

Studies on optical and electrical properties of synthesized polycrystalline CdMoO_4 and PbMoO_4

P K Pandey*, N S Bhawe & R B Kharat

Department of Chemistry, Nagpur University
Nagpur 440 033, India

Email: pandeykp2003@yahoo.co.uk

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Molybdates of Cd(II) and Pb(II) were synthesized by chemical route. The formation of CdMoO_4 and PbMoO_4 was confirmed by chemical analysis and powder X-ray diffraction (XRD) studies. Single-phase nature and purity of the molybdates was ascertained by matching their XRD data with the JCPDS data file. The powdered form of these molybdates was transformed into pellets under desired pressure using polyvinyl alcohol (PVA) as a binder. The polycrystalline pellets of these materials were then sintered at 900°C for 30 h. These molybdates in polycrystalline pellet form were characterized with respect to diffused reflectance studies, D.C. electrical conductivity and thermoelectric power measurements. The optical band gap values for CdMoO_4 and PbMoO_4 were calculated from their reflectance measurements and found to be 2.14 eV and 2.94 eV, respectively. The D.C. electrical conductivity for the pellets of these molybdates was studied over the temperature range 300-600 K. Plot of $\log(\sigma)$ vs. $(1/T)$ showed the semiconducting nature of these materials and clearly indicate a break corresponding to temperatures 408 K and 465 K, respectively, for CdMoO_4 and PbMoO_4 . The activation energies below and above this break temperature have been estimated as 1.84 eV and 4.00 eV for CdMoO_4 and 2.46 eV and 8.63 eV for PbMoO_4 .

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Cadmium molybdate (CdMoO_4) and lead molybdate (PbMoO_4) are interesting materials due to their chemical and structural properties¹⁻¹⁶. Chemical interest in mixed $\text{CdMo}_x\text{W}_{1-x}\text{O}_4$ crystals is due to their possible catalytic activity, which has been studied by Daturi and co-workers^{1,2}. For the values of x in the range of $1/8 < x < 1/4$, the catalytic activity increases. Generally, mixed metal molybdates are among the most active catalysts for olefin oxidation and ammoxidation, possessing key properties including optimum metal-oxygen bond strength and suitable solid-state redox complexes³⁻⁷. Lead molybdates are naturally occurring minerals which can also be made synthetically⁸ and which have very interesting luminescence properties⁹. PbMoO_4 single crystals

have important applications as acousto-optic modulators, deflectors and ionic conductors¹⁰⁻¹². Recently, PbMoO_4 has been demonstrated as an efficient low temperature scintillator for nuclear instrumental application¹³.

Structural interest in these materials is due to the fact that both CdMoO_4 and PbMoO_4 crystallize in scheelite type structure with space group $I4_1/a\bar{1}2$, which is number 88 in the International Tables¹⁴. Daturi and co-workers¹⁻² have reported crystal parameters of these molybdates. The structure has eight symmetry elements where each Mo site is surrounded by four equivalent oxygen sites in tetrahedral symmetry. Scheelite form of CdMoO_4 has an interesting property to transform into wolframite form under pressure¹⁵. Daturi and co-workers¹⁻² found that 50%-50% alloy takes scheelite structure while alloys with smaller Mo concentration have the wolframite form. Holzworth, *et al.*^{16,17} have studied the electronic band structures of these scheelite type materials with in the framework of density-functional theory. Optical dielectric function and reflectivity for these materials have also been reported.

Literature survey reveals that an extensive research has been carried out on the crystal growth and characterization of lead molybdate single crystals¹⁸⁻²¹ but only a few references² are available on cadmium molybdate crystal studies. Optical transmittance studies on lead molybdate single crystal have been carried out²¹ so far only to study its colouration properties. No report has been found so far on the optical and electrical characterization of the molybdates of Cd(II) and Pb(II) to determine their optical band gap and activation energies. Therefore, it was thought worthwhile to study the optical and electrical parameters of these molybdates as they have been reported as important electronic and catalytic materials. In the present investigation, CdMoO_4 and PbMoO_4 are synthesized through chemical route and their single-phase nature has been confirmed by X-Ray Diffraction (XRD) studies. These molybdates are then transformed into polycrystalline pellet form for optical and electrical studies. Finally, an attempt has been made to determine the optical band gap of these molybdates from their reflectance measurements. Electrical conductivity measurements have then been

used to determine their thermal activation energy. The dominant charge carriers in the molybdates of Cd(II) and Pb(II) have been determined by thermoelectric power (TEP) measurements within the temperature range 300-600 K.

Experimental

Molybdates of Cd(II) and Pb(II) were precipitated by the addition of hot ammonium molybdate solution to nitrates of metals at controlled pH (~ 10)¹⁸.



where, A= Cd and Pb

The white precipitate obtained was washed repeatedly with doubly distilled water and was filtered under vacuum. The powder obtained was dried in an oven at 135°C for 20 h.

An appropriate amount of the synthesized metal molybdate was taken and ground in an agate mortar using 5% aqueous solution of A.R. grade polyvinyl alcohol (PVA) as a binder²². Pellets of 1.2 cm diameter with flat parallel faces were prepared from the powder in a hydraulic press at the pressure of 2 tonnes/inch². The pellets were sintered at 900°C for 30 h by the standard technique²³.

Characterization techniques

The chemical composition of the molybdates of Pb(II) and Cd(II) was determined by estimating metal contents in them using complexometric/EDTA titration²⁴. XRD was recorded for phase identification using the Phillips PW-1710 X-ray diffractometer with CuK α line in 2 θ range 10-100°C. The X-Ray tube was operated at 35 kV, 20 mA with scanning speed 0.5 s per step. Optical diffused reflectance measurement was made with UV-Visible spectrophotometer (GBC Cintra 10e, Australia) in the wavelength range 350-800 nm using A.R. grade BaSO₄ as a reference material. The reflectance vs. wavelength so obtained was plotted graphically from which the optical band gap measurements were made. In order to determine the D.C. conductivity, a thin layer of silver paste was applied on the clean flat parallel faces of the pellets of these molybdates to provide good electrical contact²⁵. The D.C. conductivity of the pellets of the molybdates was determined in the temperature range 300-600 K in steps of 10 K by applying a steady potential difference of 2 V across the pellet. The BPL-India mega ohmmeter Model RM 160 mK-III A was used to

Table I—Analytical and other physical data of the compounds

Composition of molybdate	Percentage of metal		Optical band gap (eV)
	Found (%)	Calculated (%)	
CdMoO ₄	40.67	41.27	2.14
PbMoO ₄	56.44	56.61	2.94

measure D.C. conductivity of the molybdate pellets. The type of charge carrier was then determined by the hot probe thermoelectric power measurements.

Results and discussion

Chemical analysis and XRD powder pattern of the molybdates confirm the formation of single crystalline phase. The analytical data given in the Table I clearly indicate a good agreement between the theoretical and experimental values for the metal contents in the respective molybdates.

XRD study was carried out on the sintered molybdate powders of Pb(II) and Cd(II). The compounds were found to be polycrystalline and single phase in nature having scheelite type crystal structure. All the peaks in the diffraction pattern, as shown in Fig. 1a for PbMoO₄ and Fig. 1b for CdMoO₄, were indexed on the basis of JCPDS Data card^{26,27}. The observed 'd' values are in good agreement with the standard 'd' values. Both the compounds belong to the tetragonal crystal system with the lattice parameters; $a=b=5.17$ Å, $c=11.19$ Å, $\alpha=\beta=\gamma=90^\circ$ and volume=299.10 (Å)³. Therefore, above results confirm the complete formation of PbMoO₄ and CdMoO₄.

Optical studies

Optical reflectance measurements of both the sintered molybdates are shown in the Fig. 2 within the wavelength range 350-800 nm. The difference in the nature of the reflectance spectra of the two molecules can be explained on the basis of the band models of the molecules¹⁶. In the Pb materials, the corresponding 5 *d* states of Pb are filled, so that there is no appreciable *d*-like density in the valence and conduction band region. Although the 6 *s* states of Pb form a well-defined narrow band below the bottom of the valence band. There is some additional 6 *s* character of Pb throughout the valence band of PbMoO₄. There is also significant contribution of 6 *p* states of Pb throughout the conduction bands of these materials. Therefore, the sharp reflectance peak in PbMoO₄ is associated with 6 *s*→6 *p* transitions of Pb whereas the two main peaks in the reflectance spectra of CdMoO₄

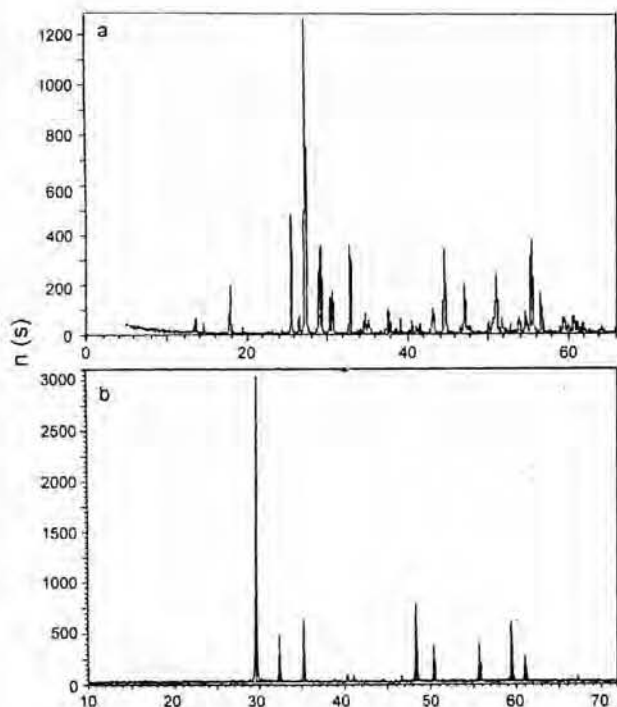


Fig. 1—Powder XRD plot of (a) polycrystalline lead molybdate and (b) polycrystalline cadmium molybdate.

Table 2—Activation energy measurements of the compounds

Type of molybdate	Activation energy (eV)		Temperature for change of slope (K)
	Intrinsic conduction	Extrinsic conduction	
CdMoO ₄	4.00	1.84	408
PbMoO ₄	8.63	2.46	465

are due to transitions between the O valence band and the crystal-field split 4 *d* conduction band^{16,17} of Mo. Some weak transitions from the 4 *d* states of Cd are also associated with CdMoO₄. The reflectance spectra were then used for the determination of optical band gap of both the molybdates²⁸⁻³⁰. The estimated values of the optical band gap energies are given in the Table 2. Both these molybdates are found to be wide band gap materials.

Electrical conductivity measurements

Figure 3 shows the variation of log (σ) with temperature for the polycrystalline pellets of PbMoO₄ and CdMoO₄. The nature of the plot indicates the semi-conducting behaviour of the material. The variation of log (σ), the conductivity with $1/T$ is linear (Fig. 3) in

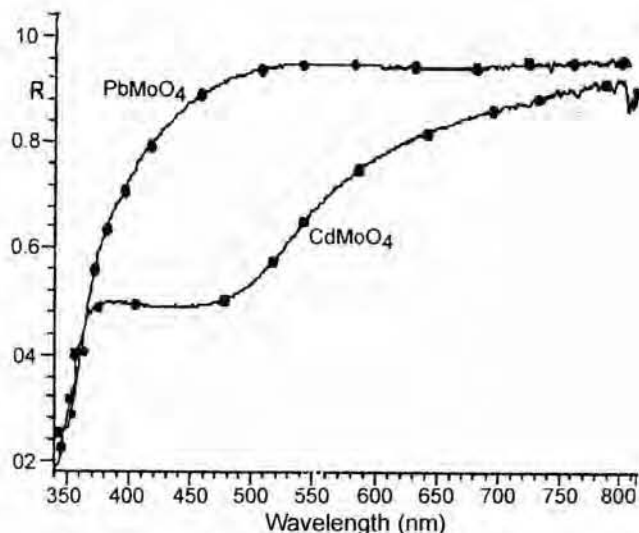


Fig. 2—Reflectance spectra of the molecules.

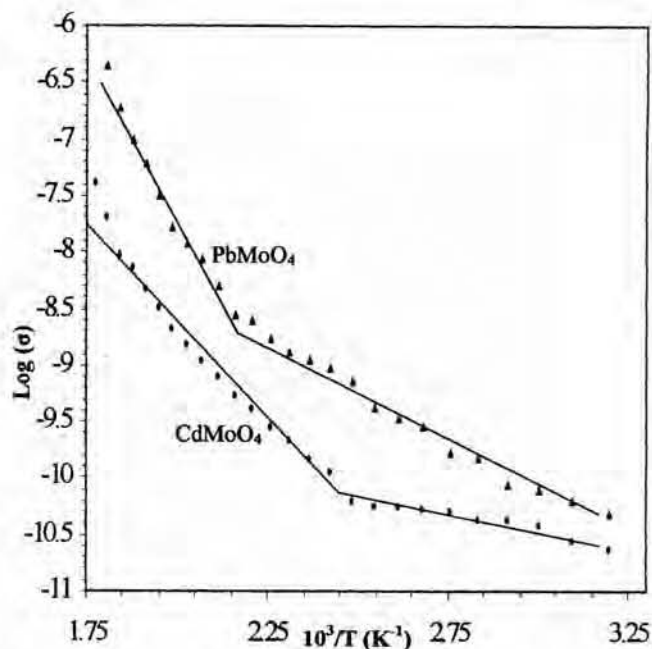


Fig. 3—Variation of D.C. electrical conductivity with temperature. two regions of temperature showing that the well known exponential law;

$$\sigma = \sigma_0 \exp (-E_a/kT)$$

where, the constants have their usual meaning, is obeyed in the two temperature ranges covered. The plot of log (σ) vs. $1/T$ gives straight lines whose slope is equal to $(-E_a/k)$.

A break is found in the plot of $\log(\sigma)$ vs. $1/T$ for both the materials. The activation energy and the temperatures for the change of slope for both the molybdates are given in Table 2. The difference in the values of optical band gap and activation energy, determined from the reflectance spectra and electrical conductivity measurements, respectively, for both the metal molybdates is attributed to different experimental condition and the source of electron excitation³¹.

The activation energy for conduction is found to be low in the low temperature region. This low temperature conductivity can be considered to be extrinsic (impurity dominated) whereas, conduction in the higher temperature range may be regarded as intrinsic³²⁻³⁴. One of the major reasons for extrinsic conductivity for these compounds may be due to the presence of other metal impurities. The mixed oxides prepared by this method may contain very small amounts of other metals since the constituent salts used for the synthesis were not of spec-pure grade. Even very small amounts of an impurity can drastically modify the electrical properties of a semiconductor. At higher temperature these atoms generally are ionized and do not show their effect³⁵. The change in conduction mechanism is indicated by change in the slope of the plot of $\log(\sigma)$ vs. $1/T$ and may depend on the hopping energy involved, structure of the compound and polaron formation. In the higher temperature region the conductivity is predominantly attributed to the O^{2-} : 2p band.

Thermoelectric power (TEP) measurements

TEP measurements for both the molybdate pellet samples were carried out using the two-probe method³⁶. The variation of thermo-emf developed across the two faces of each molybdate pellets with a change in temperature were obtained. Polarity of the thermo-voltage confirms an *n*-type semiconducting behaviour of the molybdates of Cd(II) and Pb(II). In general, the thermoelectric power depends upon carrier concentration, trap level and intergranular barrier height. In our case, the increase in TEP may be attributed to presence to M^{+2} ($M = \text{Cd}, \text{Pb}$) ions in the respective molybdates, which acts as an electron donor in these oxide materials.

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