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Research paper

Dc electrical properties of semiconducting cobalt oxide substituted lead vanadate glasses

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Abstract

Semiconducting lead vanadate glasses with CoO substitution represented as xCoO-(50-x) PbO-50V2O5 with x=5,10 and 15 mol% were prepared by melt quenching technique. They were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), differential thermal analysis (DTA) and DC electrical conductivity. The overall features of these XRD curves reveal the amorphous nature of present glasses. SEM investigations were conducted for the micro structural characterization of V2O5 crystal phases. Density was observed to decrease with an increase in CoO content. The dc electrical conductivity of the present system increases as the concentration of substitution of CoO increases with 5molpercentage to 15molpercentage.

Keywords: *Lead Vanadate; Glasses; Mott's Hopping; Dc Electrical Conductivity; Cobalt Substitution*

1. Introduction

In the conventional silicate based glasses electrical conduction takes place due to ionic transport. In semiconducting glasses, the electrical conduction is due to the transport of electrons from low valancy state to high valancy state [1-5]. The research in understanding the structural and physical properties of glasses in general and semiconducting glasses in particular has increased considerably due to the potential applications perceived for the semiconducting glasses. Some of the possible applications are in threshold switching, memory switching, electrochemical batteries etc. Studies are carried out on semiconducting glasses in bulk as well as thick film form. Among all PbO-V2O5 glasses have been of great interest due to their ease of preparation as compared to other semiconducting glasses [6-8]. In the present work we prepared the glass samples by substituting CoO in different molar ratios into a chosen glass matrix xCoO (50-x)PbO :50 V2O5 where x = 5 mole % to 15 mole % and discussed the study of compositional and temperature dependence of dc electrical properties of CoO substituted lead vanadate glasses in the temperature range 300K- 500K.

2. Experimental Details

A series of glass with the molar formula x CoO (50-x) PbO: 50 V2O5 (x=5, 10, 15 in molar ratio) were prepared. Appropriateamounts of reagent grade CoO, PbO and V2O5 were well mixed And melted in silica crucibles using an electrical furnace at a temperature ranging between 9500C-10000C range, depending
On the glass composition. The melt was swirled frequently to insure the homogeneity the melts were quenched on a large stainless steel block maintained at room temperature (≈300C) and constituting of 9mm cylindrical cavities to get samples of cylindrical shape of 2 to 3mm width. The glass samples were annealed at 1400C below the glass transition temperature for nearly 2 hours. The samples were washed with an acetone and dried. The glasses were stored in desiccators until required.

3. Results and discussion

The perfect amorphous nature of these samples which were annealed at 1400C for each composition(x=5, 10, 15mol%) is indicated in the X-ray diffractograms shown in figure 1. It is observed that density (d) decreases gradually with the increase in CoO content in the glass compositions. The chemical analysis data is given in table 1.

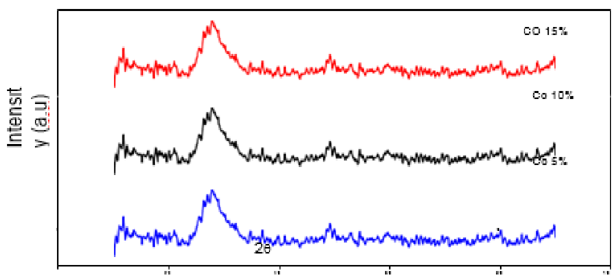

Fig. 1: X-Ray Diffractograms of Xcoo-(50-X) Pbo-50V2O5 Glass System Annealed at 1400C(X=5, 10, 15 Mol %).

The DTA patterns of these glass systems are shown in figure 2, and are slightly different when compared to those of the unsubstituted system[9]. Values of glass transition temperature Tg, crystallization temperature TC, and melting temperature for the xCoO (50-x) PbO-50V2O5 glass systems are given in table 2. The Tg values decrease with increasing of CoO content and these results suggest that CoO acts as network modifier whereas PbO acts as a network former

Table 1: Composition, Density, Concentration of V4+, Total Vanadium Ions and Their Ratio and Average Vanadium Site Separation in Coo Substituted Lead Vanadate Glass

Glass composition (mole %)			Density	$[V^{4+}]$	N	C=	R
V_2O_5	PbO	CoO	(gm/c.c)	10^{20}/c.c	10^{22}/c.c	(V^{4+}/N)	(Å)
50	45	5	5.14	2.58	1.56	0.0165	4.03
50	40	10	5.04	2.63	1.58	0.0166	4.02
50	35	15	4.96	2.72	1.60	0.0170	4.01

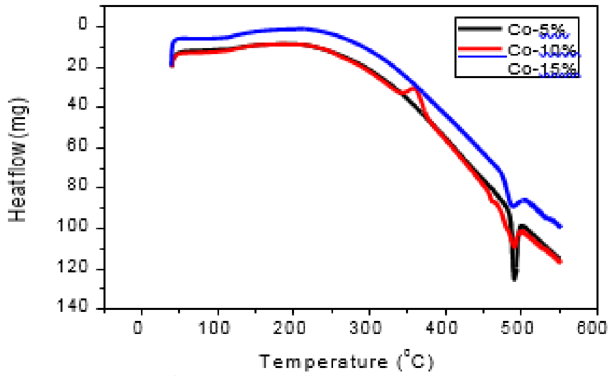

Fig. 2: DTA Curves of Xcoo-(50-X)Pbo-50V2O5 Glass System Glass Transition Temperature(TG),Crystalline Temperature (TC) and Melting Temperature(Tm) for (X=5,10,15mol%).

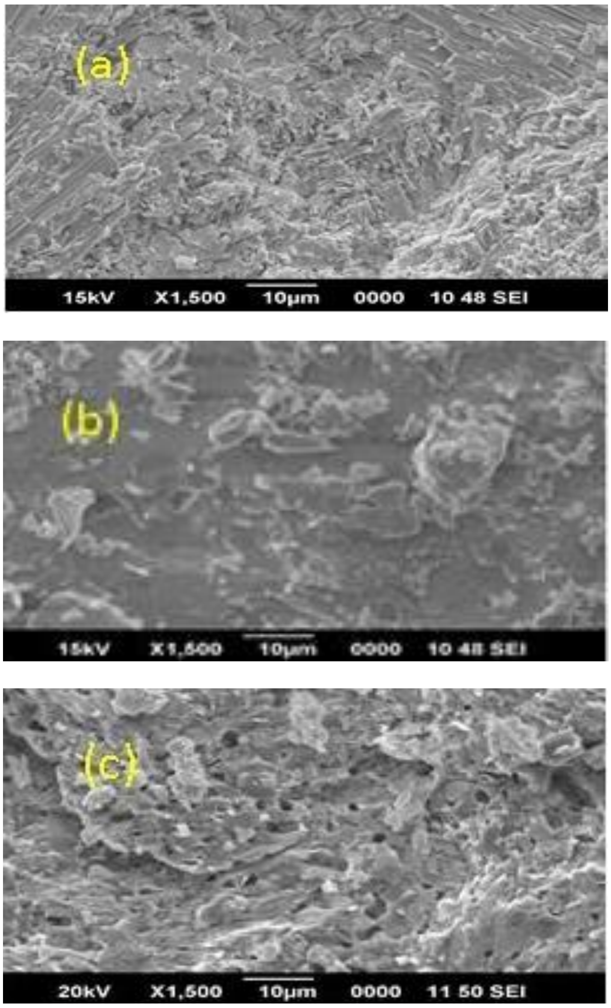

Fig. 3: SEM Micrograph for A) 5coo-45pbo-50V2O5 B) 10coo-45pbo-50V2O5 C) 15coo-45pbo-50V2O5 Glass.

Table 2: Values Of Glass Transition Temperature (TC), And Melting Temperature(Tm) for the XCOO (50-X) PBO: 50V2O5

Composition (mole %)			Tg	TC	Tm
CoO	PbO	V2O5			
5	45	50	123	212	493
10	40	50	102	355	490
15	35	50	93	315	489

Crystallization temperature TC is the maximum temperature of the exotherm, from the figure 2 it can be seen that there is only one endothermic peak corresponding to the melting point. This indicates that the CoO substituted samples behave like the eutectic composition up to x=15 mol% of substitution. Figure 3 shows the SEM micrographs of xCoO-(50-x)PbO-50V2O5 (x=5,10 and 15mol%) with heating rate upto 4 hours at 400^0C.From the micrographs of these samples, it was observed that there is some microstructural changes have been seen. The dc conductivity for glass composition is shown in figure 4, as a function of reciprocal temperature. The activation energies for different molar ratios are given in table 3. Figure 4 clearly gives the linear relationship between logσ and reciprocal of absolute of temperature. The slope of the curves, which gives the activation energy for conduction. The experimental conductivity data in such a situation are well described with activation energy for conduction given by Mott's formula [1].

$$\sigma = \sigma 0 \exp(-W/kT) \quad (1)$$

Where σ0 is pre-exponential factor, W is the activation energy and k is the Boltzmann constant

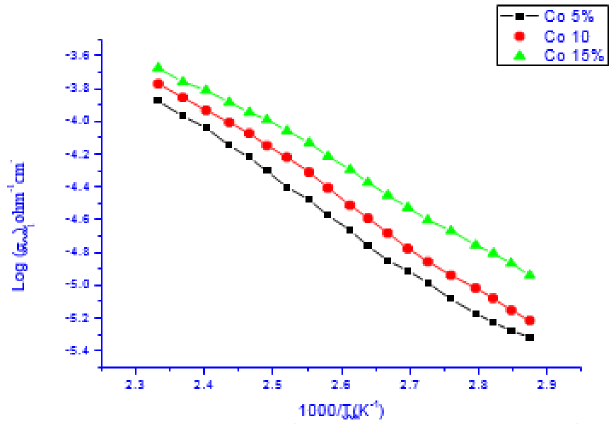

Fig. 4: Temperature Dependence of Logarithmic Dc Conductivity of Xcoo (50-X) Pbo-50V2O5 Glass System Annealed at 1400C (X=5, 10, 15mol %).

Table 3: Activation Energies Obtained at Different Temperature Regions by Fitting Mott's Model for Coo Substituted Lead Vanadate Glasses

Glass Composition (mole %)			Activation energies of the samples annealed at 140^0C O W(eV)
V2O5	PbO	Co	
50	50	-----	0.175
50	45	5	0.037
50	40	10	0.033
50	35	15	0.028

At a given temperature, the conductivity of CoO substituted glass system is slightly less than that of the unsubstituted 50PbO:50V2O5 glass system. It is clear in figure that the conductivity increases, while the activation energy decreases with the increase in the CoO content in the glass compositions. Such behavior is a feature of small polaron hopping [1]. Kinser and Wilson [10] studied the electrical properties and the corresponding microstructures of vanadium phosphate glasses and suggested that the observed conductivity maximum at C (where C=amount of V4+/amount of Vtotal) < 0.5 is a consequence of microstructural segregation [11]. Similarly, according to Anderson MacCrone in iron silicate glasses the majority of iron ions are supposed to be situated in relatively well ordered clusters which might be giving rise to high electrical conductivity in these glasses [12]. In literature there are instances of V2O5 containing glasses showing maximum conductivity at different values of C [11]. These differences are attributed to polaron-polaron interactions. [13] and short range Coulomb repulsion which modifies C in Mott's equation[1] to C(1-C)n. These examples suggest that the diffusion like conduction mechanism in the glass systems containing random distribution of ion sites may be inappropriate. These discrepancies are supposed to be explained by a model proposed by Anderson & Mac Crone

[12] In which the charge carriers move along chains of highly Conductive transition metal ions. Therefore it is possible in the present glass systems to suggest that conductive chains may be microstructure dependent and vary as microstructure varies as a function of temperature.

Different properties of CoO substituted semiconducting lead vanadate glasses have been studied. These properties include XRD, DTA, SEM, density, and dc conductivity. The overall features of these XRD curves confirm the amorphous nature of the present glass system. The DTA studies on xCoO(50-x)PbO-50V2O5 glass systems indicated that CoO is substituting for PbO without drastically affecting the microstructure of the unsubstituted lead metavanadate glass network up to x=15mol%. SEM investigations of the present glass sytem revealed that there are some micro structural changes are attributing as the substitution (CoO) concentration increases. Density was observed to decrease with an increase in CoO content in the glass composition. The temperature dependence of electrical conductivity for the present glasses increases as the CoO content increases in the glass composition.

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