

Photoelectrochemical studies on newly synthesized quaternary oxide of Ca-Mo-Cu-O.

P.M. Randiwe

Department of Chemistry
Kavikulguru Institute of Technology and Science, Ramtek
Dist -Nagpur-441106,India

ABSTRACT: A new quaternary oxide, $\text{Ca}_2\text{MoCu}_3\text{O}_8$, has been synthesized using solid state reaction between corresponding oxides and characterized by chemical analysis, X-ray diffraction, electrical conductivity. It crystallizes in a tetragonal structure with a lattice parameter $a_0 = 10.624 \text{ \AA}$ and $c_0 = 6.208 \text{ \AA}$. It is an n-type semiconductor and conducts current via different mechanism in two temperature ranges. A break is found in the plot of $\text{Log } \sigma$ vs $1/T$ at 391 k when activation energy changes from 0.269 to 1.366 eV.

The photoelectrochemical properties are reported. The material in the form of Hydrogen annealed pellet was used as photoanode in electrochemical photovoltaic (ECPV) cell. The Flat band potential was located at -0.42V.

PEC cell parameters such as Conversion Efficiency(η) and Fill Factor have been determined as 0.157% and 0.267 respectively.

Keywords: Synthesis, chemical analysis, X-ray diffraction; Electrical conductivity and Photoelectrochemical (PEC) study.

1.Introduction:

Present investigation was carried out to evaluate the performance of quaternary oxide semiconducting materials for their photo electrochemical (PEC) behavior in electrochemical photovoltaic (ECPV) cell. The development of ECPV cells has been hindered by relatively low conversion efficiency and poor stability offered by the oxides semiconducting materials.

Molybdates of Copper, Nickel and Manganese reported earlier in our laboratory by Kichambare and Kharat [1-3] showed poor solar to electrical conversion efficiency but remarkable stability found when used as photoanode in ECPV cell.

An exhaustive survey of the literature on quaternary oxides indicates that the compound $\text{Ca}_2\text{MoCu}_3\text{O}_8$, have not been synthesized before. Hence, in this paper we present the synthesis and characterization of quaternary oxide and its application as photoanode in PEC cell.

2. Experimental:

2.1. Preparation and identification

$\text{Ca}_2\text{MoCu}_3\text{O}_8$ was prepared by use of the constituent oxides (Economos 1955) by intimately mixing the AR grade oxides CaCO_3 , MoO_3 and CuO in the molar ratio 2: 1: 3 in acetone. The mixture was pressed into pellets 0.012 m in diameter in a hydraulic press at 2 ton/ In^2 using 5% polyvinyl acetate as a binder. The pellets were first slowly heated up to 300°C for about 3 h to evaporate the binder and finally fired in air at 800 and 950°C for 20 and 55 h respectively in an electric furnace [4]. They were then furnace cooled at a rate of 1°C/min. The formation of this compound was ascertained by taking powder diffraction patterns using a Phillips diffractometer model P.W. 1700 with $\text{CuK}\alpha$ radiation. The formation of the compound was taken to be completed when the reacting materials in unreacted form and more than one modification of the compound were not present, indicating the existence of essentially a single phase. The XRD patterns of the compounds were indexed using standard indexing procedures.

2.2. Fabrication of PEC cell

The compound thus prepared was used in the pellets form for the fabrication of PEC cell. The surface of the electrode was mechanically polished and the silver paste was applied on one of the surface of the pellet and fired at 50 c for 1 h to dry the silver paste. The ohmic contact between the copper wire and silver coated was made and the surface was covered with epoxy. The electrode thus formed acted as Photo anode.

The platinum electrode was fabricated by welding a platinum wire to platinum plate (1x 1cm). Three-electrode PEC cell was designed using quaternary oxides as photoanode, the metal as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode with $\text{Ce}^{+4/+3}$ redox couple was prepared from solution of Cerric (iv) ammonium sulfate and Cerium(iii) sulfate. The light source was a 150w tungsten halogen lamp (10 mWcm^{-2} intensity). The light source was illuminated through a quartz plate specially provided on the cell container. The PEC cell arrangement and subsequent measurement were made using procedures described elsewhere [5].

3. Results and discussion

3.1. Chemical analysis

The possible formal valences of the constituent atoms in the compound are $\text{Ca}_2^{3+}\text{Mo}^{6+}\text{Cu}_3^{2+}\text{O}_8$. The chemical composition of quaternary oxide was determined by estimating the metal contents using standard analytical procedure [4]. Decomposition of the material was carried out by fusion with sodium peroxide followed by double acid ($\text{H}_2\text{SO}_4 + \text{HCl}$) leaching.

Complexometric /EDTA titration method was used for the determination of Ca(II). Copper and molybdenum contents in the quaternary oxide was determined by atomic absorption spectroscopy (AAS) using a Perkin-Elmer instrument.

The percentage of Ca(II), Mo(VI) and Cu(II) were found to be 16.00 %, 18.99% and 39.38 % against 16.20%,19.39% and 38.53 %. There is thus good agreement between experimental and theoretical values.

3.2. X-ray diffraction

The d values for various planes and their relative intensities measured from the height of the peaks in the diffractogram as shown in Fig. 1, are given in Table 1. The compound is found to have a tetragonal structure with lattice parameter $a_0 = 10.624 \text{ \AA}$ and $c_0 = 6.208 \text{ \AA}$. The elemental analysis and XRD studies show that the valency of metallic ions does not change. However, more confirmation could be done using the XRF technique.

Table 1.
Results of X-ray diffraction study of $\text{Ca}_2\text{MoCu}_3\text{O}_8$

I/I_0	d_{obs}	d_{cal}	h k l	I/I_0	d_{obs}	d_{cal}	h k l
40.89	4.751	4.751	2 0 1	2.45	1.929	1.929	5 2 0
100	3.104	3.104	0 0 2	10.09	1.848	1.822	5 0 3
14.79	2.859	2.869	1 1 2	7.12	1.694	1.700	6 0 1
20.21	2.615	2.600	2 1 2	22.65	1.588	1.583	6 3 0
48.93	2.464	2.490	4 0 1	7.78	1.509	1.502	6 1 0
5.78	2.318	2.322	3 3 1	5.22	1.288	1.288	8 2 0
17.49	2.136	2.137	3 2 2	9.32	1.248	1.275	6 5 0

3.3. Electrical conductivity

Temperature dependence of the electrical conductivity is shown in Fig. 2. The variation of $\log \sigma$ against $1/T$ is linear showing that well known exponential law ($\sigma = \sigma_0 \exp(-E/KT)$) is obeyed in the temperature range covered. A break is found in the plot of $\log \sigma$ versus $1/T$ at 391°K when activation energy changes from 0.269 eV to 1.366 eV.

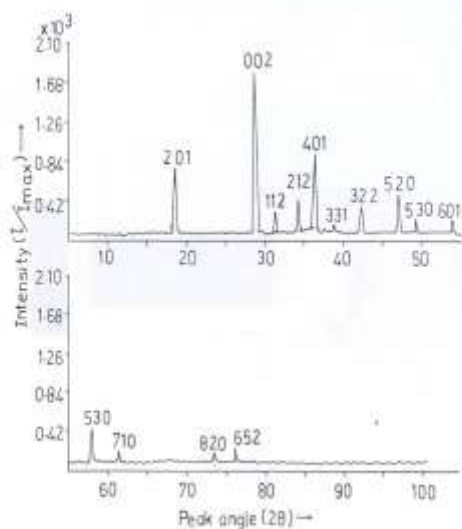


Fig.1.0 - X-ray diffraction pattern for $\text{Ca}_2\text{MoCu}_3\text{O}_8$.

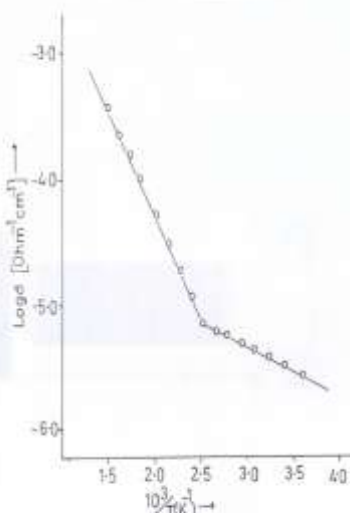


Fig.2.8 - Temperature dependence of the electrical conductivity.

Figure 1 X-Ray diffraction pattern

Figure 2. Temperature dependence of electrical conductivity

From Fig. 2 it is seen that the compound is semiconducting in nature and conducting the current via different mechanism in two temperature ranges. The low temperature conductivity can be attributed to an extrinsic type of conduction whereas conduction in the high temperature range may be regarded as an intrinsic type [6-7].

3.4 Diffuse reflectance spectra

Reflectance spectra are an efficient tool for the determination of band gap of semiconductor [8] and also to evaluate the absorption coefficient. The diffuse reflectance spectra were scanned between 200nm and 900nm using Varian DMS 80 UV-Visible spectrophotometer. It shows an intense absorption in the visible region. The band gap was calculated to be 1.536eV. The difference in the

values of band gap determined from diffuse reflectance spectra and electrical conductivity measurements are attributed to differential experimental conditions and the source of excitation of the electron.

3.5. Photoelectrochemical (PEC) studies

3.5.1 Sintering in hydrogen atmosphere.

The pellet of quaternary oxide showed high resistivity at room temperature. In order to obtain maximum photo response, the semiconductor electrode should have low resistivity [11]. Therefore, before utilizing the pellet of $\text{Ca}_2\text{MoCu}_3\text{O}_8$ as a photo anode in the PEC cell, its resistivity was lowered down to minimum practical value by sintering the pellet in hydrogen atmosphere. The optimum condition for temperature and duration of hydrogen sintering were decided by trial. Sintering at 320 C for 30 min gave the best possible results without any sign of decomposition and structural changes in the compound. These hydrogen -sintered pellets have been used for the study of PEC properties in ECPV cell.

3.5.2 Chemical stability and selection of redox couple:

Besides having a reasonable band gap, the photoelectron must be chemically stable in the electrolyte. The semiconductor sample, ie pellets of quaternary oxides were kept in 1M H_2SO_4 , 1M HCL and 1M KOH for period of 10 days and filtered solutions were analyzed using Atomic Absorption Spectroscopy (AAS) and Complexometric titration for metal ions. The resulting solution was found to be free from any metal ions confirming the stability of these quaternary oxides in H_2SO_4 , KOH and HCL. However, with higher concentrations the pellets showed sign of corrosion to varying degrees. So it was concluded that these electrodes could be used only in moderate acidic medium [9].

3.5.3 Effect of intensity illumination on short circuit current (Isc)

When the- semiconductor-electrolyte junction is illuminated with light having energy greater than the band gap of the semiconductor, electron-hole pairs are produced in the depletion region of the junction and charge separation takes place due to the local field present at the interface. When a counter electrode is immersed in the electrolyte and connected to the semiconductor, the photogenerated electron moves into the bulk of the semiconductor and through external circuit it reaches to counter electrode to reduce the oxidized species in the electrolyte[9,10] .

The Fig 3.0 shows that the photocurrent voltage curve shifts towards with the increasing light intensity. It is seen that the plot of short circuit current versus light intensity is linear up to a certain point after which it deviates from linearity. The nonlinear behavior of Isc demonstrates that the recombination of photogenerated carriers at the semiconductor electrolyte interface is limiting the rate of light intensities employed. The flattening of conduction and valance bands as a result of high illumination intensity will reduce the space charge layer field efficiency of charge carrier separation and thus reduce the Photocurrent. Hence it was decided to use 10- mWcm^2 light intensity for photo electrochemical(PEC) studies

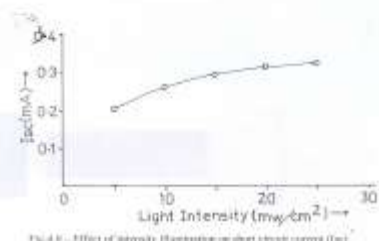


Fig. 3.0 - Effect of intensity illumination on short circuit current (Isc).

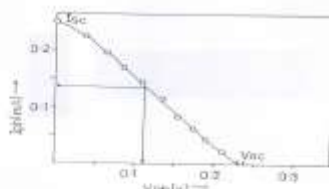


Fig. 4.0 - Current-voltage characteristics.

Figure 3. Effect of intensity illumination

Figure 4. Current-voltage characteristics

3.5.4 Power efficiency and Fill Factor

The maximum power efficiency and fill factor for the photoanode, $\text{Ca}_2\text{MoCu}_3\text{O}_8$ were calculated from the current-voltage (I-V) characteristics of the PEC cell (Fig 4.0). The photocurrent and photo voltage of the semiconductor electrode were measured at different biased potentials. The close circuit current (Isc) and open circuit voltage (Voc) of the PEC cell was found 0.390 mA and 0.519 V respectively. The maximum current (I max) and maximum voltage (V max) of the cell came out to be 0.396mA and 0.296V, respectively. Hence the fill Factor and power efficiency were calculated to be 0.267 and 0.157% respectively [11, 12, 13]

3.6 Conclusion:

It is concluded from the above studies that the solar to electrical conversion efficiency is quite low. The low value of power conversion efficiency is mainly attributed to i) high internal resistance of a cell ii) energy losses due to the photo induced redox reactions iii) optical losses due to absorption in the electrolyte, reflection from semiconductor surface etc iv) ohmic losses v) losses due to concentration polarization if the redox process is slow vi) surface recombination center on the electrolyte surface However attempts are being made to increase the conversion efficiency of $\text{Ca}_2\text{MoCu}_3\text{O}_8$ by using it in the form of the thin film or single crystal as photoanode in place of polycrystalline material.

Acknowledgements:

The author is grateful to the management, Kavikulguru Institute of Technology & Science, Ramtek, for permission and constant encouragement during the progress of this work.

References:

1. P.D.Kichambare & R.b.Kharat, J.Trans.SAEST 22(3) (1987) 89
2. P.D.Kichambare & R.b.Kharat, J.Solar Energy Mater 2(1991) 63.171-175
3. P.D.Kichambare & R.b.Kharat, J.SESI, 2 (1-2)(1988) 4
4. A. L Vogel' Text Book of Quantrtative Inorganic analysis, Third edition, ELBSand Longman, London, (1969)
5. R.I.Shuey, semiconducting Ore Minerals(Reinhold new York)1975
6. R.b.Yadao, J.phys.chem.Solid,(1983) 697 (44)
- 7 R.Bharati, R.Shankar & R.A.Singh, J.Pramana,(1980)449(49)
- 8.S.Joshi, D.laxminarayan, P.K.Garg & M.K.Agarwal, J.Indian J.Pure.Appl. Phys31 (1993) 651
9. G.kline, K.K.kam, R.Ziegler & B.A.Parkinson. solar Energy Mater, 37 (1982) 6
10. T.Sakata, T.kanvas & K.Tanimura, J.Ber.Bunsenge Phys Chem, 486(1979)83
11. M.A.butler & D.B.Gineley, J.Indian Chem. Soc.125(20(1978)228
12. P.D.Kichambare & R.b.Kharat, J.Solar Energy Mater 2(1988) 49
13. Yu.V.Pelskov, Solar Energy Conversion, A photoelectrochemical approach, springer, Berlin, (1990).

