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Synthesis of Single Crystalline Delafossite $CuCrO_2$ by sol-gel growth

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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 $Cu(NO_3)_2.3H_2O$ and $K_2Cr_2O_7$ 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 ºC for four hours in air to obtain the black shiny $CuCrO_2$ crystals. The temperature was slowly ramped up at 5 ºC per minute to reach 1200 ºC 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, λ = 1.54060 Å) operating at 40 kV and 30 mA. Data was collected in the 2-theta range of 10-80^0 by scanning every 0.05^0 for 10.16 s. Diffuse reflectance measurements were performed using 60 mm Integrating sphere attachment in Jasco V-650 spectrophotometer (λ – 200 to 870 nm).

From the observed reflectance (R), the Kubelka–Munk function ($\alpha/S = ((1 - R)^2/(2R))$ was derived and plotted versus energy in eV [(wavelength in nm) X (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 ^{0}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 $CuCr_2O_4$ and contains delafossite phase as the product. The powder pattern was indexed in hexagonal setting and the lattice parameters, a = b = 2.972 Å, c = 17.065 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.

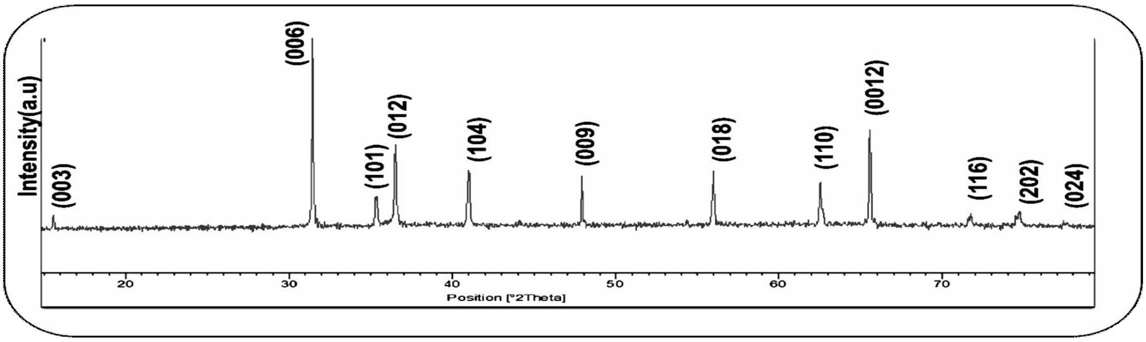

Figure 1. X-ray powder diffraction pattern of Delafossite $CuCrO_2$

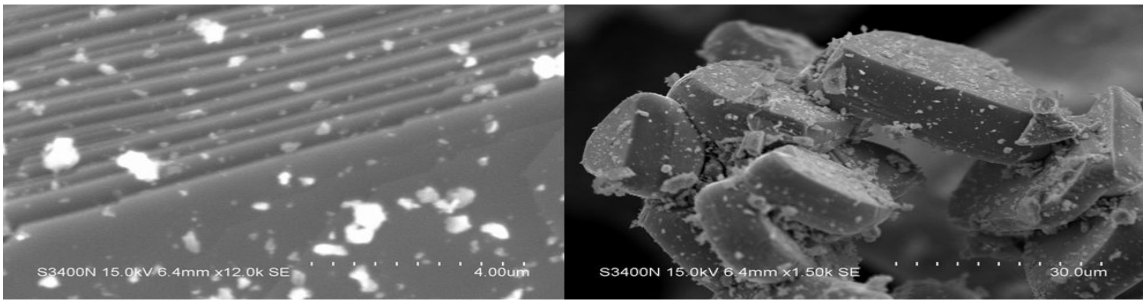

Figure 2. SEM images of Delafossite $CuCrO_2$

From diffuse reflectance measurement, the obtained Kubelka - Munk transformed absorption (α/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.

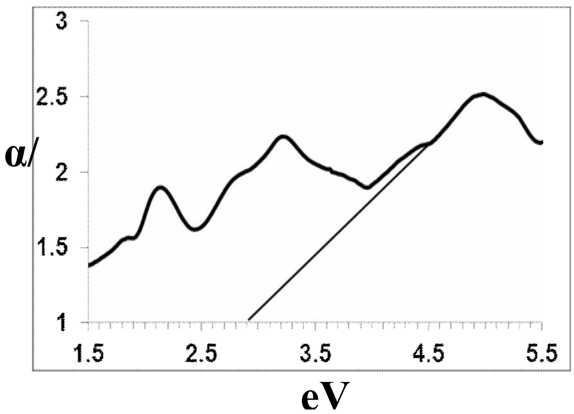

Figure 3. UV-Vis diffuse reflectance spectra of Delafossite $CuCrO_2$

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.

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