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EPR and optical absorption studies on Chromium ions in mixed alkali Cadmium phosphate glasses

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It was observed by earlier workers, that some glasses with two alkali oxides exhibit mixed alkali effect. To see whether such effect manifests in the cadmium phosphate glasses, EPR and optical absorption studies are carried out using Cr^{3+} ion as dopant. Studies on the systems x Li_2O + (20-x) Na_2O + 20 CdO + 59.5 P_2O_5 + 0.5 Cr_2O_3 ($5 \leq x \leq 15$) clearly indicated the presence of mixed alkali effect with x=10.

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1. Introduction

Mixed–alkali effect in glasses has attracted much attention, due to it's technological and theoretical interests in describing the physics and chemistry of glasses. The mixed alkali effect (MAE) corresponds to the nonlinear variation of certain physical properties with the relative alkali content in glasses containing two or more different types of alkali ions [1-3]. Many physical properties measured in mixed-alkali systems show initial non-linear growth and subsequent reversal in trends leading to a maxima or minima as a function of modifier fraction [1].

By changing the chemical composition, the local environment of the transition metal (TM) ion incorporated into the vitreous network can also be changed, leading to local ligand field inhomogeneities. These structural modifications are well reflected in the EPR and absorption spectra of TM paramagnetic ions in glasses. Cadmium phosphate based glasses have been used as matrices for the growth of cadmium selenide quantum dots. As the reports on studies concerned with the structure and properties of phosphate glasses are rather meagerly available in literature, we undertook the study of Cadmium phosphate based glasses through EPR and optical investigations as these studies are important and useful to gain insight into the microscopic mechanisms responsible for the effect. In the present investigation the nature of the site symmetry of Cr^{3+} ions in lithium-sodium mixed alkali cadmium phosphate glasses (hereafter referred to as LiNaCdP1, LiNaCdP2 and LiNaCdP3) is studied from the nature and splitting of EPR and optical bands at three concentrations with a view to establish the mixed alkali effect .

2. Experimental

The starting materials used in the present study are Analar grade Li_2CO_3 (99.9%), Na_2CO_3 (99.9%), CdO (99.9%) and P_2O_5 (99.9%). The host glass composition is taken as x Li_2O + (20-x) Na_2O + 20 CdO + 59.5 P_2O_5 + 0.5 Cr_2O_3 ($5 \leq x \leq 15$). For each concentration the mixture is first sintered at 700 K after thoroughly mixing it using standard procedures. The resulting sample is kept in a platinum crucible and then melted in an electric furnace at 1250 K for nearly 2hours. Glass is formed by quenching the melt at room temperature in air. The glass so formed is annealed at 550 K for 30 minutes. To ensure the amorphous nature of the glass ,X-ray diffraction studies are performed on a PHILIPS X'PERT PRO X-RAY diffraction system. EPR spectra are recorded at room temperature on JES-FA series X-band EPR spectrometer having 100 kHz field modulation. Optical absorption spectra of these glasses are recorded at room temperature on JASCO (V-530) spectrophotometer in UV-VIS region.

3. Results and discussion

Powder XRD spectra are recorded for the three Cr^{3+} doped LiNaCdP glass samples and a typical one is shown in Fig.1.

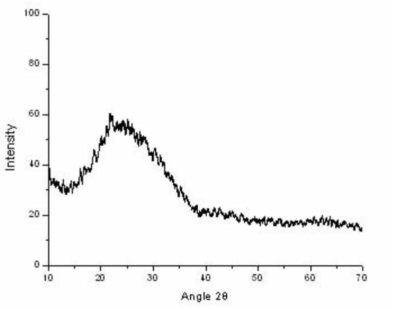

Fig 1. Powder XRD pattern of Cr^{3+} ions doped LiNaCdP glass

The observed X-ray patterns of the samples studied in the present investigation indicate that the samples are vitreous. The optical absorption spectrua (900-200 nm) of the Cr^{3+} doped mixed alkali cadmium phosphate glasses exhibit only two bands with the band at higher energy shown in Fig 2.

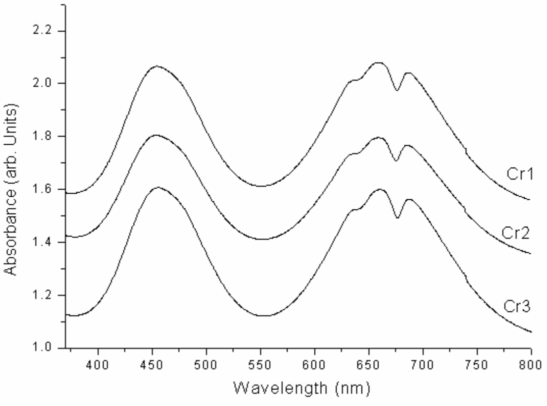

Fig 2. Optical absorption Spectra of Cr^{3+} ions doped LiNaCdP glasses(Cr_1:LiNaCdP$_1$, Cr2:LiNaCdP$_2$, Cr_3: LiNaCdP$_3$).

The low-energy band in the optical spectrum shows fine structure. By the crystal field theory ,Cr^{3+} ions are usually assumed to occupy approximately octahedral symmetry sites in inorganic solids. This is due to the ionic radius and the strong ligand field stabilization energy of Cr^{3+} ions in sixfold coordination. The parity-forbidden d–d transitions can be due to partially allowed by the weak distortion of the crystal field or by instantaneous distortion due to molecular vibrations [5-7]. The assignment of the bands is given in Table 1.

The Cr3+ ions in octahedral symmetry are characterized by three spin-allowed transitions ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$. In the present case, only two bands are observed about to first two transitions. In the profile of ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ it is well known that the spectrum of Cr^{3+} doped glasses exhibits two dips [8]. These dips are due to the Fano anti-resonances resulting from the interaction of the ${}^2T_{1g}(G)$ and ${}^2E_g(G)$ with vibrationally broadened ${}^4T_{2g}$ (F) state [9]. Band assignment of the optical spectra supposing Cr^{3+} ions to be located at nearly octahedral sites are shown in Table 1:

Table 1. Band assignment of the optical absorption spectra of Cr^{3+} ions.

	Band position		
Electronic transition	LiNaCdP$_1$ (cm^{-1})	LiNaCdP$_2$ (cm^{-1})	LiNaCdP$_3$ (cm^{-1})
${}^4A_{2g} \rightarrow {}^2E_g(G)$	14810.7(14753)	14767.0(14798)	14767.0(14751)
${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ (ν_1)	15124.4(15120)	15170.3(15170)	15147.4(15150)
${}^4A_{2g} \rightarrow {}^2T_{1g}(G)$	15645.2(15400)	15669.7(15455)	15620.7(15403)
${}^4A_{2g} \rightarrow {}^4T_{1g}(F)(\nu_2)$	21923.8(21919)	22020.4(22021)	21972.0(21972)

On the basis of the preceding band assignment the crystal field parameter Dq is evaluated from the band position of ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ as 10Dq. The Racah inter-electronic repulsion parameter B can be evaluated from:

$$B = (2\,\nu_1{}^2 + \nu_2{}^2 - 3\,\nu_1\,\nu_2) / (15\,\nu_2 - 27\nu_1)$$

Here ν_1 and ν_2 represent the energies of ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ respectively.

The Racah parameter *B* can be regarded as a measure of inter-electronic repulsion in the d shell; the larger the *B* value, the more the electrons are localized on the transition-metal ion. Based on the above assignments the energy matrices of d^3 configuration are solved for different values of crystal filed (Dq) and inter electronic repulsion (B and C) parameters. A good fit with the experimental results is obtained. The calculated bands are presented (within brackets) in Table 1.

Table 2. Spectroscopic properties of Cr^{3+} in different phosphate glass systems.

Phosphate glass System	Dq (cm-$_1$)	B (cm-$_1$)	C (cm-$_1$)	Dq/B (cm-$_1$)
LiNaCdP1	1512	712	3195	2.123
LiNaCdP2	1517	719	3195	2.11
LiNaCdP3	1515	715	3188	2.117

By comparing the *B* values (Table 2), we can say that the ionic contribution to the chemical bonds between Cr^{3+} ions and the ligands is high for LiNaCdP2 glass(x=10) sample. In glass phases, Cr^{3+} ions occupy a variety of sites with different crystal field strengths due to site variability and compositional disorder [10]. The first excited state is ^2E in high field sites and $^4T_2$ in low field sites [11]. The relative energies of the excited $^4T_2$ and ^2E states depend on the crystal field strength. Here the crystal field strength Dq/B also shows the dependence of mixed alkali variation effect for x=10 glass sample which is related to Cr^{3+} doped phosphate glasses by Haouari et. al. [12].

EPR spectrum of Cr^{3+} ions doped mixed alkali cadmium phosphate glasses are shown in Fig. 3 for all the samples.

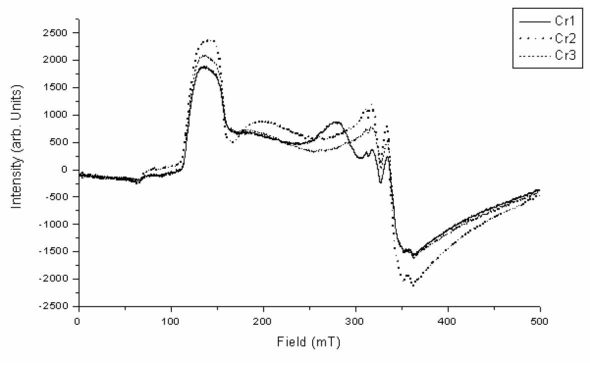

Fig 3. Powder EPR spectra of Cr^{3+} ions doped LiNaCdP glasses (ν=9.446GHz) (Cr1:LiNaCdP1, Cr2:LiNaCdP2, Cr3: LiNaCdP3).

In all the spectra, the glass samples shows two resonance signals at g ~ 4.8 and g ~ 2.0, which are broad and asymmetric at low and high magnetic fields. For LiNaCdP1(Cr1) sample, resonance signal at g ~ 2.3 exists because of some copper impurity in Na_2O. When the concentration of Na_2O is reduced in composition, the signal at g ~ 2.4 is also reduced. The Cr^{3+} free ion, with its three unpaired electrons usually considered in distorted octahedral sites. In an octahedral field its ground state is $^4A_{2g}$ level. In the presence of low symmetry component and spin orbit coupling, the four-fold degeneracy spin states split into two Kramer's doublets. In glasses a large separation between the two doublets leads to the resonance around g ~ 2 and 5 at room temperature [13,14]. These resonances for Cr^{3+} ions may exist in glasses as both isolated Cr^{3+} ions in the glassy network and exchanged coupled Cr^{3+} - Cr^{3+} pairs aggregation together [15]. In the present study the obtained values are given in Table:

Table 3. Effective g values for the different phosphate glass systems.

Glass system	Effective *g* values	
LiNaCdP1(x=5)	4.994	1.981
LiNaCdP2(x=10)	4.80	1.966
LiNaCdP3(x=15)	4.944	1.974

In this table the g values near 4.8 are assigned to the isolated Cr^{3+} ions and those near to 2.0 are assigned to exchange coupled Cr^{3+} ions based on Haouari etal's assignments [12] and which also suggested by Ardelean et. al. [16] and explained the existence of Cr^{5+} for lower concentrations of Cr_2O_3 [17,18]. The large line- widths in the EPR spectra in these glasses at g ~ 4.8 is a typical feature of glasses [12]. These are due to the random variation of crystal field parameters at various sites. Crystalline systems do not exhibit the broad feature. From this study we also conclude that Cr^{3+} ions have distorted octahedral environment for all the samples.

There is some considerable decrease in g values for x=10 sample and increase in intensity of absorption in the spectrum. This resulting decrease of covalent nature for x=10 sample compared to others is an evidence to the presence of mixed alkali effect.

The inter-electronic repulsion parameters obtained from optical absorption bands are a measure of ionic nature of the samples. The observations indicate that for x=10 composition the ionic nature shows a peak as we vary the concentration from x=5 to 15. Usually the increase in Li_2O concentration increases the conductivity of the sample at a certain concentration. In the present case it is observed that for $x < 10$ and for $x > 10$, the Li ions are involved in a sort of binding with some Cr^{3+} ions thereby inactivating them. The reduction of intensities in EPR spectra at x=5 and x=15 can be considered as an evidence for this. The bonding between Li and Cr ions is reducing the ionic nature of the glass sample is indicated by a rise in g value of the Cr^{3+} ion. From these observations we may be concluded that mixed alkali effect will not change the environment of Cr^{3+} ions in cadmium phosphate glasses but changes the ionic conductivity and spectral intensity. Both optical absorption and EPR data also confirm these results.

The effective *g* factor for a transition-metal ion by correlating both EPR and Optical data is proportional to g_0 where

$$g_0 = g_e - \frac{8\alpha\lambda}{\Delta}. \qquad (1)$$

Here g_e is the free electron g factor ($g_e = 2.0023$), λ is the spin–orbit coupling constant (91 cm^{-1} for Cr^{3+} ions) , Δ is the energy difference between the ground and the excited electronic levels. The parameter α is characteristic of the ionic contribution to the chemical bond between the Cr^{3+} ion and the ligands. The larger the value of α, the stronger the ionic contribution to the chemical bond and the smaller the value of the *g* factor. The *g* values found in this work (table 3) confirm that the ionic contribution to the chemical bond is high for x=10 glass sample compared to others. The α values evaluated are 0.442, 0.756 and 0.588 for LiNaCdP1, LiNaCdP2 and LiNaCdP3 glasses respectively, which supports high ionic contribution for x=10 glass sample. These results report the mixed alkali effect for present cadmium phosphate glass samples at equal concentration of alkali content.

4. Conclusions

From EPR and optical absorption spectra, we concluded that Cr^{3+} ions are located in sites with nearly octahedral symmetry in the present glass systems. EPR spectrum of the Cr^{3+} ions in mixed alkali cadmium phosphate glasses show the broad nature at room temperature and exhibits two resonance signals at $g \sim 4.8$ and $g \sim 2.0$ due to isolated Cr^{3+} ions and exchanged coupled Cr^{3+} ions. Four characteristic bands for Cr^{3+} ions are assigned from optical absorption spectrum. From these bands, the inter-electronic repulsion and crystal field parameters are evaluated. By comparing the EPR and optical absorption spectra and the resulting spectral values, mixed alkali effect has been explained in the mixed alkali cadmium phosphate glasses.

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