

Production of CuAlO_2 in powder, bulk and nanofiber forms

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A study was carried out on the production of CuAlO_2 by using 3 different production routes namely, hydrothermal synthesis, conventional solid state reaction and electrospinning process. For hydrothermal synthesis, commercially available metal salts, Cu_2O powder and chemically precipitated CuO nanoparticles were used as precursors. Bulk CuAlO_2 samples were prepared via solid state reaction route by ball milling and high temperature sintering of CuO and Al_2O_3 powders. CuAlO_2 ceramic mats were synthesized by electrospinning process with the assistance of polyvinylpyrrolidone, as a template polymer. Highly crystalline mesh structured fibers were obtained after sintering of polymer/equal moles of copper chloride and aluminum nitrate composite in air. In the current work, solid state reaction and electrospinning processes yielded phase pure CuAlO_2 in hexagonal symmetry. On the other hand, products obtained from hydrothermal synthesis were CuO , Cu_2O and $\text{Al}(\text{OOH})$, which did not yield CuAlO_2 under current experimental conditions. Detailed qualitative X-ray diffraction analysis revealed the need of specific ionic species in the solution within a narrow temperature-composition-pH window to obtain phase pure CuAlO_2 employing hydrothermal conditions.

Key words: CuAlO_2 , p-TCO, Hydrothermal synthesis, Solid state reaction, Electrospinning process.

Introduction

Today the need for wide band gap semiconductors is increasing due to increase in the use of optoelectronic devices in practical applications. Transparent conductive oxides (TCOs) combine electrical conductivity and optical transparency in the same material. Thanks to these properties they are being used extensively in solar cells, flat panels, electromagnetic shielding, light emitting diodes and heat sources [1]. These well-known and widely used TCOs are mostly based on tin-, indium-, and zinc-oxide [2] and all are n-type semiconductors. Since the discovery of p-type conductivity in a highly transparent thin film of copper aluminum oxide (CuAlO_{2+x}) [3] a considerable effort has been spent on the production of p-type TCOs and great progress has been achieved on the synthesis conditions. Among these TCOs, CuAlO_2 is the first and most popular one due to high transparency in visible region and good conductivity [4], in addition, it has also promising photovoltaic [5], gas sensing [6], and thermoelectric [7] properties. Therefore, CuAlO_2 and other p-type TCO materials have attracted considerable scientific and technological attention.

Up to now, the preparation of CuAlO_2 thin films has mainly been carried out by vacuum based techniques including pulsed laser deposition [8-10], sputtering [11-

13], and chemical vapor deposition [14, 15]. Conventional solid state synthesis, hot pressing and pulsed electric current sintering was employed to obtain bulk samples of CuAlO_2 for the purpose of understanding the origin and details of thermoelectricity [16-18]. Sol-gel processing was also used extensively as an alternative and competitive approach to prepare thin films of copper aluminum oxide during the last decade [19-23]. Electrospinning process (employing polyvinyl alcohol as a template polymer) and ion exchange mechanism were shown to be suitable methods to obtain nanofibrous mats and powders of CuAlO_2 , respectively [24, 25]. Although hydrothermal method provides the advantage of production close to ambient temperatures, there are only a few studies exist in literature focusing on the production of CuAlO_2 based on hydrothermal treatment [26-29] and only 2 of them has been reported with conversion efficiency above 95% [28, 29]. Further, the reaction/precipitation temperature in these 2 studies was above 350°C , which generally requires special sealing gaskets and highly corrosion resistant hydrothermal vessels. The difficulty in the production of CuAlO_2 with this method is probably due to the problems encountered on the stabilization of the valency of the copper ion in the monovalent (Cu^+) state in the solution, [30] which makes hydrothermal synthesis of CuAlO_2 far from reproducibility at low temperatures.

Based on the above observations, in an effort to develop CuAlO_2 in different forms for different kind of applications, the current study was undertaken on powder, bulk and nanofiber processing. The paper reports the results for 3 different production methods namely,

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hydrothermal synthesis, conventional solid state sintering and electrospinning process using a variety of precursors.

Experimental Procedure

Hydrothermal synthesis

Hydrothermal reactions were carried out in a custom-made high pressure vessel equipped with a 150 mL PTFE liner, heating system, temperature controller, and pressure gauge. The system is capable of carrying out experiments up to 250 °C under 100 bar pressure. Temperature of the solution can be measured directly with a K-type thermocouple that was immersed into the system. In this part of the study 23 runs were performed in total. Some of the selected reaction conditions are summarized in Table 1. 4 series of experiments were performed using commercially available chemical reactants, Cu₂O powders and chemically precipitated CuO nanoparticles as precursors. Chemical reagents used in the experiments are of analytical grade and used without further purification.

In the first set of experiments (runs 1, 2 and 3), the solution was prepared by using *copper nitrate hemipentahydrate* (Cu(NO₃)₂ · 2.5H₂O-98%) and *aluminum nitrate nonahydrate* (Al(NO₃)₃ · 9H₂O-99%) as metal sources and *sodium hydroxide* (NaOH-99%) pellets as a mineralizer. For run 3, *formic acid* (CH₂O₂-98%) was also added into the solution as a reducing agent to control the chemical state of copper under hydrothermal conditions [28, 31]. First, metal sources were mixed and dissolved in deionized water. During stirring process, some amount of NaOH pellets and formic acid were added to the solution. After complete dissolution of the precursors, the solution was transferred to the hydrothermal unit and heating/

holding steps were performed as given in Table 1.

In the second set of hydrothermal experiments (runs 4 and 5), commercial Cu₂O powders (–200 mesh, 99%) and Al(NO₃)₃ · 9H₂O were used as metal sources. First, the Al-source was dissolved in deionized water. During stirring process, Cu₂O powders were added slowly into the solution to provide a complete dispersion. Finally, NaOH pellets were dissolved and the solution was transferred to the hydrothermal unit.

For runs 6 and 7 the so called “teflon pouch” method was adapted from literature [27]. For this set of experiments certain amount of precursors and NaOH were weighed and placed in a 1.0 mm thick walled teflon cup. This cup was sealed with an Al-foil on top and placed into the hydrothermal unit filled with 70 mL of deionized water. Hydrothermal vessel was sealed and first heated to 150 °C at a rate of 10 °C/min and held for 4 h at this temperature to allow the permeation of water into the teflon cup. This was followed by a higher temperature step performed for 48 h according to Table 1.

In the fourth set of hydrothermal experiments, initially CuO nanoparticles were obtained by chemical precipitation method described in detail elsewhere [32] and these nanoparticles were used as a copper source in the solution for hydrothermal treatment. In a typical synthesis for CuO, first 4 mmol of *copper acetate monohydrate* (Cu(OOCCH₃)₂ · H₂O- > 98%) and 1 mL *glacial acetic acid* (CH₃COOH- > 99.5%) were mixed with 200 mL deionized water. The turquoise colored solution was rapidly heated to 95 °C by using a hot plate and held 10 min at this temperature. Simultaneously, 0.75 g of NaOH was dissolved in 20 mL of deionized water at room temperature and mixed by pouring into the boiling solution under vigorous stirring. Although, the dark brown precipitates formed immediately after the

Table 1. Reaction conditions used for hydrothermal synthesis.

Run no	Precursors						Temperature (°C)	Time (h)
	Cu(NO ₃) ₂ (mmol)	Al(NO ₃) ₃ (mmol)	CuO (nanoparticles) (mmol)	Cu ₂ O (com. pow.) (mmol)	CH ₂ O ₂ (mL)	NaOH (g)		
1	15	15				10	220	60
2	15	15				13	220	60
3	15	15			5.7	6	220	60
4		15		7.5		6	220	60
5		15		7.5		10	220	60
6		10		5		1.4	150 220	4 48
7		10		5		2.8	150 220	4 48
8		1	1				215	24
9		1	1		0.4		215	24
10		1	1		0.4	0.082	215	24
11		1.9	1.9		0.71	0.154	215	48

addition of NaOH, the solution was stirred further and held at 95 °C for the next 15 min before cooling. After being kept 6 h at room temperature, the precipitate was collected by centrifuging and rinsed with distilled water and ethanol, respectively. Finally, CuO nanoparticles were dried at 80 °C in an oven for 12 h. Solutions for hydrothermal synthesis were prepared by dissolving $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 15 mL deionized water and dispersion of CuO nanoparticles in 10 mL deionized water in separate beakers. Then these 2 solutions were mixed and stirred for 50 min. At this instance, initially CH_2O_2 and after 5 min NaOH pellets were added to the solution. After being stirred for 1 h in total, the solution was transferred to hydrothermal vessel and experiments were performed according to the conditions mentioned in Table 1.

In hydrothermal experiments the total volume of the solutions was fixed to 100 mL for all runs, except runs 6 and 7. For these runs the amount of water inside the system was 70 mL. For all experiments, hydrothermal system was cooled down to room temperature naturally. The precipitates were centrifuged and washed with deionized water and then the product was dried at 80-85 °C in an oven for an overnight.

Solid-state reaction

Bulk CuAlO_2 samples were synthesized via conventional solid state reaction using commercially available CuO and Al_2O_3 powders, both -200 mesh in size and with 99% purity. Appropriate amount of powder samples to provide stoichiometric CuAlO_2 were mixed with ethanol in a polypropylene jar and ball milled for 24 h by using 6 mm diameter ZrO_2 grinding media. Ball milling was carried out with a ball-to-powder ratio of 20. The milled powders were dried in an agate mortar under continuous hand grinding/mixing and calcined in an alumina crucible at 500 °C in air for 3 h to remove organic residues and then at 800 °C for a dwell time of 2 h. The calcined powders were cooled down to room temperature and compacted by uniaxial pressing under a pressure of 20 MPa to obtain bulk pellets. These compacts were heated to 1200 °C at a rate of 10 °C/min and sintered for 24 h in air and then furnace cooled. Some samples were prepared by repeating the milling and calcination steps more than 2 times and finished with sintering again at 1200 °C.

Electrospinning process

CuAlO_2 nanofibrous mats were prepared by electrospinning of a solution typically containing 5 mmol Cu ($\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$, 5 mmol aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -99%), 1.0 g polyvinylpyrrolidone (PVP, $M_w = 1.3 \times 10^6$) as a template polymer and 10 mL of deionized water. Aluminum chloride was dissolved into water first, and then copper acetate was added and mixed for 1 h to obtain a clear solution. PVP was

added to this solution under vigorous stirring to achieve a complete homogenous mixture. After stirred for 5 h at room temperature, the viscous solution was transferred to a syringe having a 22 gauge stainless steel needle. The tip was electrified using a high-voltage DC supply (Spellman SL30) under an applied voltage of 15 kV. The solution was pumped continuously using a syringe pump (KD Scientific) at a rate of 0.1 mL/h. The fibers were collected on an aluminum foil placed at a distance of 15 cm from the needle tip. The product was dried in an oven for 12 h at 90 °C under vacuum and heat treated at 400 °C in air for 5 h to remove organics. The pretreated dark colored nanofibrous mats were peeled off the substrate foil, placed in an aluminum crucible and heated to 1100 °C at a heating rate of 10 °C/min and kept in this temperature for 5 h. Light gray product was collected after furnace cooling to room temperature. Sintered mats were hand ground into powder form in an agate mortar for XRD measurements.

In the current work, all products (as-precipitated, as sintered or as-heat treated) were characterized by X-ray diffraction (XRD) using a BRUKER D8 ADVANCE diffractometer operating at 40 kV, 40 mA. Measurements were taken in Bragg-Brentano mode with $\text{Cu-K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation. The scanning speed was set 2 °/min from 20 to 80 °. The microstructure of the samples was investigated by using a SM Zeiss LS-10 scanning electron microscope (SEM).

Results and Discussions

Hydrothermal synthesis

In this work, hydrothermal reaction conditions are summarized in Table 1. X-ray diffraction patterns of the obtained precipitates are given in Figure 1(a-d). Hydrothermal synthesis as a function of NaOH and CH_2O_2 was performed at 220 °C for a reaction time of 60 h and 20 bar pressure, in order to investigate the effect of NaOH and CH_2O_2 on the formation of CuAlO_2 from $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. As shown in Figure 1(a,a), product with 10 g NaOH was single phase CuO (JCPDS card no: 48-1548) and as NaOH was increased to 13 g, a partial reduction reaction occurred yielding Cu_2O . As a result Cu_2O peaks (JCPDS card no: 05-0667) appeared in the pattern in addition to CuO peaks, Figure 1(a,b). No peaks related to aluminum compounds are observed in the patterns; however, this does not rule out the existence of amorphous material. A similar observation was also reported in literature [28]. On the other hand, with the addition of formic acid, the chemistry of the precipitates showed a significant change. As seen in Figure 1(a, c) the pattern covers phases of Cu_2O , Cu and AlOOH , (Cu; JCPDS card no: 04-0836 and AlOOH ; JCPDS card no: 21-1307). This implies that addition of CH_2O_2 leads to reduction of CuO to Cu. It

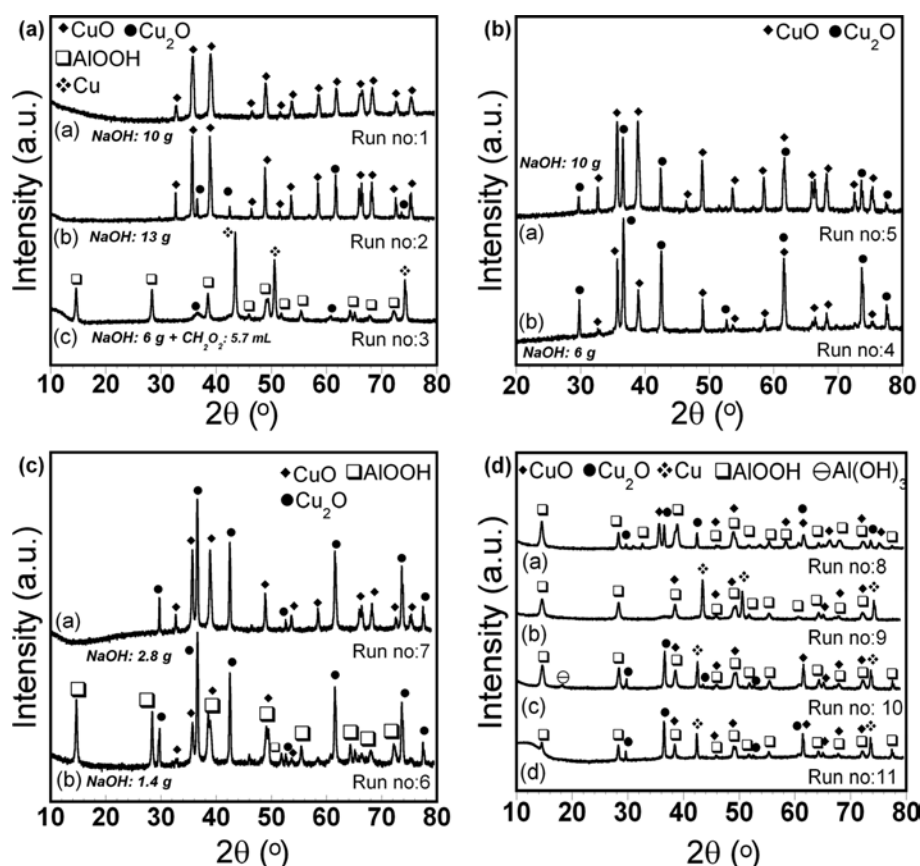


Fig. 1. XRD patterns of products obtained from hydrothermal synthesis with precursors, (a) 15 mmol $\text{Cu}(\text{NO}_3)_2$ + 15 mmol $\text{Al}(\text{NO}_3)_3$, (b) 10 mmol $\text{Al}(\text{NO}_3)_3$ + 5 mmol Cu_2O , (c) 15 mmol $\text{Al}(\text{NO}_3)_3$ + 7.5 mmol Cu_2O , (d) 1 mmol $\text{Al}(\text{NO}_3)_3$ + 1 mmol CuO nanoparticles.

also shows that CH_2O_2 plays an important role on the formation of crystalline AlOOH in the presence of some NaOH , via increasing the stability of this compound under hydrothermal conditions employed. Similar runs with different amounts of NaOH and formic acid were also performed however the results which are not given here yielded similar end products without CuAlO_2 formation.

Figure 1(b) shows XRD data for the products obtained from Cu_2O powders and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ after 60 h of hydrothermal reaction at 220 °C. As shown in Figure 1(b,a), products with 10 g NaOH are only Cu_2O and CuO . This result indicates occurrence of a partial oxidation reaction yielding CuO . It is believed that the observed oxidation stems from the presence of the nitrate in the Al -source which acts as an oxidizer [24]. In case of 6 g NaOH addition, oxidation to CuO could still be observed but with decreased amount of CuO formation, Figure 1(b, b). Similarly, Figure 1(c) shows XRD data for the products obtained from Cu_2O powders and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ via teflon pouch method. The X-ray pattern with 2.8 g of NaOH addition reveals the formation of CuO . This is consistent with the X-ray results obtained above from runs 4 and 5, Figure 1(c, a). There are still intense peaks belonging to Cu_2O in the pattern after 48 h of hydrothermal reaction at

220 °C, indicating only partial oxidation reaction and transformation to CuO . With lower NaOH concentrations, the same phase distribution was observed, but in this case, the intensity of CuO peaks are significantly lower as seen in Figure 1(c, b). In addition, there are peaks belonging to AlOOH , which demonstrates the higher tendency of boehmite precipitation at lower NaOH concentrations.

For runs 8-11, chemically precipitated CuO nanoparticles were used as copper source in the solution as mentioned above in the experimental section. XRD data and SEM image of the as-precipitated CuO nanoparticles are given in Figures 2(a) and 2(b), respectively. The XRD pattern in Figure 2(a) identifies that the product is monoclinic CuO (JCPDS 48-1548, Tenorite). The SEM image given in Figure 2(b) suggests formation of CuO particles in nanometer sizes with equiaxed morphology. Sizes of the nanoparticles as measured by SEM indicate a narrow distribution changing from 10 to 40 nm diameter. These nanoparticles were subjected to hydrothermal synthesis in the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as aluminum metal source. NaOH and CH_2O_2 amounts were changed as given in Table 1. Figure 1(d,a) refers to an XRD pattern of sample without NaOH and CH_2O_2 . According to XRD analysis, without NaOH and CH_2O_2 , CuO was partially reduced to Cu_2O and Al -precipitates as AlOOH . When only CH_2O_2 was used, almost all CuO reduced to

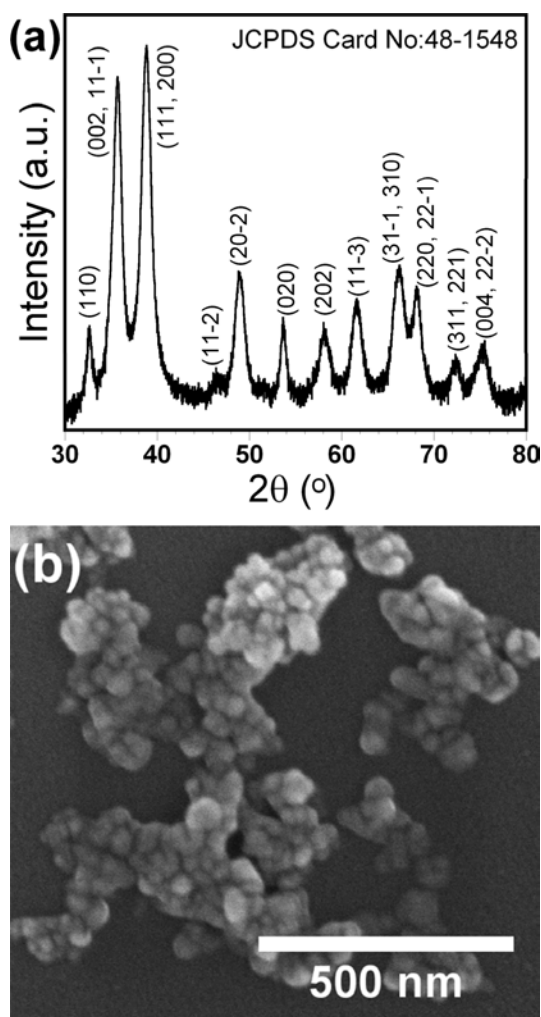


Fig. 2. (a) XRD pattern and (b) SEM image of chemically precipitated CuO nanoparticles.

metallic Cu.

Figures 1(d,c) and 1(d,d) represents the effect of reaction time on the final phase distribution of the product. The diffractogramme after 24 h of reaction at 215 °C, covers phases of CuO, Cu₂O, Cu and AlOOH, Figure 1(d,c). When the reaction time was increased further to 48 h, a very similar phase distribution was observed. This result shows that the reduction and oxidation reactions were almost completed within the first 24 h. After this stage stable precipitates of the aforementioned species formed, which probably inhibits the formation and precipitation of the desired CuAlO₂ phase.

Solid-state reaction

Bulk CuAlO₂ pellets were produced via conventional solid state reaction by using commercially available Cu₂O and Al₂O₃ powders. Figures 3(a) and 3(b) shows X-ray diffraction data of these pellets after sintering. Figure 3(a) represents the phase distribution in the sample after 24 h of milling, 2 h calcination at 800 °C and 24 h sintering at 1200 °C. The circles on the

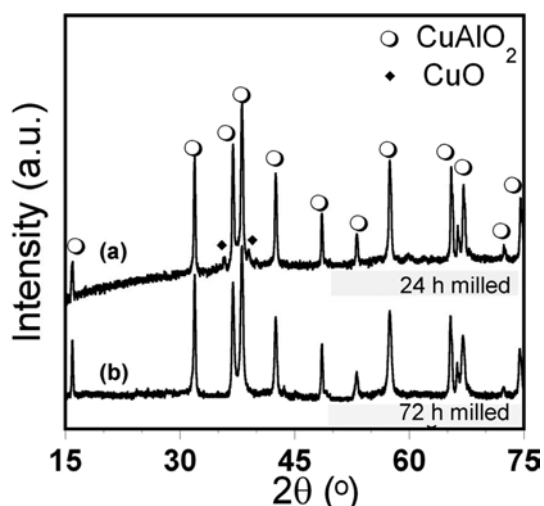


Fig. 3. XRD patterns of sintered bulk CuAlO₂ pellets (a) 24 h ball-milled, 800 °C calcined, 1200 °C sintered, (b) ball-milled and calcined for 3 times followed by 1200 °C sintering. Note that CuO phase still exists in (a).

pattern refer to CuAlO₂ peaks (JCPDS card no: 75-2356). On the other hand, there are still small peaks belonging to CuO appears in the pattern, indicating the formation of CuO as a secondary phase. Formation of such side phases is a common problem also reported in literature during the production of CuAlO₂ via solid state reaction route [16, 33]. Secondary phases are generally not desired in p-type TCOs due to their low electrical conductivity which yields a decreased conductivity of the final product [34]. In a recent study, bypassing of calcination step showed to be an effective way on the elimination of these side phases [17]. In the current work, the secondary phase (i.e., CuO) was eliminated by repeating the milling and calcination steps for 3 times. Once the sample was milled and calcined at 800 °C for 2 h, it was crushed and milled again and then calcined at 800 °C. This process repeated once more prior to final sintering at 1200 °C. The X-ray data belonging to this sample is given in Figure 3(a). All peaks on the pattern are well matched with single phase CuAlO₂. No peaks related to CuO compound are observed in the pattern implying the formation of single phase CuAlO₂. The discussion given above revealed the necessity of long processing time and high energy consumption to obtain phase pure CuAlO₂ via conventional solid state method. In addition, contamination of the sample during milling and high temperature sintering have to be taken into consideration for this approach.

Electrospinning process

CuAlO₂ nanofibers were prepared by electrospinning of an aqueous solution containing metal sources and PVP. Figure 4(a) shows X-ray data of sintered CuAlO₂ nanofibrous mat at 1100 °C for 5 h. All the diffraction peaks can be indexed as CuAlO₂ in hexagonal

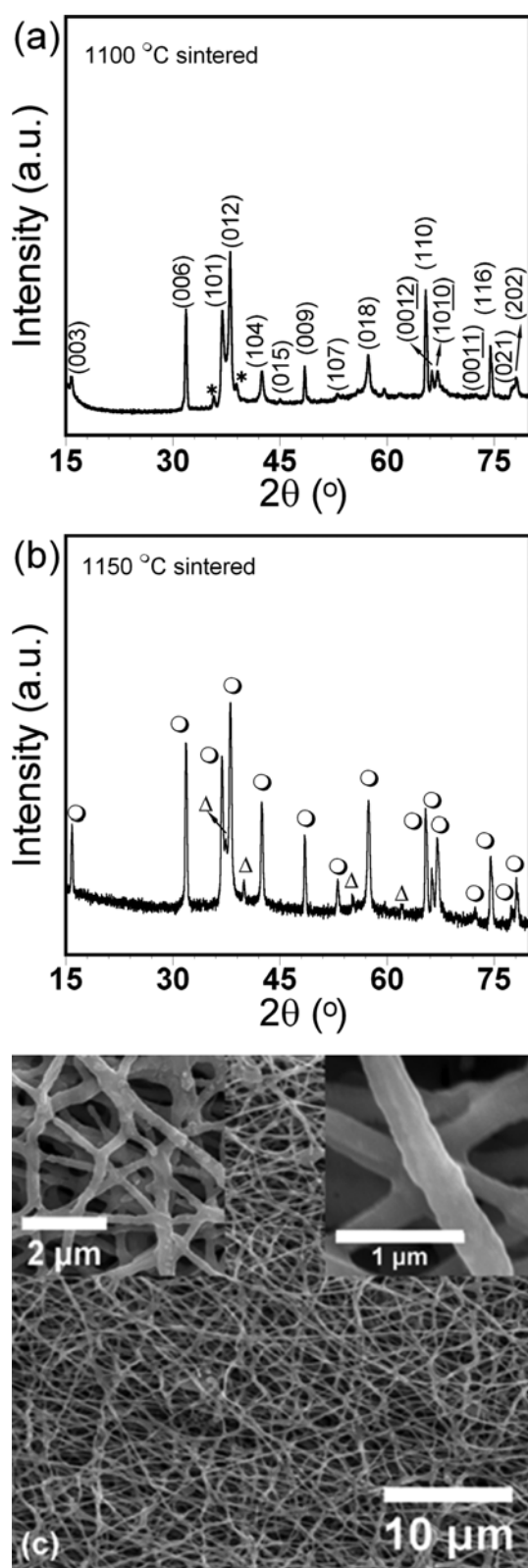


Fig. 4. XRD patterns (a) sintered 5 h at 1100 °C and (b) sintered 10 h at 1150 °C, (c) SEM image of sintered CuAlO_2 nanofibrous mats. Star denotes CuO, open circle and triangle both denote CuAlO_2 (see text for details). The inset images for (c) reveal the morphology of fibers at higher magnifications.

symmetry (JCPDS card no: 75-2356) except for very small 2 peaks marked with (*) which belongs to the

CuO phase located at $2\theta = 35.5^\circ$ and 38.8° . To eliminate the retained CuO phase samples were sintered at 1150 °C for 10 h. The XRD pattern of a representative sample is given in Figure 4(b). The peaks marked with open circle belongs to CuAlO_2 (JCPDS card no: 75-2356). In addition, 4 more peaks located at $2\theta = 37.3^\circ$, 39.9° , 55.1° and 62.0° can be observed on this pattern. These peaks corresponds to the diffraction of (101), (102), (105) and (106) planes of CuAlO_2 , also in hexagonal symmetry with c -axis equals to 11.293 Å (JCPDS card no: 75-1792). This symmetry is probably more stable at higher temperatures and sintering of the sample at 1150 °C caused an atomic rearrangement and formation of CuAlO_2 with a reduced c -axis. Zhoe et al. [24] mentioned in their study that the sintered fibers showing a preferred orientation and diffraction of (003), (006), (009) and (0012) planes exhibited stronger intensity than that of the (101) and (102) planes, which were similar to the CuAlO_2 films deposited on the sapphire surface. On the contrary, in our study sintering of the sample both at 1100 and 1150 °C yielded diffraction of (012) plane with the highest intensity, which was similar to the bulk CuAlO_2 sample obtained via solid state sintering. This difference may be emerged due to employing different kind of materials and template polymer in our and their study. Figure 4(c) presents SEM micrograph of CuAlO_2 nanofibers after sintering. The inset images reveals the morphology of the fibers at higher magnifications. As can be seen from the images, the electrospinning process leads to formation of a fabric like highly porous mesh structure with interconnected fibers at various lengths. The integrity of the nanofibers is preserved after sintering. The surface of the nanofibers are rather smooth. It is well known that, ceramic nanofibres obtained by electrospinning generally consist of tiny crystallites attached randomly to each other [35]. These crystallites are generally too small to observe with SEM. On the other hand, a smooth surface with lack of porosity, such as in the inset at Figure 4(c), observed at high magnifications may imply a well packed high density structure. SEM examination of sintered nanofibres also showed a size distribution in terms of individual fiber diameter between 150-300 nm.

Conclusions

In this study, 3 different production routes were applied to obtain phase pure CuAlO_2 . The methods employed were hydrothermal synthesis, conventional solid state sintering and electrospinning. Detailed X-ray diffraction studies of final products have shown that;

1-Under the experimental conditions employed in this work, hydrothermal treatment of various precursors did not yield any CuAlO_2 product. This result indicates that

the successful formation of CuAlO_2 under hydrothermal conditions strictly depends on the type of starting materials, pH of the solution and the temperature range applied. Considering the literature and the results obtained from this study, if temperatures around 200°C will be used for reaction, oxide precursors have to be used and reactive species for the formation of CuAlO_2 have to be preserved in the solution during the heating stage. On the other hand, using commercial salts as metal precursors, the reaction temperature has to be much higher, at least equals to the critical point of the liquid phase used in the hydrothermal treatment. These results in total revealed the need of specific ionic species in the solution within a narrow temperature-composition-pH window to obtain phase pure CuAlO_2 employing hydrothermal conditions.

2- CuAlO_2 bulk samples can be produced successfully from relatively cheap oxide powders via traditional solid state sintering, and the method can easily be adapted to mass production. On the other hand, long mixing/grinding and repeated calcination steps prior to final high temperature sintering are necessary to prevent the formation of side phases. This necessity may lead to the contamination of the sample and a significant increase in the production costs.

3-Electrospinning of an aqueous solution containing the metal precursors and PVP yielded the successful formation of a composite structure in the form of nanofibrous mat. Polycrystalline nanofibers (diameter of $\sim 150\text{-}300\text{ nm}$) as confirmed by XRD were formed after sintering of the calcined samples in air at 1150°C for 10 h. SEM revealed that the sintered fibers were continuous with smooth surfaces. The highest temperature and duration of sintering are lower when compared to the temperature and time for the formation of phase pure CuAlO_2 via solid state reaction. The study suggests that polyvinylpyrrolidone could be used as a template polymer for electrospinning of CuAlO_2 as it would yield well structured nanofibers. We also have shown that using of different metal precursors and template polymer in electrospinning process may result in the formation of CuAlO_2 with different symmetry.

Based on the current work, we have shown that solid state sintering and electrospinning methods can be used to obtain phase pure CuAlO_2 ceramics with high reproducibility. These approaches can be applied to produce bulk/mesh as well as powder form of the material, which may be useful for gas sensing or catalyst applications. We are currently studying on the optimization of production parameters of other delafossite oxides by electrospinning to examine their electrical and optical properties in more detail for variety of applications.

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