Sol-gel and Hydrothermal Synthesis of Metal Oxides Precursors for CuMO$_2$ (M = trivalent metal) type Delafossite Oxides

A Project Report Submitted to Indian Institute of Technology Hyderabad

In Partial Fulfillment of the Requirements for

The Degree of Master of Science

By

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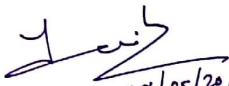
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May 2018

Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of Dr. *Tk. Prakash*

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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Approval Sheet

This thesis entitled as "Sol-gel and Hydrothermal Synthesis of Metal Oxides Precursors for $CuMO_2$ (M = trivalent metal) type Delafossite Oxides" is approved for the degree of Master of Science.

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Abstract

The ternary p-type transparent conducting oxides $CuMO_2$ (M = trivalent metals) with delafossite type structures are essential for a variety of applications such as liquid crystal displays, touch screens, gas sensors, thermoelectric devices, solar cells, dilute magnetic semiconductors, light-emitting diodes, etc., In this work, we have attempted to synthesize four ternary delafossite oxides namely $CuFeO_2$, $CuInO_2$, $CuScO_2$, and $CuYO_2$ using a low cost and relatively lower temperature method. The precursors for all these four compounds were synthesized via the sol-gel method. The powder X-ray diffraction technique was used for the phase identification. The $CuFeO_2$ and $CuScO_2$ phases were obtained by annealing of the precursors obtained by the sol-gel method in the air. However, other secondary phases were also observed along with the target phases, $CuFeO_2$ and $CuScO_2$. The $CuInO_2$ and $CuYO_2$ phases could not be stabilized using our reaction conditions. The Hydrothermal method has also been used for the synthesis of $CuInO_2$ and $CuYO_2$, but only mixed binary oxides were formed.

INTRODUCTION

The CuFeO$_2$ phase was the first delafossite type oxide discovered by Charles Friedel in 1873 but was named after French mineralogist Gabriel Delafosse who solved the crystal structure of this compound [1]. Since then a series of the similar type of ternary oxides (with general formula CuMO_2, where M being +3 cations) were synthesized with delafossite type structure [2].

(a)   (b)
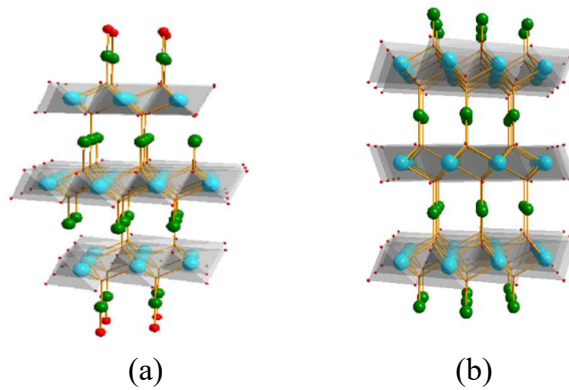
Fig 1: Structures of 3R(a) and 2H(b) forms of CuMO_2 type delafossites with the c axis vertical.

The crystal structures of these CuMO_2 oxides show an alternative layered structure where Cu atoms are situated between the edge-sharing MO_6 octahedral layers forming O-Cu-O pillars (Fig1). This octahedral layer of MO_6 can be stacked in two different ways. For ABABAB type stacking the form is known as a 3R or rhombohedral, and if the stacking is ABCABC type, then it is known as a 2H or hexagonal.

The CuMO_2 delafossite structures can be stabilized with a variety of M^{3+} cations such as Al^{3+}, In^{3+}, Sc^{3+}, and Mn$^{3+,}$ etc. [3-6]. In this study, we have focused on the synthesis of Fe, In, Sc, and Y containing CuMO_2 compounds. It has been suggested that covalent Cu-O bonds in these structures give rise to a valence band (VB) favorable for good p-type conductivity. In CuMO_2 delafossites,

the O-Cu-O linkages are very weak, and the Cu-Cu interactions are also considered as a very weak bonding interaction. No such bonding is expected from the formal $d^{10}s^0$ electronic configuration of Cu^{+1}. However, the *d-s* hybridization that occurs due to the two-fold linear coordination of copper to oxygen results in the transfer of some electron density from the $3d$ shell to the $4s$ shell [7]. As a result, there is some weak bonding between the Cu atoms. Hence, these compounds show anisotropic conductivity. Also, the presence of these Cu-Cu interactions provides a pathway for the holes to move [7].

The CuMO$_2$ delafossites have direct and indirect band gaps in the range of 1-2 eV and 3.3-4.3 eV, respectively [8-9]. The band theory of solids suggests that the band gap of materials must be above 3.1 eV to be optically transparent in the visible region. Owing to this large band gap CuMO$_2$ delafossites are about 60-80% transparent while being conducting at the same time [10]. Due to these properties, the CuMO$_2$ delafossites are considered as transparent conducting oxides (TCO's). Hence, these materials have a variety of applications such as liquid crystal displays, touch screens, gas sensors, thermoelectric devices, solar cells, dilute magnetic semiconductors, light-emitting diodes, etc. [11-12].

In recent years Cu based delafossites have attracted a lot of attention due to their excellent optical, electronic, and multiferroic properties. As a result, various methods for the synthesis of these compounds have been explored and reported in the literature. The conventional solid state method and the metathesis synthetic pathways are not preferred for the synthesis of these phases due to the need for very high-temperature heat treatment, and often pure phase synthesis is not possible using these methods. Other reported synthetic methods are all related to the laser deposition methods in a vacuum or an inert atmosphere [13-15]. These types of techniques require

very demanding experimental setup and hence unfavorable for commercial synthesis on a large scale.

The goal of this project is to develop a low cost and relatively lower temperature demanding method which can be applied to synthesize delafossite phase materials in significant amount. To achieve this goal, we have explored the sol-gel method where metal reagents are chosen according to the final product requirements. In a typical sol-gel method [16-18], the stoichiometric amounts of reactants are dissolved in water followed by the formation of an organic gel framework by the use of citric acid and ethylene glycol. This process itself makes the metal components get mixed homogeneously. The resulting gel is then heated in air to obtain a fine powder precursor that is further heat treated at the desired temperature and atmosphere to obtain the final product. The precursors obtained via this method are having the smaller particle size and high reactivity. Hence, in the final step lesser vigorous conditions are needed for good yield. Thin films and nanostructures of the solid state compounds could also be synthesized using these precursors.

The efficacy of the hydrothermal method is also investigated for the synthesis of delafossite oxides. This method utilizes water under high pressure and at temperatures above its standard boiling point as a means of speeding up the reactions between solids. The water is used as a solvent as well as for pressure transmitting medium. This method is particularly useful for the synthesis of phases which are unstable at the higher temperature. Most of the $CuMO_2$ type delafossites are found to be unstable above 1100°C. Thus, this process was used for the synthesis of delafossite phases which are unreported. This technique is also useful for the single crystal growth and to control the particle size and morphology.

EXPERIMENTAL DETAILS

1.Sol-Gel Method of synthesis

Chemicals: The following reagents were used for the synthesis via the sol-gel process: $Cu(NO_3)_2.3H_2O$ (98%, AVRA), $Fe(NO_3)_3.9H_2O$ (98%, SRL), $In(NO_3)_3.xH_2O$ (99.9%, SRL), $Sc(NO_3)_3.xH_2O$(99.9%, Kemphasol), $Y(NO_3)_3.6H_2O$ (99.9%, SRL), Ethylene Glycol (98%, AVRA), Citric Acid (99%, SRL), 250ml evaporating dish.

(a)Synthesis of CuFeO₂:

The following reagents were used for the synthesis: $Cu(NO_3)_2.3H_2O$, $Fe(NO_3)_3.9H_2O$, Ethylene Glycol, and Citric Acid. The amount of water in the Cu and Fe source were first determined using the thermogravimetric studies (Fig 2).

In a 250 mL evaporating dish, a stoichiometric amount of $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ (8×10^{-3} M of each reagent) were dissolved in the deionized water. The citric acid (30gms) and 3ml of ethylene glycol were added to the resulting solution. The clear solution was then stirred on a magnetic stirrer for overnight at room temperature (RT). This solution was stirred at 50°C for one day. A blue colored Cu-Fe precursor gel was formed. The temperature was then
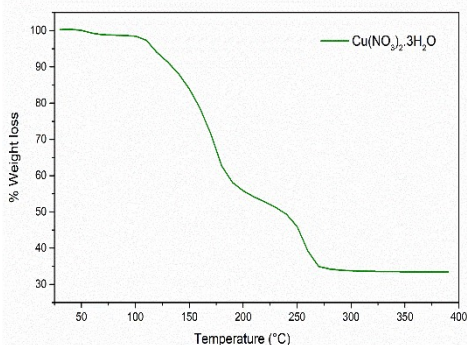
**Fig 2:** TGA graph of $Cu(NO_3)_3.3H_2O$

8

slowly increased by 5°C in every 2 hours to make sure that all the NO_2 and H_2O molecules are out of the system. At 150°C, a viscous brown colored sticky product was formed. This condensed gel was burned at 600°C for 6 hours in air to get rid of all the organic materials. The brown colored ash like the product was obtained that was finely ground and compacted into 3mm pellets under 2 tons of pressure. These pellets were then heated at 1150°C for 4h in the air to synthesize polycrystalline $CuFeO_2$.
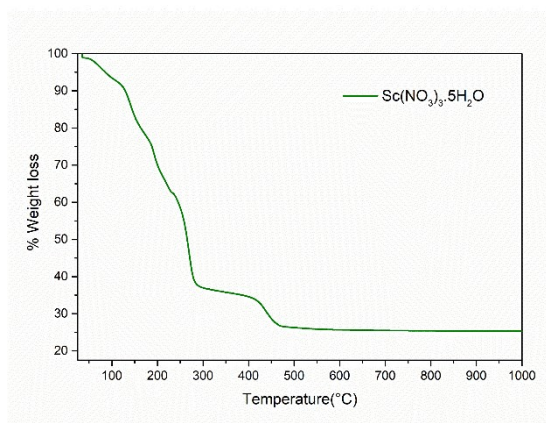
(b)Synthesis of CuInO₂:

For the sol-gel preparation of this material previously mentioned method was used. Commercially available $In(NO_3)_3 \cdot xH_2O$ was subjected to thermal analysis. This process shows 30% mass loss (Fig 3) before 200°C which corresponds to a loss of 3 water molecules. The $Cu(NO_3)_2 \cdot 3H_2O$ and $In(NO_3)_3 \cdot 3H_2O$ were taken in a 1:1 ratio. Black colored Cu-In oxide precursor powder was prepared in the same way mentioned earlier. The resulting powder was annealed at 900°C, 1000°C , and 1150°C for 18 h in the air.
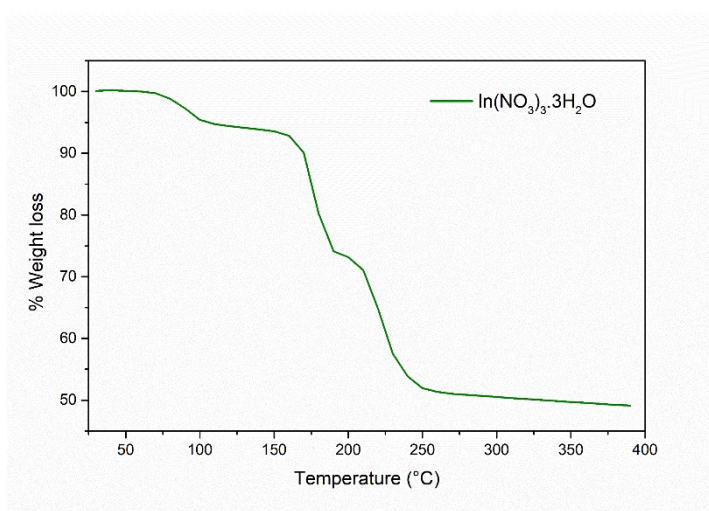
Fig 3: TGA graph of $In(NO_3)_3 \cdot xH_2O$

(c)Synthesis of CuScO₂:

Commercially available $Sc(NO_3)_3.xH_2O$ loses 75% of its mass on thermal analysis (Fig 4) which accounts for five water molecules considering the decomposition of $Sc(NO_3)_3$ [27]. In a 100 mL evaporating dish, $Cu(NO_3)_2.3H_2O$ and $Sc(NO_3)_3.5H_2O$ were taken in 1:1 ratio (1.55×10^{-3} M of each) and then 3gm of citric acid and 0.3ml of ethylene glycol were added in deionized water. By following the similar method black colored Cu-Sc oxide precursor powder is obtained. By annealing a small amount of this precursor at 1100°C for 24 h in the air, a mixed powder was obtained. This powder was again annealed at 1100°C for 24 h in the air.


Fig 4: TGA graph of $Sc(NO_3)_3.xH_2O$

(d)Synthesis of CuYO₂:

For the preparation of Cu-Y precursor similar method is that was described earlier. Commercially available $Y(NO_3)_3.6H_2O$ and $Cu(NO_3)_2.3H_2O$ were used. The thermal gravimetric analysis of $Y(NO_3)_3.6H_2O$ shows a loss of 71% of its mass on heating (Fig 5). This accounts for six water molecules and loss of nitrates [26]. The gel produced black colored precursor on burning at 600°C

in the air. This black colored powder was made into compacted pellets under pressure for further reactions.
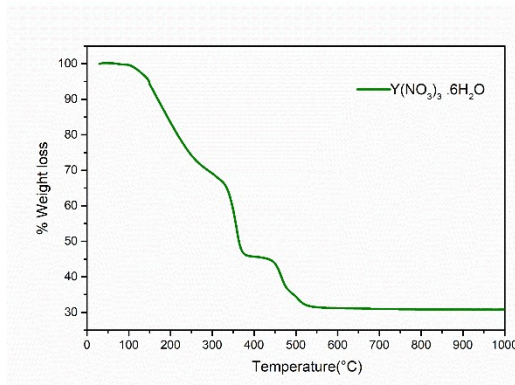
Fig 5: TGA graph of $Y(NO_3)_3.6H_2O$

2.Solid State Synthesis

The starting materials: $Cu(NO_3)_2.3H_2O$ and $In(NO_3)_3.3H_2O$ were weighed in a 1:1 (1 mM of each) molar ratio, mixed, and ground in a mortar & pestle for 15 mins. This mixture was then annealed at 1100°C for 24h in the air. A green colored powder was obtained which was characterized by the powder X-ray diffraction (PXRD) technique.

3.Hydrothermal Synthesis

(a)Low-temperature synthesis of CuInO₂

A stoichiometric mixture of $Cu(NO_3)_2.3H_2O$ and $In(NO_3)_3.3H_2O$ in a molar ratio of 1:1 (1.2 mM of each) was added in a 50ml Teflon vessel. Subsequently, 7.5 ml of deionized water, 7.5 ml of absolute ethanol, 3.75 ml of ethylene glycol and 75 mg of PEG was added to the vessel. Then 11 mL of 0.5M KOH solution was added drop by drop to maintain the pH of the solution at 8. The autoclave was kept at 190°C for 60 h. A mixture of ethanol and water was used as a solvent in

hydrothermal synthesis. As ethanol has lower (22.39 mN/m) surface tension than water (77.82 mN/m), the addition of ethanol decreases the surface tension of solvent which could help to increase the reaction kinetics and avoid agglomeration of particles. The resulting products were washed with aqueous ammonia and dilute nitric acid followed by washing with water. Finally, a grey colored powder was collected after drying at 70°C for 4 h.

(b)Low-temperature synthesis of CuYO$_2$

Copper nitrate and Yttrium nitrate was taken in 1:1 ratio and dissolved in deionized water inside a 50 mL Teflon vessel. A small amount of ethanol (5 mL) was added to it. Then 5 mL of ethylene glycol was introduced into the solution as a reducing agent.Solution pH was adjusted to 5 by drop by drop addition of 0.5 M KOH solution. A Benchmeter calibrated pH meter was used for the pH measurement. The reaction was kept at 210°C for 48 h. The final product was washed with absolute ethanol and then with Deionized water. The Reddish white colored product was collected after drying at 70°C for 4 h. A second reaction was kept under the similar conditions, with the solution pH fixed at 6.5. The resulting product obtained after washing and drying were greenish in color.

Characterizations

(a)Powder X-ray diffraction (PXRD): An X-ray diffraction pattern is a set of peaks each of different intensity and position (d-spacing or Bragg angle, θ). For a given sample the peak positions are constant, but intensities do vary with instrument sample quality, etc. All the resulting products were initially characterized by PXRD to determine the phase(s) present in the obtained samples by using a Pananalytical X'pertPro diffractometer with K$_\alpha$ radiation (λ=1.5418 Å)

operated at 40kV and 30mA with a scan rate of 0.1°/sec within the range of 10° to 70° at room temperature. The patterns obtained were plotted using software OriginPro 9.0. Phase identification was made by using Match.3 [28]

(b)TGA: Thermal Gravimetric Analysis is a technique for measuring the change in weight of a substance as a function of temperature and time. The sample usually tiny amount is heated at a constant rate of increasing heat until it decomposes. At that temperature, a weight plateau is observed. From this thermal analysis, compositional properties can be calculated. This temperature plateau can vary according to heating rate and atmosphere. TGA studies for all the commercially available reagents were done using a PerkinElmer instrument (Model-SDT Q600 V 20.9 Build 20) within the range of room temperature to 800°C using the scan rate of 10°C/min in the N_2 flow of 20.00 ml/min.

RESULTS & DISCUSSION

CuFeO₂

The PXRD studies show that mostly CuO, α-hematite and spinel phase $CuFe_2O_4$ are present in the sample (gel) annealed at 600°C for 6 h in the air (Fig 6). Subsequent heat treatment of this precursor at 1150°C for 4 h in the air results in the formation of delafossite phase $CuFeO_2$ as a major phase. Other Cu and Fe based materials were also present as minor phases. $CuFeO_2$ has a rhombohedral crystal
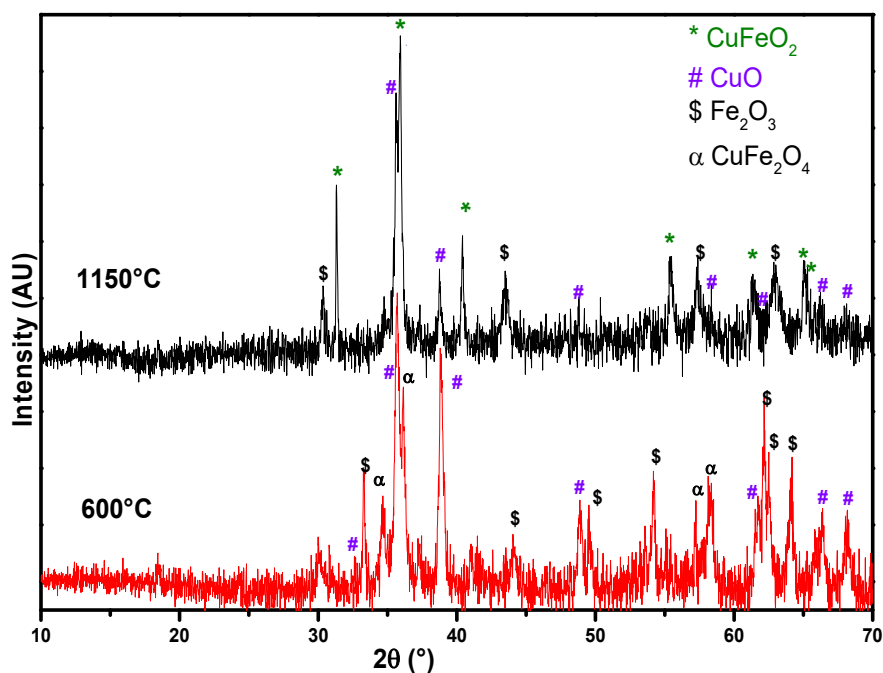

Fig 6: The PXRD patterns for Cu-Fe precursor and prepared mixed phase $CuFeO_2$

structure. The compound adopts the **R-3m** space group with cell parameters of a = 5.96 Å & α = 29.430°. In case of the sample heated at 600°C, Cu(II)oxide was found (Figure 6). As the

temperature is increased above 1100°C, Cu(II) gets reduced into Cu(I). Some of the copper oxide and iron oxide do not react due to which mixed phases were found.

CuInO₂

Fig 7 shows the presence of CuO and In_2O_3 in the sample obtained after firing sol-gel mixture at 600°C for 6 h in the air. This sample was further heated at 900°C & 1000°C in the air for 18 h, resulting in the formation of green colored $Cu_2In_2O_5$ as can be seen from the PXRD pattern.
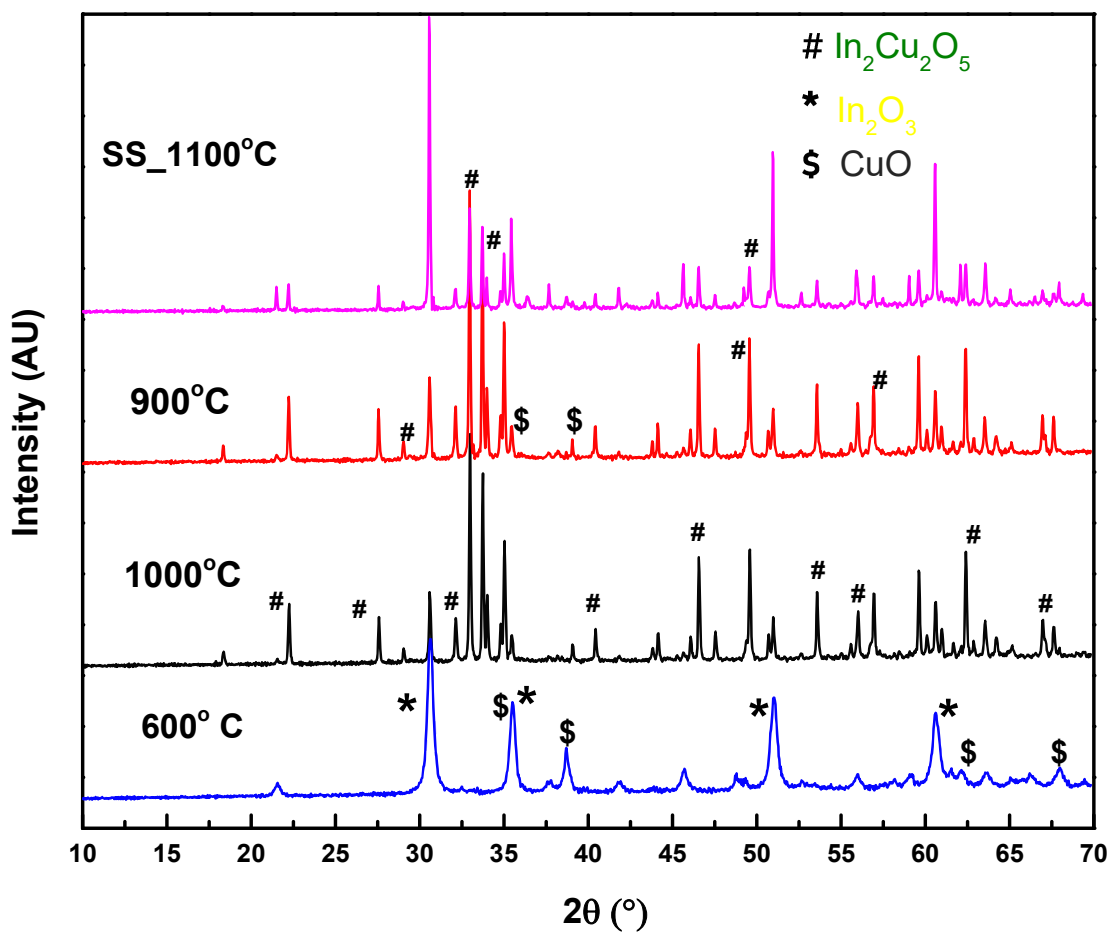
Fig 7: The PXRD patterns of Cu-In precursor, and resulting samples after different heat treatment; The Uppermost pattern was obtained for the result of solid-state synthesis.

The sample obtained by the solid-state method by heating the reactants at 1100°C for 24 h in the air also yielded the same green colored phase $Cu_2In_2O_5$. The primary phase in the product obtained by the solid state method is In_2O_3, but in case of sol-gel, the major phase was $Cu_2In_2O_5$ with a small amount of CuO & In_2O_3 phases. $Cu_2In_2O_5$ if heated at above 1100°C in the air resulted in the decomposition of the material to CuO and In_2O_3, this observation suggests that the $Cu_2In_2O_5$ phase is not stable at the high temperature. Hence, $CuInO_2$ phase could not be obtained by the solid-state method by heating in the air.

CuScO₂
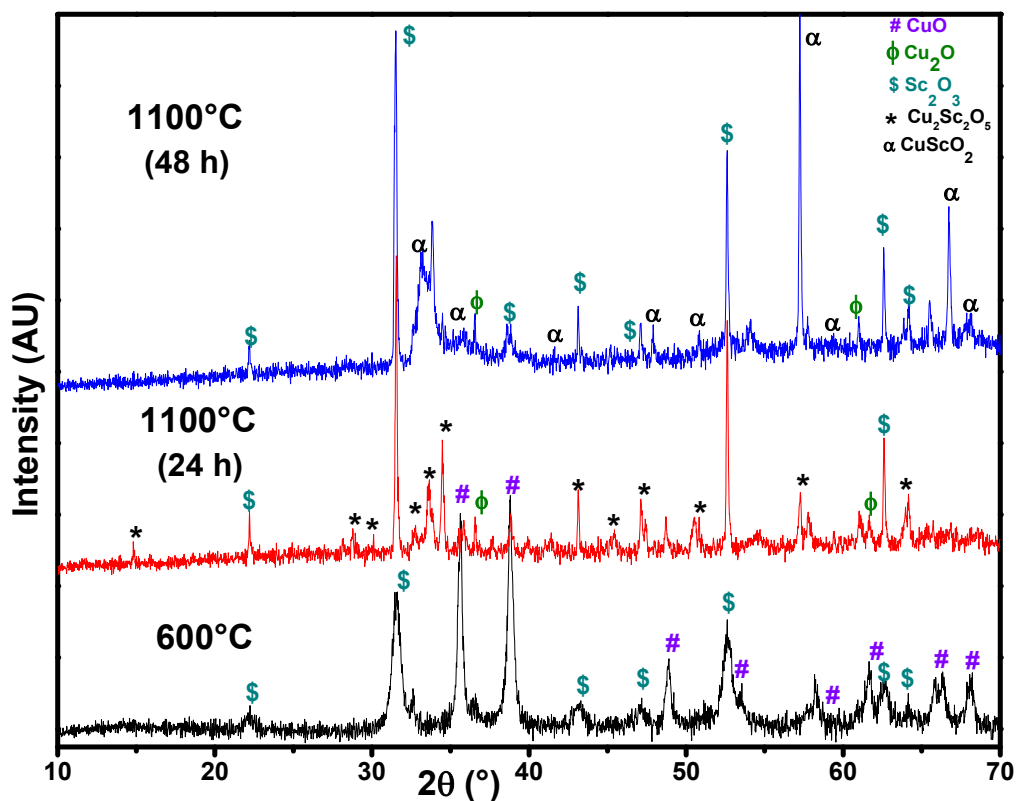
Fig 8: The PXRD patterns of as synthesized precursor by a sol-gel method, Cu₂Sc₂O₅ phase & mixed layer phase containing CuScO₂.

The PXRD studies primarily show CuO and Sc_2O_3 phases in the precursor formed at 600°C for 6 h in the air (Fig 8). Annealing this precursor further at 1100°C in the air for 24 h gives $Cu_2Sc_2O_5$ as a major phase with unreacted Cu_2O and Sc_2O_3 phases. At 1100°C, the Cu(II) gets reduced to Cu(I), but $CuScO_2$ was not found in the partially green colored product. Reduction of $Cu_2Sc_2O_5$ at 1100°C in the air for another 24 h gives mixed layer delafossite phase. This mixed layer product was mainly dominated by the 2H type of structure. Samples prepared in the air were gray, presumably due to slight oxidation of Cu(I) to Cu(II) on cooling in the air.

To synthesize $CuScO_2$, the sample must be heated in the air above 1000°C because Cu(I) in this system oxidizes to Cu(II) at lower temperatures. However, the temperature was further increased to 1150 °C to avoid forming a mixed-layer phase. Complete decomposition of the delafossite structure occurred when heating was performed in the air at temperatures exceeding 1200 °C.

CuYO₂

The PXRD plot (Fig 9) shows that CuO and Y2O3 phases are present in the precursor formed at 600°C for 6 h in the air.
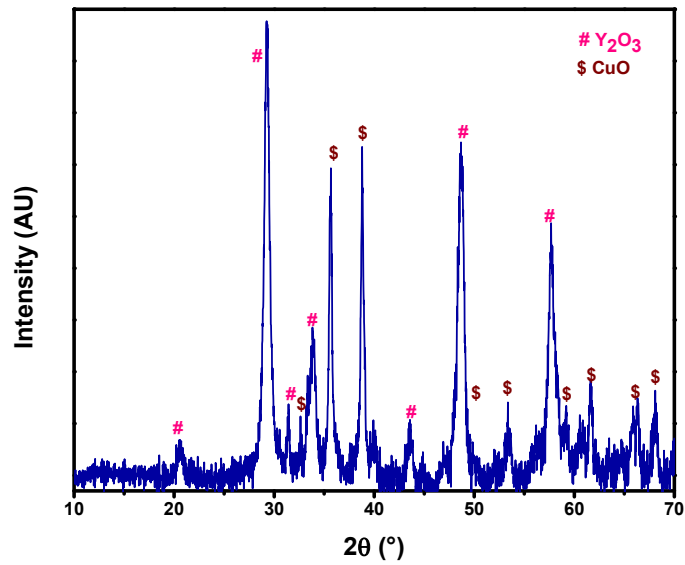

**Fig 9:** The PXRD pattern of Cu-Y precursor formed by using the sol-gel method

Hydrothermal Chemistry

The hydrothermal synthesis of complex metal oxides presents a challenge: the hydrolysis and oxidation state of two or more metal species must be controlled. Thus, it is difficult to find a universal set of synthetic conditions that can be applied to oxides even of the same family [19-20].

Consideration of Cu(I) hydrolysis. The Pourbaix diagram [21] for copper was referenced to approximate stable hydrothermal conditions for Cu(I) species. At room temperature, Cu(I) is not stable at any pH in aqueous solution, easily disproportioning into Cu (0) and Cu(II). However, at higher temperature Cu(I) is stable on a broader pH range and at 200°C, the primary species in solution will be Cu(I) (aq) when the pH < ~6.8. Above this pH, the stable Cu(OH) (aq) has low solubility (~1×10^{-3} to 1×10^{-4} mM) and readily precipitated as Cu_2O. The presence of soluble alcohols (ethylene glycol, ethanol,etc.), which act as reducing agents, also further stabilizes Cu(I).

Consideration of Y(III) & In(III) Hydrolysis

Yttrium in alkaline condition tends to form YOOH species which crystallizes very efficiently. Hence, the pH of the solution must be controlled to avoid the formation of YOOH [23]. The solubility of indium hydroxide in KOH solutions does not exceed 2×10^{-3} mole/liter [24]. Hence, the challenge for synthesis using the hydrothermal method lies in the fact that both copper and indium hydroxide are not simultaneously present in the solution.
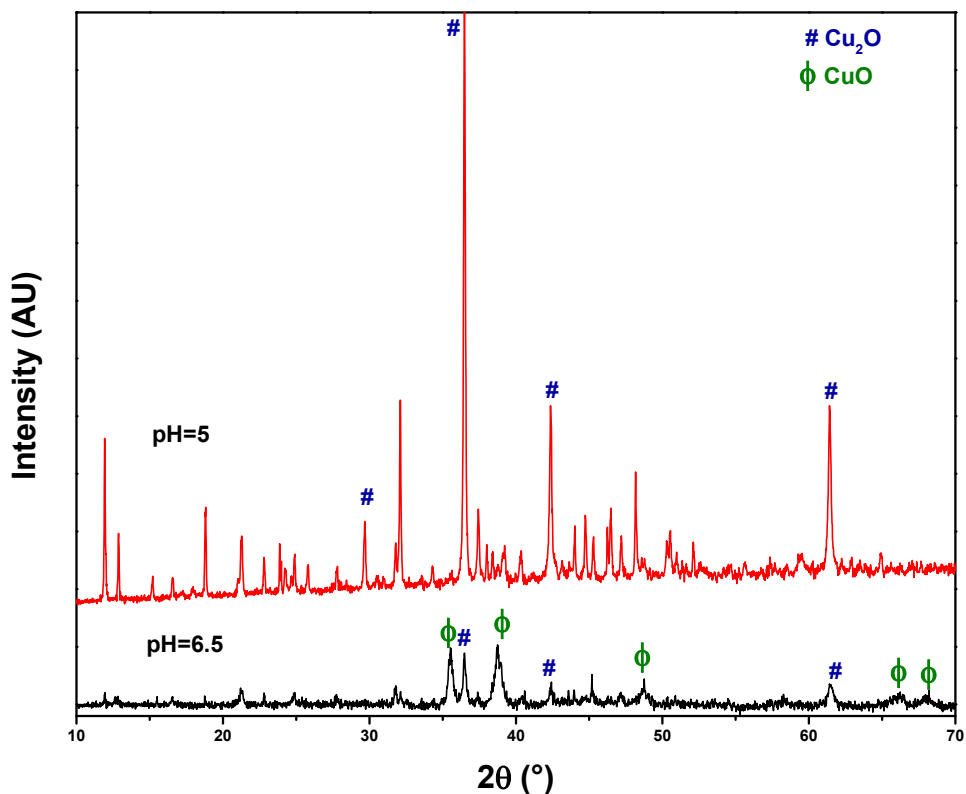
Fig 10: The PXRD pattern of resulting product obtained from hydrothermal synthesis at different pH condition

At pH=5, mixed phases (Fig 10) were obtained containing Cu_2O and a Y species. Upon hydrothermal heating under controlled pH condition Cu(II) reduces to Cu(I) and stabilizes. But, $Y(OH)_3$ is not stabilized in solution. Thus Cu(I) species can not react with $Y(OH)_3$ to form delafossite phase.

At pH=6.5(Fig 10), CuO is a primary phase, which supports the theoretical information that the Cu(I) is not stable at a higher pH. The green color is observed due to the formation of $Cu_2Y_2O_5$. Again due to the absence of Cu(I) species delafossite phase does not form.
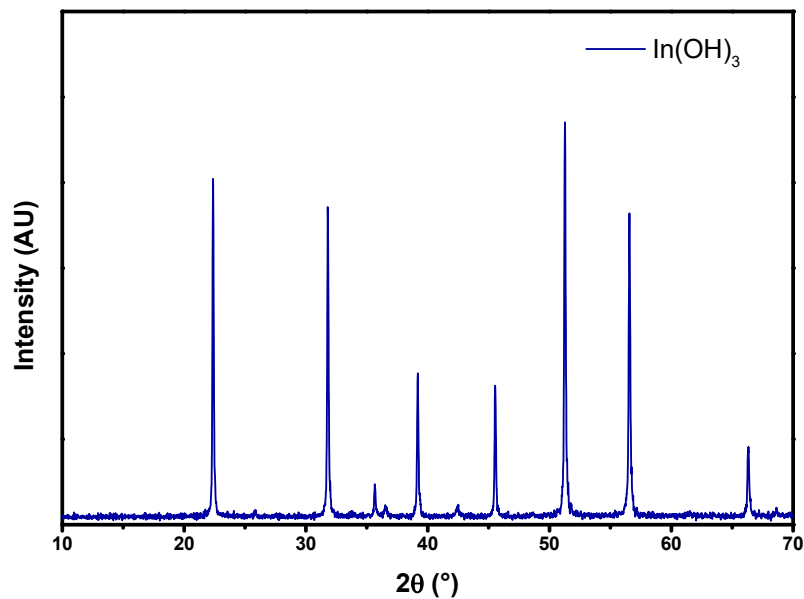
Fig 11: PXRD pattern of the product obtained from hydrothermal synthesis at alkaline pH condition of the Cu-In system

At pH=8, Cu(I) species is not stable. And as the solubility of $In(OH)_3$ is very low in alkaline condition, these two species do not react to form delafossite phase $CuInO_2$.

After washing the sample with dilute ammonia (dissolved all the unreacted copper), only $In(OH)_3$ phase was observed in the PXRD pattern (Fig 11).

CONCLUSIONS

In the present study, we attempted to find out low cost and scalable synthesis of pure phase delafossite oxides. The oxide precursors for $CuFeO_2$, $CuInO_2$, $CuScO_2$, and $CuYO_2$ were prepared by the sol-gel method. Our method was successful for the synthesis of $CuFeO_2$ and $2H\text{-}CuScO_2$ along with small amount of secondary phases. However, the $CuYO_2$ and $CuInO_2$ phases could not be synthesized by heating the precursors in the air atmosphere.

The Hydrothermal method for the synthesis of these delafossite oxides at low temperature was also explored. Unfortunately, a suitable pH condition for the reaction could not be found. As a result, only binary oxides were obtained.

Future work

To obtain the single-phase delafossite oxides, the reaction condition will be optimized in the future. The heat treatment of the precursors will be carried out under the controlled partial pressure of O_2 using a suitable oxygen buffer/getter. The hydrothermal synthesis will also be optimized by tuning the pH of the solution.

References:

(1) 1839: Gabriel Delafosse et Alfred Des, Cloizeaux. Institut de minéralogie et de physique des milieus condensés, 19 March 2009.

(2)Meagen, A.; .Marquardt, N.; Ashmore, A.;Cann, D.P. *Thin Solid Films*, **2006**, *496*, 146-156.

(3) Yao, Y.; Xie, G.; Song, N.; Yu, X.; Li, R. *Advanced Materials Research*, **2012**, *399*, 2241-2244.

(4) Godinho, K. G.; Morgan, B. J.; Allen, J. P.; Scanlon, D. O.; Watson, G. W. *Journal of Physics: Condensed Matter*, *23,* **2011**, 334201.

(5) J Li et al. *solid state sciences,* **2004,** *6*, 831-839.

(6) Zhang, Q.; Xiong, D. *Journal of Materials Science: Materials in Electronics*, **2015**, 1-5.

(7) Rogers, D. B.; Shannon, R. D.; Prewitt, C. T.; Gillson, J. L.; *Inorg. Chem.* **1971**, *10*, 723.

(8) Gillen, R.; Robertson, J. *Physical Review B: Condensed Matter and Materials Physics*, **2011**, *84*, 035125.

(9) Kawazoe, H.; Yasukawa, M.; Hyodo, H.; *Nature,* **1997**, *389*, 939–942.

(10) Ueda, K.;Hase, T.; Yanagi, H.; *J. Appl. Phys,* 2011, **89**, 1790– 1793.

(11) Yu, M. Y.; Natu, G.; Ji, Z.Q.; Wu, Y. Y.; *J. Phys. Chem. Lett*. **2012**, *3* 1074–1078.

(12) Zheng, S. Y.; Jiang, G. R.; Su, J. R.; *Mater. Lett,* **2006**, *60*, 3871–3873

(13)) Singh, M.; Singh, V.N.; Mehta, B.R. *J. Nanosci. Nanotechnol.* **2008**, *8*, 3889-3894.

(14) Chuai, Y.H.; Shen, Hong-Z.; L.; Ya-D.; Hu, B. *RSC Advances*, **2015**, *5*, 49301-49307.

(15) Younsi, M.; Manaa, S. *Energy Procedia*, **2013**, *36*, 638-641.

(16) Danks, A. E.; Hall, S.R.; Schnepp, Z.; *Mater. Horiz*., **2016**, *3*, 91—112.

(17) Pechini, M. P.; *US Patent, 3330697A*, **1967.**

(18) Avnir, D.; Coradin, T.; Lev, O.; Livage, J.; *J. Mater. Chem*.,**2006**, *16*, 1013–1030.

(19) Yu, M.; Draskovic, T. I.; Wu, Y. **2014**, *Inorg. Chem,* **2014**, *53*, 5845-5851.

(20) Shahriari, D. Y.; Barnabe, A.; Mason, T. O.; Poeppelmeier, K. R. *Inorg. Chem.* **2001**, *40,* 5734−5735.

(21) Beverskog, B.; Puigdomenech, I. *J. Electrochem. Soc.* **1997,** *144*, 3476−3483.

(22) Jedidi, A.; Rasul, S.; Masih, D.; Cavallo, L.; Takanabe, K. *J. Mater. Chem. A,* **2015**, *3*, 19085-19092.

(23) Tsukada, T.; Venigalla, S.; Morrone, A.; Adair, J. *J. Am. Ceram. Soc.,* **1999,** *82,* 1169–74

(24) White, S.J.O.; Hemond, H.F. *Critical Reviews in Environmental Science and Technology*, **2012**, *42*, 155-186.

(26) Melnikov, P.; Nascimento, V.; Consolo, Z. Z. Silva, F. A. *J. Therm Anal Calorim*, **2012**, *3,* 2236.

(27) Melnikov, P.; Nascimento, V.; Consolo, Z. Z.; Silva, F. A. *J. Therm Anal Calorim*, **2014**, *7,4272.*

(28) Prof. Dr. G. Bergerhoff Software-Entwicklung and CRYSTAL IMPACT K. Brandenburg & M. Berndt GbR.

(29) Yanagi, H.; Hase, T.; Ibuki, s.; Ueda, K.; Hosono, H.; *Appl.Phys. Lett*., **2001**, **78**, 1583.

(30) Huda et al.; *PHYSICAL REVIEW B*., **2009**, *80,* 035205.