



INFLUENCE OF Cs⁺ DOPING ON STRUCTURAL AND ELECTRICAL PROPERTIES OF HYDROTHERMALLY GROWN MOLYBDENUM HETEROPOLYOXOMETALATE

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Abstract:

In present investigation, thin films of molybdenum heteropolyoxometalate viz. undoped phosphomolybdic acid [H₃(PMo₁₂O₄₀)] and Cs⁺ doped phosphomolybdic acid [Cs₃(PMo₁₂O₄₀)] were deposited at optimum deposition conditions by hydrothermally growth process using aqueous solutions. Structural and electrical properties of undoped and Cs⁺ doped molybdenum heteropolyoxometalate thin films have been investigated. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were used to study the structural properties of the materials. Morphological study shows that, with Cs⁺ doping grain becomes spherical than undoped one. X-ray diffraction study revealed that, the material is polycrystalline in nature having simple cubic spinel structure. After doping Cs⁺ intensity of prominent peak (311) increases and other peaks are suppressed indicating intercalations of Cs⁺ in the octahedral lattice of phosphomolybdate anion without change in crystal structure. The optical absorption study revealed that, there is decrease in band gap (E_g) of material after doping Cs⁺. DC electrical conductivity shows that, after Cs doping conducting and semiconducting behavior is observed at lower temperature. TEP study shows that, there is improvement in the p-type conducting behavior after Cs doping. The TGA-DTA study revealed that, after doping Cs⁺, stability of Cs₃(PMo₁₂O₄₀) material increases and the material is thermally stable up to 687.61°C.

Keywords: Hydrothermal, heteropolyoxometalate, thin films, electrical conductivity.

1. Introduction:

The heteropolyoxometalate (HPOM) materials of Vanadium, Molybdenum and Tungsten are an exciting class of materials whose properties are intermediate between atoms or molecules and bulk materials [1]. Metal ion doped HPOM materials are technologically important due to its high electrical and thermal conductivities [2], redox ion exchange behaviors [3-5]. The heteropolyanions of V, Mo, and W find applications in biochemical industrial catalysis, proton conductor [6], ion exchange materials, thin layer chromatography, materials for separation of amino acids [7]. Heteropolyoxometalates (HPOM), in addition to their considerable applications in catalysis and medicine, are attracting attention for advanced materials.

So, in the present investigation, we are reporting influence of Cs⁺ doping on structural and electrical properties of hydrothermally grown molybdenum heteropolyoxometalate thin films.

2. Materials and Methods

2.1 Thin film deposition of PMA

For the deposition of thin films of undoped phosphomolybdic acid (PMA), 0.05M solution of phosphomolybdic acid (H₃PMo₁₂O₄₀) in acetone was taken in a 100 cm³ capacity glass beaker. The cleaned and dried glass as well as FTO substrate was dipped in above solution, and by using dip and dry technique yellow colored and uniform thin films were prepared. The deposited thin films

were dried in oven at 75°C. Thickness of the film was measured by using surface profilometer.

2.2 Thin film deposition of CsPMA

The cesium doped molybdenum HPOM (CsPMA) thin films were deposited on FTO substrates. The aqueous solution of 0.05M phosphomolybdic acid (H₃PMo₁₂O₄₀) and disodium salt of ethylene diamine tetra acetic acid (EDTA) was used as a complexing agent. A complexing agent of about 20 ml is obtained by mixing PMA (0.05M) and EDTA (0.1M) this mixing solution was adjusted to pH of about 9.5 by adding drop wise ammonia. Resulting solution of complexing agent along with 20 ml CsCl (0.2M) was poured in the Teflon of autoclave arrangement set up. Precleaned fluorine doped tin oxide (FTO) substrates were immersed vertically in autoclave containing reaction mixture and temperature was kept at 150°C for three hours. After cooling deposited thin films were washed with distilled water and dried. The dried films were annealed at 200°C by keeping in a furnace. Thickness of the deposited films was measured by surface profilometer. The DC electrical conductivity of the films were measured by using two probe method in the range from room temperature to 285 °C. TEP measurement of the sample were carried out at taking 10 °C difference between hot and cold end.

3. Result and Discussions:

3.1 Optical characterization:

Fig.1 shows the plot of $(\alpha h\nu)^2$ verses $h\nu$ for PMA and CsPMA thin films. The presence of single slope in the curves suggest that films are single phase in nature and type of transition is direct and allowed. From Fig. 1 it was found that for Cs⁺ doped material optical band gap is 2.06 eV and is lower as compared to 2.33eV of undoped PMA [8-9].

3.2 Morphological Analysis:

The morphological investigations of PMA and CsPMA HPOM materials were analyzed by SEM technique. The scanning electron microphotographs of undoped and Cs⁺ doped PMA thin films annealed at 200°C for 2 hours are shown in Fig.2a and Fig.2b. From these figures it is found that, there is uniform distribution of grains for Cs⁺ doped PMA as compared to undoped one. The grains of Cs⁺ doped material becomes spherical this indicates that Cs⁺ plays an important role to improve structural and electrical properties. Spherical grains achieve good electrical properties.

3.3 Compositional analysis by EDS:

Required atomic percentage of phosphorus, oxygen, molybdenum and cesium composition under investigation was confirmed by analyzing annealed thin films on Energy Dispersive X-ray Analyzer. Fig.3 (a) and 3(b) shows the EDS spectra of PMA and CsPMA.

The EDS pattern shows the presence of O, P, Mo and Cs in the films without any major impurity. Table 1 shows theoretical and practical atomic percentage of O, P, Mo and Cs.

3.4 Structural analysis of PMA and CsPMA by XRD:

The X-ray diffractograms of PMA and CsPMA are presented in Fig. 4. The presence of prominent peak having 311 planes in the XRD pattern shows that the material possesses simple cubic spinel structure. The crystallite size, lattice constant and average grain size of PMA and CsPMA are shown in Table 2 which indicate that, after Cs⁺ doping crystallite size (D), lattice constant (a) and average grain size (Ga) values decreases [10].

3.5 DC Electrical conductivity

The electrical conductivity (σ) was measured as a function of temperature in the range from room temperature to 252 °C for PMA and CsPMA. The conductivity data have been analyzed to distinguish between possible mechanisms in the material. The plot of $\log \sigma$ verses $1000/T$ for PMA and CsPMA is shown in Fig.5.

The plot of $\log \sigma$ verses $1000/T$ of PMA shows that, in the lower temperature range (112

°C to 197 °C) conductivity increases with increase in temperature indicating conducting behavior of the material. At higher temperature range (197 °C to 252 °C) conductivity decreases with increase in temperature indicating semiconducting behavior of the material.

The plot of $\log \sigma$ verses $1000/T$ of CsPMA shows that, in the lower temperature range (67 °C to 147 °C) conductivity increases with increase in temperature indicating conducting behavior of the material. This may be due to increasing the mobility of the electron in the material. At higher temperature range (147 °C to 252 °C) conductivity decreases with increase in temperature indicating semiconducting behavior of the material. This may be due to carrier concentration of electron and hole.

From Fig.5 it is found that, after Cs doping conducting and semiconducting behavior is observed at lower temperature. The activation energies in ferrimagnetic and paramagnetic regions are calculated from slope of the plot $\log \sigma$ verses $1000/T$ and are tabulated in Table 3.

From Table 3 it is observed that activation energies of PMA and CsPMA, in paramagnetic region are found more than in ferrimagnetic region. This can be attributed to the effect of magnetic ordering in the conduction process. From conductivity plot it is observed that after doping Cs heteropolyoxometalate material shows conducting nature at lower temperature than undoped material. This is due to lower concentration of hopping mechanism due to anions [11].

3.6. Thermoelectric power (TEP) of phosphomolybdic HPOM material:

Seebeck coefficient of a material was determined from the plot of the measured seebeck voltage verses the temperature difference across the material. We measured the seebeck coefficient (S) of the PMA and CsPMA in the range 300K to 550K which is shown in Fig.6. Undoped HPOM material (PMA) shows n-type behavior in the temperature range 311K to 331K and p-type behavior in the range 331K to 350K. After 350K material not shows conducting behavior. After Cs doping material shows p-type behavior in the temperature range 300K to 473K. Hence there is improvement in the p-type conducting behavior after Cs doping [12].

3.7 TGA-DTA measurements:

Thermal stabilities of PMA and CsPMA were determined by TGA-DTA measurements. Fig.7 (a) and Fig.7 (b) shows TGA-DTA curves for PMA and CsPMA respectively. TGA-DTA curves shows that, PMA is thermally stable up to 417.35 °C while CsPMA is thermally stable up to 687.61 °C.

Table 1: Theoretical and practical atomic percentage of O, P, Mo and Cs.

Elements	Theoretical atomic %	Practical Atomic %
O	25.50	67.82
P	2.01	2.76
Mo	50.36	22.34
Cs	22.13	7.09

Table 2: Effect of Cs⁺ doping on crystallite size, lattice constant and average grain size.

Sample	Crystallite size 'D' (nm)	Lattice constant 'a' (Å)	Average grain size 'Ga' (nm)
PMA [H ₃ (PMo ₁₂ O ₄₀)]	44.38	11.31	1530
CsPMA [Cs ₃ (PMo ₁₂ O ₄₀)]	31.34	10.89	1031

Table 3: Observed variation of ΔE for PMA and Cs PMA material.

Sample	Transition Temp. (°C)	Activation energy ΔE (eV)		ΔE = E _p - E _f
		Ferrimagnetic	Paramagnetic	
PMA	197	0.1001	0.3348	0.2347
CsPMA	147	0.08	0.4673	0.3873

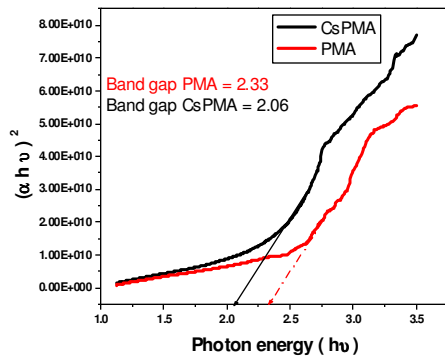


Figure 1: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for PMA and CsPMA thin films.

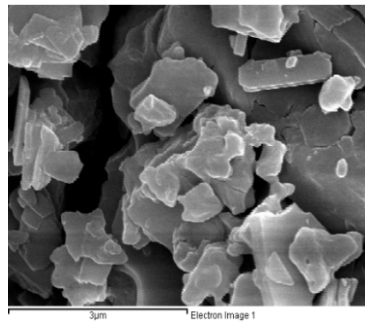


Figure 2: (a) SEM of PMA

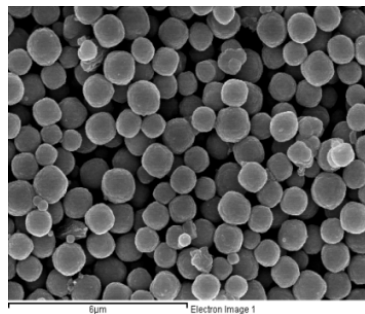


Figure 2: (b) SEM of CsPMA

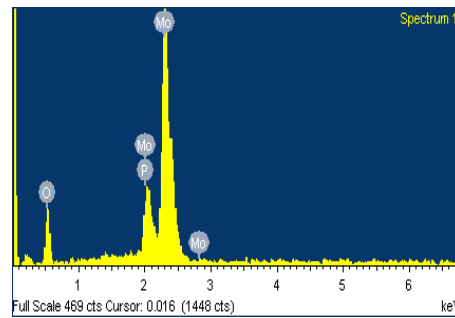


Figure 3: (a) EDS of PMA

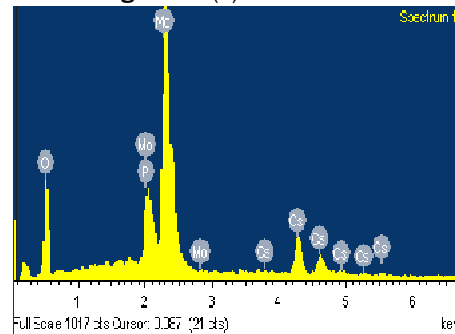


Figure 3: (b) EDS of CsPMA

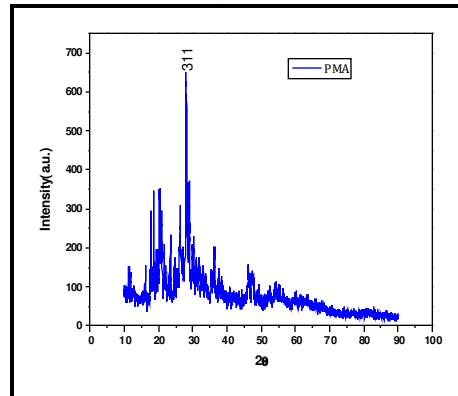


Figure 4: (a)

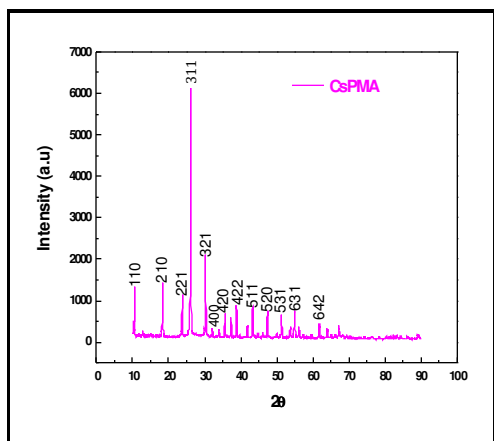


Figure 4: (b)

Figure 4: (a and b) XRD of phosphomolybdic acid (PMA) and Cs⁺ doped phosphomolybdic Acid (CsPMA)

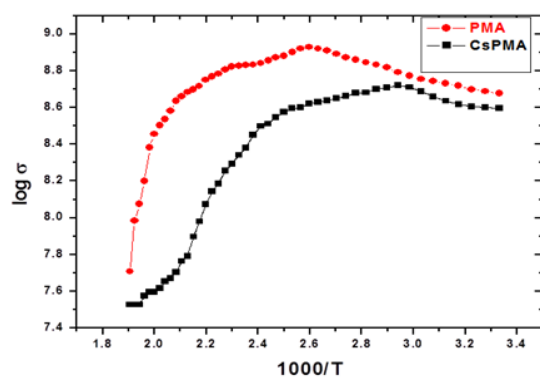


Figure 5: log σ versus $1000/T$ plots for PMA and CsPMA material

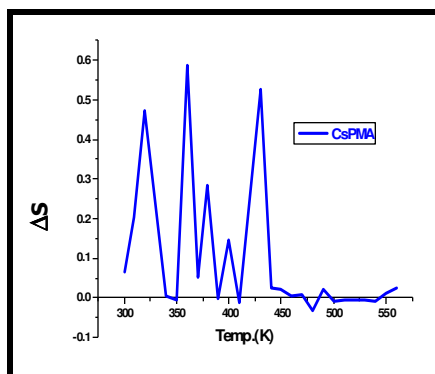
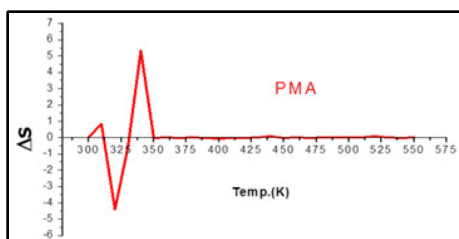


Figure 6: Temperature dependence of the seebeck coefficient of PMA and CsPMA material.

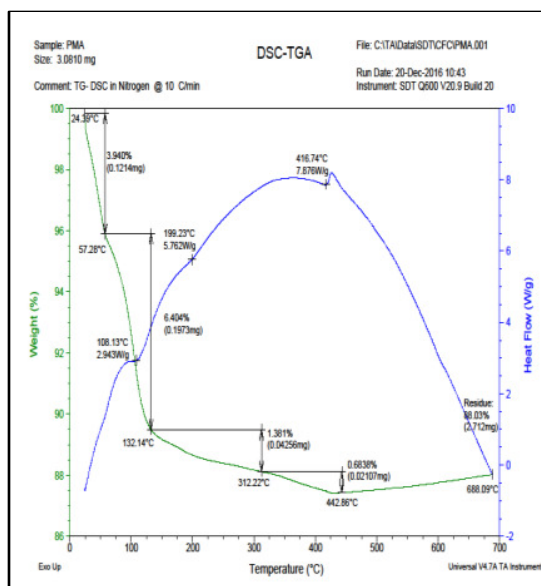


Figure 7: (a) TGA-DTA curve PMA

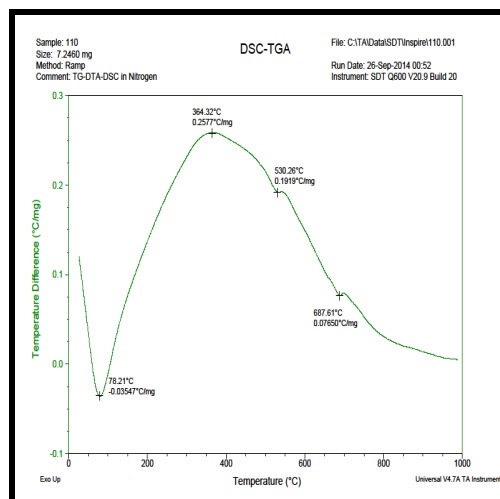


Figure 7: (b) TGA-DTA curve CsPMA

4. Conclusion:

Thin films of the PMA and CsPMA were prepared by hydrothermal process. X-ray diffraction study confirms well formation of simple cubic spinel spherical nanocrystals. Band gap, crystallite size, lattice constant decreases with Cs⁺ doping. DC electrical conductivity shows that, after Cs doping conducting and semiconducting behavior is observed at lower temperature. TEP study shows that, there is improvement in the p-type conducting behavior after Cs doping. Thus Cs₃(PMo₁₂O₄₀) HPOM material is applicable for fabricating semiconducting and switching devices.

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