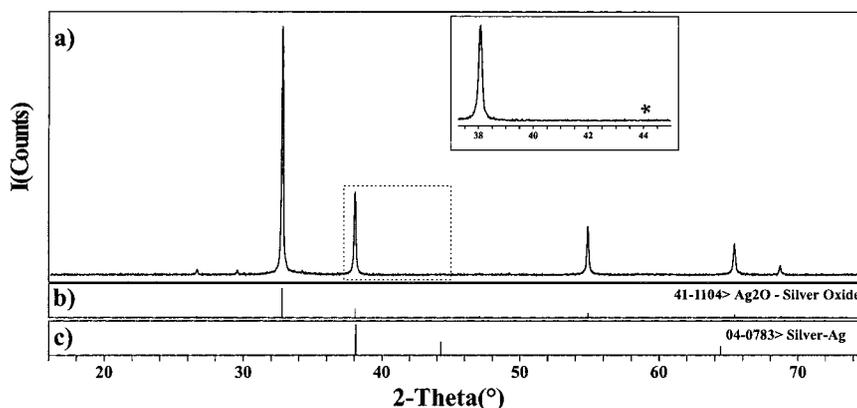
Fig. 3. (a) Powder XRD pattern for typical Ag_2O as received from vendor ($K\beta$ transition at $2\theta = 29.413°$), with inset from $37.5 < 2\theta < 45.5°$ illustrating location, marked by asterisk, where (200) reflection of metallic Ag would appear. Calculated positions, both indexed and showing relative intensities marked by vertical bars, of (b) Ag_2O (JCPDS #41–1104) and (c) Ag (JCPDS #04–0783).

the addition of excess Ag_2O and increased NaOH(s) in the current work did not eliminate the presence of trace amounts of metallic silver. Post-synthesis leaching in dilute nitric acid led to reduced amounts of metallic silver, but at the expense of significant dissolution of the delafossite phase.

TEM studies of samples from several vendors (D.F. Goldsmith, Alfa-Aesar, Fisher and Acros Organics) reveal Ag_2O to be the source of the silver impurity. It is important to note that, in previous reports [11,21,22], the presence of metallic silver was believed to be an artifact of the synthesis, i.e. that it was an unwanted side product arising from the decomposition of a small amount of Ag_2O. This conclusion is most likely a consequence of the difficulty in detecting the presence of Ag in Ag_2O by conventional techniques such as PXRD or elemental analysis. Unless significant amounts are present, metallic silver in Ag_2O would not be observed by PXRD, owing to peak overlap of the most intense reflection for Ag, which is the (111) peak, located at $2\theta = 38.116°$, $d(\text{Å}) = 2.3590$ Å, and the (200) reflection of Ag_2O, occurring at $2\theta = 38.066°$, $d(\text{Å}) = 2.3620$ Å. (Fig. 3). Resolving these two peaks ($\Delta d/d = 1.3 \times 10^{-3}$) would be

extremely difficult using any available powder X-ray diffractometer. With electron microscopy, however, this problem can be avoided. Micrographs of several grains reveal the presence of globules, attached to the surface of larger Ag_2O particles, which by electron diffraction are shown to be metallic silver. (Fig. 4).

Attempts at oxidizing the Ag globules within the Ag_2O, in an oxygen atmosphere at temperatures up to 280 °C, were only partially successful. The size range of the globules decreased from 100–250 to 20–70 nm, but were not completely removed (Fig. 5). It has been proposed that, in air at elevated temperatures (but below the decomposition temperature of 300 °C), Ag_2O undergoes slow dissociative evaporation into O_2 molecules and free Ag atoms, which immediately condense as metallic silver [25]. Condensation occurs owing to the low-volatility of the gaseous Ag atoms and the lack of highly reactive species in the surroundings. Under the hydrothermal conditions presented here, where no oxidizing agents are available to react with metallic silver, it is not surprising that attempts to synthesize $AgInO_2$ using
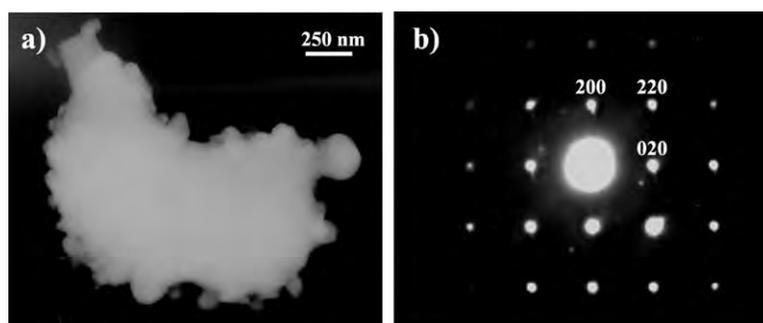
Fig. 4. Electron micrographs of (a) an image of a typical Ag_2O grain, as received from vendor, and (b) a diffraction pattern, along the [001] zone axis of Ag, as taken from a globule.
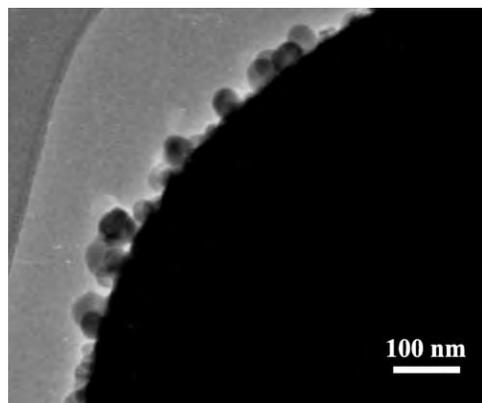
Fig. 5. TEM image of an oxidized Ag_2O particle illustrates the presence of Ag globules on the grain edge.

a source of Ag_2O that contained trace amounts of silver metal resulted in a small, but detectable, amount of silver metal in the $AgInO_2$ product.

4. Conclusions

Delafossite-like $AgInO_2$ was synthesized in high yield by a new hydrothermal technique that had previously been applied only to Cu-based delafossites. The presence of metallic Ag in the product is similar to what has been reported in previous hydrothermal work. TEM studies, on various sources of Ag_2O, demonstrated that the impurity can be attributed to unoxidized Ag globules within Ag_2O and not to a side product of the reaction. Attempts to remove this impurity by heating the Ag_2O in an O_2 atmosphere were unsuccessful, although the number and size of the Ag globules were reduced. It is unlikely that a pure sample of Ag_2O can be obtained through oxidation of the Ag globules, owing to the mechanism by which Ag_2O decomposes into metallic Ag on heating to temperatures approaching 300 °C. New routes towards pure starting materials are warranted.

Preliminary results show that applications of this single-step hydrothermal technique towards the low temperature synthesis of other Ag-based delafossites, including aliovalent substitution of the B-site cation, are promising. The synthetic, structural, and electro-optical details will appear in forthcoming contributions.

Acknowledgements

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