Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 173 (2003) 355–358
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Synthesis of 3R-Cu$MO_{2+\delta}$ (M = Ga, Sc, In)

Sangmoon Park and Douglas A. Keszler*

Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331-4003, USA

Received 27 June 2002; received in revised form 6 February 2003; accepted 13 February 2003

Abstract

Improvements have been made in the single-phase synthesis of 3R $CuScO_2$ and $CuInO_2$ by the metathesis reaction between CuCl and AMO_2 (A = Li, Na; M = Sc, In). A new flux-assisted procedure has also been devised for the preparation of single-phase $CuGaO_2$ at temperatures near 600°C. Oxygen insertion into $CuScO_2$ and $CuInO_2$ has been examined by heating samples in air to a temperature of 450°C. A single phase of composition $CuInO_{2.67}$ can be produced by this method, while oxygen uptake for $CuScO_2$ under similar conditions results in the production of CuO and Sc_2O_3.

1. Introduction

Chemical and physical properties of numerous compounds CuMO_2 (M = +2, +3, +4 cation) crystallizing in the structure of delafossite, $CuFeO_2$ [1], have been examined [2,3]. In particular, the compounds $CuScO_2$ and $CuInO_2$ have recently been studied as transparent p-type conductors [4,5]. Their bulk synthesis, however, has been a challenge. The Sc derivative exists in two polytypes—2H and 3R. The 2H form can be stabilized by incorporation of small amounts of Mg, but up to now, no method has been reported for the synthesis of single-phase 3R material. The preparation of $CuInO_2$ has likewise been difficult because of its relatively low decomposition temperature −600°C.

A low-temperature substitution reaction

$$CuCl + AMO_2 = CuMO_2 + ACl (A = Li, Na;\ M = In, Sc)$$

has been described for synthesis of these compounds, but its use has resulted in the generation of multiphase products, i.e., following the procedures of Doumerc et al. [6] we observe residual Sc_2O_3 and Cu_2O in the preparation of $CuScO_2$, and residual In_2O_3 and Cu_2O are observed in the preparation of $CuInO_2$ [7]. In principle, the substitution reaction should provide a simple means for the realization of single-phase products; for $CuScO_2$, the reaction affords only the 3R polytype as part of the product mixture, and the reaction occurs below the decomposition temperature of $CuInO_2$. The synthetic challenge is then to simply improve the yield of the substitution process, and, as we describe below, this can be done in a straightforward manner. In addition to improving the low-temperature metathesis reaction, a new, flux-assisted method is described for the synthesis of the Ga derivative, $CuGaO_2$, providing a procedure that should be applicable to the preparation of a variety of other delafossites and similar Cu oxides. The lower temperatures of this process relative to standard solid-state techniques may provide a means for better stoichiometry control, considering the volatility of Cu oxides at elevated temperatures. Given the availability of single-phase 3R Sc and In delafossites, we have also examined their oxidation on heating in air to form Cu$MO_{2+\delta}$, which is of interest for affecting their electrical properties by introducing p-type carriers.

2. Experimental

For the preparation of $CuScO_2$ and $CuInO_2$, the reagents Sc_2O_3 (Stanford Materials 99.9%), In_2O_3 (Cerac 99.99%), Li_2CO_3 (Cerac 99.999%), Na_2CO_3 (Cerac 99.995%), and CuCl (Alfa 99%) were used. $NaInO_2$ and $LiScO_2$ were prepared by heating the appropriate stoichiometric quantities of Na_2CO_3, Li_2CO_3, In_2O_3, and Sc_2O_3 in alumina crucibles at 1000°C for 12 h. $LiScO_2$ and $NaInO_2$ were loaded with 30 mol% excess CuCl in separate alumina tubes, which

*Corresponding author. Fax: +1-541-737-2062.
E-mail address: douglas.keszler@orst.edu (D.A. Keszler).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(03)00110-5

were subsequently sealed inside evacuated silica tubes. The Sc mixture was then heated for 12 h at 700°C, and the In mixture was heated for 3 h at 600°C. The cooled products were vigorously stirred in 2 M NH_3(aq) for several hours to remove LiCl, NaCl, and excess CuCl.

For the preparation of $CuGaO_2$, the reagents Ga_2O_3 (Cerac 99.995%), Cu_2O (Cerac 99%), CuCl (Alfa 99%), and KCl (MCB Reagent) were used. Products were characterized from reactions of 80 wt% (Ga_2O_3 + Cu_2O)/20 wt% (0.7 CuCl + 0.3 KCl) and 80 wt% (Ga_2O_3 + Cu_2O)/20 wt% (0.3 CuCl + 0.7 KCl). The mixtures were heated in sealed, evacuated silica tubes from 300°C to 800°C for 15 h. The products were stirred in 2 M NH_3(aq) overnight to remove the flux components. All samples were characterized by X-ray diffraction on a Siemens D-5000 powder system, both before and after washing in NH_3(aq).

Oxygen uptake in production of $CuMO_{2+\delta}$ (M = Sc, In; $\delta > 0$) was determined by heating samples at 250°C, 300°C, 350°C, 400°C, and 450°C for 3 days at each temperature. The same sample was used for each successive heating step so that each was heated for a total of 15 days. The powders were weighed and ground after each heat treatment.

3. Results and discussion

As shown by the diffraction patterns in Figs. 1 and 2, application of the metathesis reactions

$$LiScO_2 + CuCl = CuScO_2 + LiCl$$

$$NaInO_2 + CuCl = CuInO_2 + NaCl$$

can lead to the production of single-phase 3R-delafossites $CuScO_2$ and $CuInO_2$. In each X-ray pattern, there is no evidence of other phases such as In_2O_3, Sc_2O_3, and Cu_2O or the 2H polytype of $CuScO_2$. The presence of In_2O_3, Sc_2O_3, or Cu_2O in the products, as noted by others [7], likely arises from reaction between the alkali–metal reagents and the container SiO_2. Indeed, when heating the reagents directly in silica tubes, severe attack of the tube is readily noted. To circumvent these side reactions, the reagents are first placed in an alumina tube, which is subsequently sealed inside the silica tube, providing a physical barrier between the reagents and the silica. The net result is a straightforward application of the substitution reaction (cf., cell parameters in Table 1).

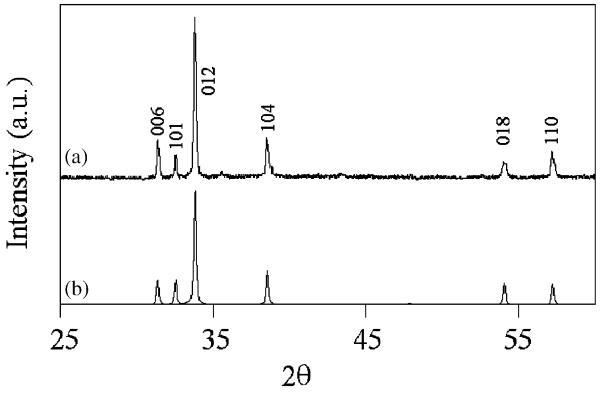

Fig. 1. (a) Experimental X-ray diffraction pattern for 3R $CuScO_2$. (b) Simulated X-ray diffraction pattern for 3R $CuScO_2$ (for structural data, see Ref. [6]).

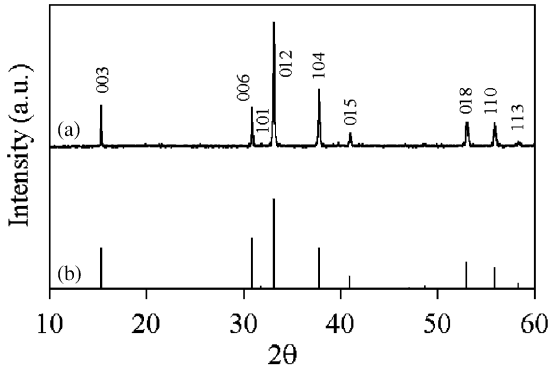

Fig. 2. (a) Experimental X-ray diffraction pattern for 3R $CuInO_2$. (b) Simulated X-ray diffraction pattern from data in Table 3 of Ref. [7].

Table 1
Cell parameters and δ values for $CuMO_{2+\delta}$ (M = Sc, In)

$CuMO_2$	a (Å)	c (Å)	V (Å^3)	δ
M = Sc	3.2160(6)	17.077(3)	152.96(5)	0
250°C	3.2180(6)	17.081(3)	153.18(5)	<0.01
350°C	3.2183(6)	17.086(3)	153.26(5)	0.06
400°C	3.219(2)	17.089(9)	153.3(1)	0.26
	3.253(7)	17.06(4)	156.3(6)	
450°C	3.253(8)	17.05(4)	156.3(7)	Decomposition
M = In	3.2869(9)	17.349(4)	162.32(7)	0
250°C	3.2904(4)	17.376(2)	162.92(3)	<0.01
350°C	3.2916(9)	17.370(3)	162.98(7)	0.09
400°C	3.2950(5)	17.382(2)	163.44(4)	0.32
	3.3240(8)	17.387(3)	166.37(6)	
450°C	3.3222(2)	17.355(1)	165.89(2)	0.67

We note that the resulting $CuScO_2$ powder exhibits a light gray-blue color. This color likely results from the presence of a small amount of unreacted or excess Cu compound in the sample, as heating the powder in a sealed, evacuated tube across a temperature gradient of 50°C at 1000°C leads to a color that is more aptly described as off white, a result that is consistent with the reported band gap, >3 eV [8]. (A transparent, brown discoloration, similar in appearance to Cu_2O, was noted at the cooler end of the silica tube.) The $CuInO_2$ product exhibits a rather deep off-yellow color, a result that is consistent with the reported absorption spectrum of thin films [5].

The success of these metathesis processes derives from the topochemical nature of the reactions. The Sc–O and In–O structural connectivities in $LiScO_2$ [9] and $NaInO_2$ [10], respectively, match those in the corresponding materials $CuScO_2$ and $CuInO_2$; in the metathesis process only the coordination environments of the Li(Na) and Cu atoms change. For the preparation of $CuGaO_2$, a corresponding topochemical substitution is not possible, since the compounds $MGaO_2$ (M = Li, Na, K) crystallize with tetrahedral coordination of the Ga atoms [11]; application of the low-temperature replacement process does not lead to a delafossite product. Reaction temperatures near 900°C are used to prepare the compound directly from the solids Cu_2O and Ga_2O_3 [12]. To promote the reaction between Ga_2O_3 and Cu_2O at lower temperatures, we have used a flux-assisted approach with the KCl–CuCl system [13], which exhibits a deep eutectic ($T_m = 125$°C) near 30 mol% KCl/70 mol% CuCl. By using a mixture of 20 wt% eutectic and 80 wt% Cu_2O:Ga_2O_3, we observe production of $CuGaO_2$ at temperatures near 400°C; the product is retained on heating the mixture to 800°C. Refined cell parameters for the phase are $a = 2.9767(7)$ and $c = 17.174(3)$ Å. In the KCl-rich flux, however, the results are much different. At the composition 70 mol% KCl/30 mol% CuCl, the liquidus occurs at approximately 540°C. In the 80/20 wt% mixture of this KCl/CuCl composition and Cu_2O:Ga_2O_3, no reaction between Cu_2O and Ga_2O_3 is observed at 400°C. Just below the liquidus at 500°C, Cu_2O and Ga_2O_3 react to form $CuGaO_2$, while at temperatures above the liquidus, the major peaks in the X-ray diffraction patterns of the products correspond to Ga_2O_3. So, above the liquidus, Cu_2O is preferentially dissolving in the flux, leaving Ga_2O_3 as the precipitated product. To promote the smooth formation of $CuGaO_2$ from Cu_2O and Ga_2O_3, the flux should be more concentrated in Cu, i.e., near the eutectic point. Considering the reduced reaction temperatures relative to other techniques, the useful solubility of an oxide containing an M^{3+} cation, and the ability to readily dissolve the flux for isolation of the product, the synthesis method should be generally applicable to the preparation of other delafossite compounds and related oxides.

Since single-phase 3R $CuInO_2$ and $CuScO_2$ powders are now available, we have done a cursory examination of the oxidation products that occur on heating in air. The results are summarized in Table 1. As noted in the experimental section, all samples were heated at each of the indicated temperatures for 3 days. For $CuScO_2$, heat treatment at 250°C affords a discoloration of the sample from white to gray and a very small increase in mass. At 350°C, the sample has turned black, and the mass increase corresponds to a stoichiometry of $CuScO_{2.06}$. The increasing trend in the cell parameters following these heat treatments is consistent with a small solubility of O atoms in the 3R structure. At 400°C, the stoichiometry is $CuScO_{2.26}$, but the X-ray pattern can be accounted for on the basis of a two-phase mixture comprised of lightly and heavily O-doped phases. At 450°C, decomposition begins with appearance of CuO and Sc_2O_3 in the diffraction pattern; the heavily-doped O phase, however, is still discernable, and no change in unit-cell volume is observed between 400°C and 450°C. We note that the poor fit of the data to the larger hexagonal cell at 400°C and 450°C provides some evidence that the symmetry of this phase could be lower than indicated by the hexagonal cell.

The results for air oxidation of $CuInO_2$ are slightly different from those of $CuScO_2$. Up to 350°C, a volume increase is observed, but the O concentration is higher than that of $CuScO_{2+\delta}$ (cf., Table 1). At 400°C, the material separates into a two-phase product of lightly and heavily-doped O components. In contrast to $CuScO_2$, the O-rich form of $CuInO_{2+\delta}$, $\delta = 0.67$ exhibits a higher thermal stability, providing a single-phase product at 450°C that is nicely indexed with a hexagonal cell. The differences between $CuInO_2$ and $CuInO_{2.67}$ are readily apparent from comparison of their X-ray patterns in Fig. 3. Reflections of the type (00l) exhibit only minor shifts on O insertion, whereas reflections of the type $k, l \neq 0$ exhibit significant shifts. The shifts indicate that the cell is preferentially expanding in the ab plane upon O insertion. In the two-phase regions of the phase diagrams for the Sc and In analogues, the diffraction patterns are essentially composites of the two patterns of Fig. 3.

The results on oxidation of $CuScO_2$ are qualitatively similar to those previously reported [14] for samples heated in flowing O_2(g) at 400°C, where a large volume increase was observed, corresponding to an expansion of the a-axis and a slight contraction of the c-axis (cf., Table 1). The maximum O incorporation in the previously reported study corresponds to $\delta = 0.37$, a value that exceeds our observation of $\delta = 0.26$. This

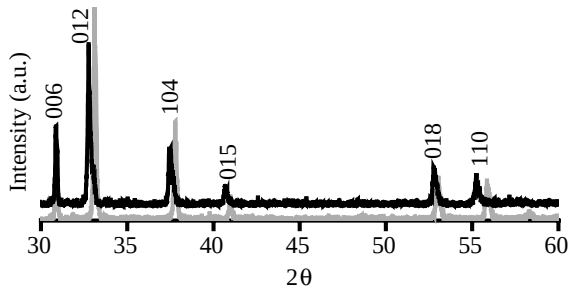

Fig. 3. X-ray diffraction patterns for $CuInO_{2+\delta}$. Black line represents $\delta = 0$, and gray line represents $\delta = 0.67$.

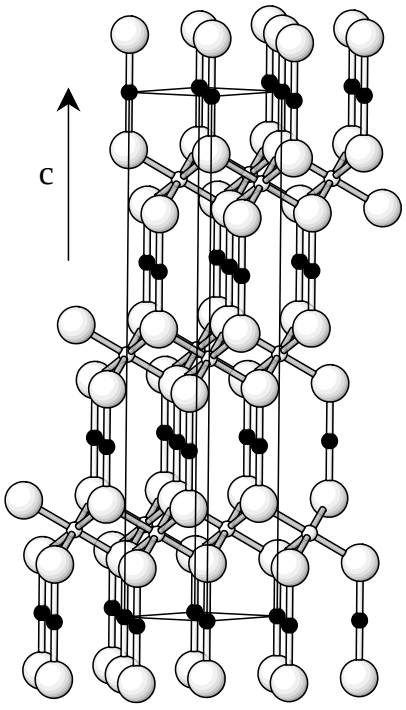

Fig. 4. Drawing of the structure of delafossite. Large open circles represent O atoms, small filled circles represent Cu atoms, and small open circles represent *M* atoms such as Sc or In.

result is expected, as we heated samples in air rather than O_2(g), and O insertion in the Sc compound is kinetically slow. The observation of a two-phase region in this system is also consistent with a previous report on the compounds $LaCuO_{2+\delta}$ and $CuYO_{2+\delta}$ [15]. The results on $CuInO_{2+\delta}$ follow those of the Sc analog, but higher O concentrations are more readily realized in the In derivative. This higher concentration can be associated with the larger crystal radius of In ($r = 0.93$ Å) vs. Sc ($r = 0.87$ Å) [16] and the larger cell volume of $CuInO_2$ (cf. Table 1). The delafossite structure (Fig. 4) contains hexagonal arrays of Cu(I) atoms that can be oxidized. O incorporation occurs through placement of atoms in triangular hollows formed by nearest-neighbor Cu atoms. In the Sc derivative, these nearest-neighbor Cu⋯Cu distances are shorter than those in the In compound, as seen by comparing the lengths of the *a* axes (Table 1), likely contributing to the slower kinetics of O insertion. Similarly, for $CuGaO_2$ with its even shorter *a*-axis, heating in air under the same conditions does not produce a measurable increase in mass; O insertion does not occur under these conditions. In air at 800°C, the compound is simply oxidized to CuO and $CuGa_2O_4$.

4. Conclusions

Single-phase 3R forms of $CuScO_2$ and $CuInO_2$ can readily be prepared by a relatively low-temperature metathesis reaction; care must be taken to prevent reaction of the reagents with the container. A flux-assisted method can be used to prepare $CuGaO_2$ at temperatures as low as 600°C. O insertion proceeds more readily in the In derivative relative to that of the Sc derivative because of the larger size of the In atom. This larger size also leads to a higher thermal stability of the oxidized In delafossite.

Acknowledgments

This work was supported by the US National Science Foundation (DMR-0071727). We thank Professors A.W. Sleight and J. Tate for many technical discussions at OSU on delafossite compounds.

References

[1] A. Pabst, Am. Mineral. 23 (1938) 175–176.
[2] R.D. Shannon, D.B. Rogers, C.T. Prewitt, Inorg. Chem. 10 (1971) 713–718.
[3] R. Nagarajan, N. Duan, M.K. Jayaraj, J. Li, K.A. Vanaja, A. Yokochi, A. Draeseke, J. Tate, A.W. Sleight, Int. J. Inorg. Mater. 3 (2001) 265–270.
[4] N. Duan, A.W. Sleight, M.K. Jayaraj, J. Tate, Appl. Phys. Lett. 77 (2000) 1325–1326.
[5] H. Yanagi, T. Hase, S. Ibuki, K. Ueda, H. Hosono, Appl. Phys. Lett. 78 (2001) 1583–1585.
[6] J.P. Doumerc, A. Ammar, A. Wichainchai, M. Pouchard, P. Hagenmuller, J. Phys. Chem. Solids 48 (1987) 37–43.
[7] M. Shimode, M. Sasaki, K. Mukaida, J. Solid State Chem. 151 (2000) 16–20.
[8] A. Draeseke, H. Yanagi, D. Tucker, D. Easley, D.H. McIntyre, J. Tate, J. Li, A.W. Sleight, Bull. Am. Phys. Soc. 47 (2002) B23/13.
[9] R. Hoppe, B. Schepers, H.J. Roehrborn, E. Vielhaber, Z. Anorg. Allg. Chem. 339 (1965) 130–143.
[10] E. Hubbert-Paletta, R. Hoppe, G. Kruezburg, Z. Anorg. Allg. Chem. 379 (1970) 255–261.
[11] M. Marezio, Acta Crystallogr. 18 (1965) 481–484; H. Mueller, R. Hoppe, Z. Anorg. Allg. Chem. 611 (1992) 73–80.
[12] C. Sandonnini, Gazz. Chem. Ital. 44I (1914) 307.
[13] G. Gessner, Silikattechnik 21 (1970) 45–46.
[14] M. Elazhari, A. Ammar, M. Elaatmani, M. Trari, J.P. Doumerc, Eur. J. Solid State Inorg. Chem. 34 (1997) 503–509.
[15] R.J. Cava, H.W. Zandbergen, A.P. Ramirez, H. Takagi, C.T. Chen, J.J. Krajewski, W.F. Peck, J.V. Waszczak, G. Meigs, R.S. Roth, L.F. Schneemeyer, J. Solid State Chem. 104 (1993) 437–452.
[16] R.D. Shannon, C.T. Prewitt, Acta Crystallogr. Sect. B 25 (1969) 925–929.