Synthesis of Single Crystalline Delafossite CuCrO$_2$ by sol-gel growth

Satish Bolloju, R. Srinivasan*

Department of Chemistry, BITS-Pilani Hyderabad campus, Jawahar Nagar Village, Shameerpet Mandal, Hyderabad-500 078, India.

*Corres.author: rsvasan@hyderabad.bits-pilani.ac.in

Abstract: Delafossite CuCrO$_2$ having layered crystal structure composed of CrO$_6$ octahedra and CuO$_2$ linear units is an important delafossite oxide studied extensively by physicists and chemists. Black shiny CuCrO$_2$ crystals were obtained by calcining the precursor at 1200 °C for four hours in air. From X-ray powder diffraction studies, all the reflections could be indexed to the delafossite-type structure CuCrO$_2$ (space group: R-3m (166); JCPDS # 89-0539). The unit-cell parameters were found to be $a = b = 2.972$ Å, $c = 17.065$ Å. The high intensity (006) reflection indicated that the crystal growth is along the c-axis. The direct band gap was found to be 2.9 eV from the solid UV-Vis diffuse reflectance spectra measurements.

Keywords: Sol-Gel, Delafossite, CuCrO$_2$, Powder XRD, Layered, Oxides.

Introduction and Experimental:

Delafossite Cu’Cr$^{3+}$O$_2$ is a p-type semiconductor oxide with stable structure and possess interesting technological applications such as catalyst [1], photocatalyst [2], sensors [3], transparent p-type conducting oxides [4], and opto-electronic materials [5]. Delafossite CuCrO$_2$ crystallizes in a layered structure comprising of alternate layers of CrO$_6$ octahedra and CuO$_2$ linear units. It is studied in different forms like powder [1-2], single crystal [6], and thin film [7] by physicists and chemists. Sol-gel synthesis is one of the most useful techniques to grow single crystals. In this work, the sol–gel synthesis and its characterization by powder XRD, Scanning Electron Microscopy, FT-IR and Diffuse Reflectance Spectroscopy are presented.

Stoichiometric amount of 1:1 Cu(NO$_3$)$_2$.3H$_2$O and K$_2$Cr$_2$O$_7$ were dissolved in the distilled water and stirred well for proper mixing. Two equivalents of citric acid was added into that solution while stirring. Similar to the sol-gel procedure followed for citric acid–nitrate route [8], the mixed solution was placed in a hot water bath to evaporate the water content. But there was no clear transparent gel formation in this case, but only a paste-like formation was observed. Up on drying in a lab oven, a powder precursor was obtained. This precursor was calcined in an alumina crucible at 1200 °C for four hours in air to obtain the black shiny CuCrO$_2$ crystals. The temperature was slowly ramped up at 5 °C per minute to reach 1200 °C and allowed to dwell for four hours before cooling down to room temperature by itself. XRD data was carried out with a PANalytical XPERT-PRO Diffractometer (Cu Anode, $\lambda = 1.54060$ Å) operating at 40 kV and 30 mA. Data was collected in the 2-theta range of 10-80° by scanning every 0.05° for 10.16 s. Diffuse reflectance measurements were performed using 60 mm Integrating sphere attachment in Jasco V-650 spectrophotometer ($\lambda = 200$ to 870 nm).
From the observed reflectance (R), the Kubelka–Munk function \( \frac{\alpha}{S} = \frac{(1 - R)^2}{2R} \) was derived and plotted versus energy in eV \([(\text{wavelength in nm}) \times (\text{energy E in eV}) = 1239.9]\) to determine the band gap.

**Results and Discussion:**

Black shiny crystals were obtained when the precursor was heated for four hours at 1200 °C. X-ray powder measurement was done for the crushed crystals. All the reflections could be indexed to the delafossite type structure CuCrO\(_2\) (space group: R-3m (166); JCPDS card no. 89-0539) as shown in the Figure 1. The powder pattern was devoid of any side phase such as spinel CuCr\(_2\)O\(_4\) and contains delafossite phase as the product. The powder pattern was indexed in hexagonal setting and the lattice parameters, \(a = b = 2.972 \text{ Å}, c = 17.065 \text{ Å}\) are in perfect agreement with those previously reported. Optical images taken using confocal microscope indicated the plate-like crystal formation. SEM images recorded for the crystalline sample are shown in the Figure 2. The layered arrangement and plate-like formation are illustrative from the SEM images.

![X-ray powder diffraction pattern of Delafossite CuCrO\(_2\)](image1)

**Figure 1. X-ray powder diffraction pattern of Delafossite CuCrO\(_2\)**

![SEM images of Delafossite CuCrO\(_2\)](image2)

**Figure 2. SEM images of Delafossite CuCrO\(_2\)**

From diffuse reflectance measurement, the obtained Kubelka - Munk transformed absorption \(\frac{\alpha}{S}\) was plotted versus energy in eV and the band gap was then determined using a standard method in which the absorption edges were extrapolated to zero. The direct band gap was found to be 2.9 eV as shown in the Figure 3. FT-IR spectra measured for the pellets showed characteristic peaks around 721 and 552 cm\(^{-1}\) corresponding to CrO\(_6\) octahedral stretching modes.

![UV-Vis diffuse reflectance spectra of Delafossite CuCrO\(_2\)](image3)

**Figure 3. UV-Vis diffuse reflectance spectra of Delafossite CuCrO\(_2\)**
Conclusion:

Black shiny crystals of CuCrO\(_2\) were obtained by sol-gel growth. SEM images exhibited the layered structure of delafossite CuCrO\(_2\). The direct band gap was found to be 2.9 eV. Further experiments are going on to crystallize Mg doped CuCrO\(_2\). Also it would be interesting to study the conducting properties of the doped and undoped crystalline materials.

Acknowledgements:

The authors acknowledge the financial support by Department of Science and Technology, Government of India. HCU, Alagappa University and Karunya University for characterization studies.

References: