

## OPTICAL ABSORPTION OF $\text{AlF}_3\text{-YF}_3\text{-PbF}_2\text{-MF}_2\text{-MgF}_2$ (M= Ca, Sr and Ba) GLASSES DOPED WITH CHROMIUM IONS

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Fluoroaluminate glasses in the  $\text{AlF}_3\text{-YF}_3\text{-PbF}_2\text{-CaF}_2\text{-MgF}_2$ ,  $\text{AlF}_3\text{-YF}_3\text{-PbF}_2\text{-SrF}_2\text{-MgF}_2$  and  $\text{AlF}_3\text{-YF}_3\text{-PbF}_2\text{-BaF}_2\text{-MgF}_2$  systems have been doped with 0.2 and 0.3 mol %  $\text{CrF}_3$  and their optical absorption has been studied. The absorption spectrum displays two strong and broad bands corresponding to the electronic transitions  ${}^4\text{A}_{2g}({}^4\text{F}) \Rightarrow {}^4\text{T}_{2g}({}^4\text{F})$  and  ${}^4\text{A}_{2g}({}^4\text{F}) \Rightarrow {}^4\text{T}_{1g}({}^4\text{F})$  of the  $\text{Cr}^{3+}$  ions in a nearly octahedral environment. Crystal field and Racah parameters were determined. They depend on the nature of the earth alkali cation and also on chromium concentration, which suggests that local field and covalent character also change.

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### 1. Introduction

Optical properties of rare earth and transition metal ions in Heavy Metal Fluoride Glasses (HMFG) have been intensively investigated by various authors [1-7]. These optical properties include transparency (both in the U.V and Visible spectra), IR transmission and multiphonon absorption edge, and ability to host lanthanides and transition metals as luminescent centres. This feature is essential for use in glass laser technology[8], optical sensing and solar concentrator [9]. In addition to these potential applications,  $\text{Cr}^{3+}$  ions are also useful as a spectroscopic probe for obtaining information about the local environment in amorphous materials [10-12].

Chromium ion, a paramagnetic transition metal ion, when dissolved in glass matrix in very small quantities has a strong influence on optical transmission and leads to coloured glasses. In most glasses [13-16],  $\text{Cr}^{3+}$  ions occupy sites that have a nearly perfect octahedral symmetry because of the strong ligand field stabilization energy of  $\text{Cr}^{3+}$  in a six-fold coordination [15].

The aim of this study is to investigate the optical absorption of the  $\text{Cr}^{3+}$  cations in  $\text{AlF}_3\text{-YF}_3\text{-PbF}_2\text{-MF}_2\text{-MgF}_2$  (M= Ca, Sr and Ba) glasses, using the crystal field theory to account for the observed d-d transitions.

### 2. Experimental

Sample compositions, expressed in mol % are the followings:  $30\text{AlF}_3\text{-}10\text{YF}_3\text{-}30\text{PbF}_2\text{-}10\text{CaF}_2\text{-}20\text{MgF}_2$ ,  $30\text{AlF}_3\text{-}10\text{YF}_3\text{-}30\text{PbF}_2\text{-}10\text{SrF}_2\text{-}20\text{MgF}_2$  and  $30\text{AlF}_3\text{-}10\text{YF}_3\text{-}30\text{PbF}_2\text{-}10\text{BaF}_2\text{-}20\text{MgF}_2$ . The method used for glass synthesis is based on the ammonium bifluoride processing that has been described elsewhere [17]. Starting materials are anhydrous fluorides (Al,Sr,Mg) and oxides (Y,Pb,Cr). After the fluorination stage at  $350^\circ\text{C}$ , the mixture is melted under a controlled atmosphere. Then the melt is poured into a brass mould and annealed at a temperature slightly below the glass temperature  $T_g$ . The samples used in this work were doped with 0.2 and 0.3 at %  $\text{Cr}^{3+}$ .

The absence of peak structure in X-ray diffraction pattern of the samples confirmed the absence of crystalline phase. The absorption spectra were recorded using a Varian Cary 5G spectrophotometer operating between 350 nm and 800 nm.

### 3. Theoretical background

Electronic configuration of Cr (III) ( $d^3$ ) gives rise [18-19] to the free ion terms,  $^4F$  and  $^4P$  with  $^4F$  as the ground level. On applying the octahedral ligand field, the  $^4F$  term splits into  $^4A_{2g}$ ,  $^4T_{2g}$ ,  $^4E_{2g}$  and  $^4T_{1g}$  states, whereas  $^4P$  term transforms as  $^4T_{1g}$  state. Luminescence of  $Cr^{3+}$  originates from the lowest excited states. From the energy diagram it is seen that, for low ligand field systems ( $Dq/B < 2.3$ ), one may observe the  $^4T_{2g}(^4F) \Rightarrow ^4A_{2g}(^4F)$  fluorescence whereas, for high ligand field ( $Dq/B > 2.3$ ), it is the  $^4E_{2g}(^4F) \Rightarrow ^4A_{2g}(^4F)$  phosphorescence. For intermediate ligand field ( $Dq/B \sim 2.3$ ) both fluorescence and phosphorescence may occur.

### 4. Results

At room temperature, absorption spectra exhibit two bands corresponding to spin allowed optical transitions, respectively:  $^4A_{2g}(^4F) \longrightarrow ^4T_{2g}(^4F)$  and  $^4A_{2g}(^4F) \longrightarrow ^4T_{1g}(^4F)$  in order of increasing energy. Typical spectra of samples doped with 2%  $Cr^{3+}$  are shown in figure 1.

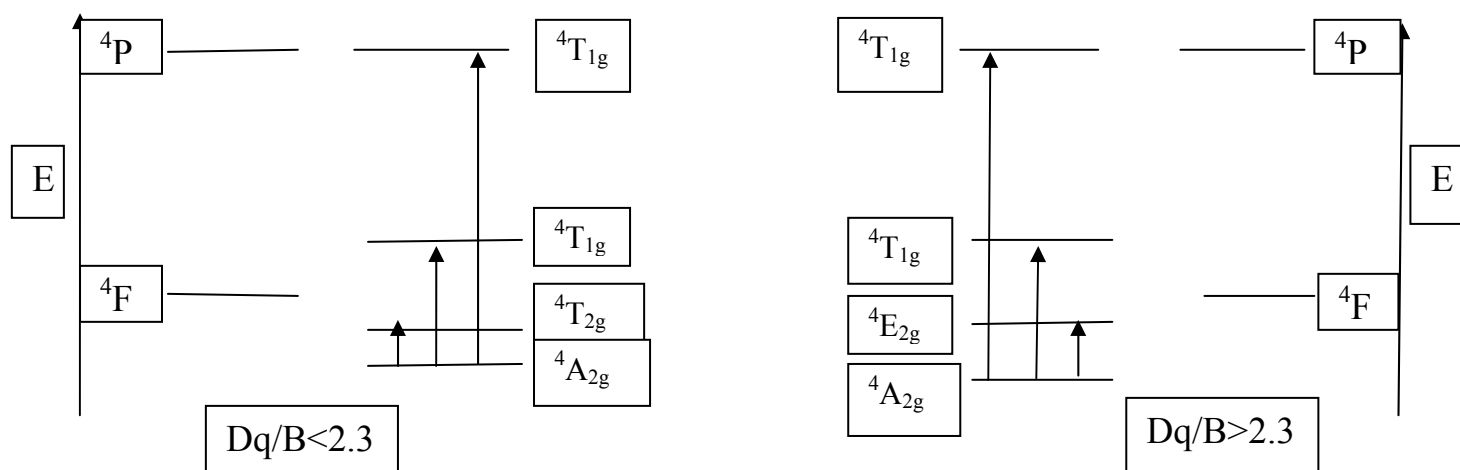


Fig. 1. Electronic transitions of  $Cr^{3+}$  ion in  $d^3$  configuration

The average values of the energy levels are reported in table 1. Similar dips in the absorption of  $Cr^{3+}$  in fluoride glass were attributed to effects of the anti resonance process described in the literature [20]. The ligand field parameters  $Dq$  (crystal field splitting energies) and  $B$  (Racah repulsion) are evaluated by using the Tanabe Sugano matrix elements [19]. The energies of these transitions and the values obtained are also given in table 1. The nephelauxetic ratio  $\beta'$  has been obtained using the relation  $\beta' = B(\text{complex}) / B_0(\text{free ion})$  [24], where  $B_0$  is the value of the Racah parameter for the free ion. For  $Cr^{3+}$  free ion, Racah parameter,  $B_0$ , is  $918\text{cm}^{-1}$  [19].

Table 1. Experimental energy levels and parameters ( $\text{cm}^{-1}$ ) of  $30AlF_3-10YF_3-30PbF_2-10MF_2-20MgF_2: CrF_3$  ( $M = Ca, Sr$  and  $Ba$ ) glasses

Energy levels	$^4T_{2g}(^4F)$	$^4T_{1g}(^4F)$	$Dq$	$B$	$Dq/B$	$\beta'$
0.2Cr Ca	16129	23155	1616	727	2.21	0.791
0.2Cr Sr	16051	23265	1605	755	2.12	0.822
0.2Cr Ba	16000	23466	1600	796	2.01	0.867
0.3Cr Ca	15748	22675	1574	719	2.18	0.783
0.3Cr Sr	15673	22727	1567	739	2.12	0.805
0.3Cr Ba	15625	22831	1562	765	2.04	0.833

Calculations also predict a third band due to  ${}^4\text{A}_{2g}({}^4\text{F}) \longrightarrow {}^4\text{T}_{1g}({}^4\text{P})$  transition in the absorption spectra of Cr-doped silicate glasses [26]; this band could not be observed as its wavelength lies well below the cut-off value. Nevertheless these observations are consistent with the assumption that chromium ions  $\text{Cr}^{3+}$  ( $d^3$ ) are mainly in the octahedral environment in these vitreous matrices.

## 5. Discussion

Crystal chemistry of chromium (III) is very close to that of aluminium and many of their complexes are isostructural. For this reason,  $\text{Cr}^{3+}$  may be considered as a local probe to collect structural information about aluminium. While there is little doubt about  $\text{Al}^{3+}$  coordination number that is known to be six, questions arise as to the character of the chemical bonding and its dependence on glass composition. Indeed, the main features of the absorption spectra of  $\text{Cr}^{3+}$  in fluoride glass can be interpreted on the basis of the crystal-field theory. Because of the structural disorder inherent to glass structure we might expect that the octahedral sites available to  $\text{Cr}^{3+}$  ions are less regular than those observed in crystalline compounds. While distortion is expected to be small, the present data do not allow evaluating the possible deviation from the perfect octahedral symmetry.

Considering an octahedron, the crystal-field parameter  $10\text{Dq}$  may be estimated from the energy of the  ${}^4\text{A}_{2g}({}^4\text{F}) \Rightarrow {}^4\text{T}_{2g}({}^4\text{F})$  band. Its value is inversely proportional to the fifth power of the  $\text{Cr}^{3+} - \text{F}^-$  distance [21]. The obtained experimental results show the decrease of the  $10\text{Dq}$  parameter, as the ionic radius of the modifier increases, according to the sequence:  $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$  (Table 1). These results suggest that the size of the  $\text{Cr}^{3+}$  ions also increases, resulting in larger  $\text{Cr}^{3+} - \text{F}^-$  distances, following the evolution of the modifiers. [22]. In the same way, the Racah parameter  $B$  increases with cation size.

The lowest value of  $\beta'$  is observed for calcium glass and the highest for barium glass (table 1), which relates to the covalent contribution to the bond between the  $\text{Cr}^{3+}$  and its ligands [24-25]. From these results it can be concluded that glasses containing calcium are more covalent in nature whereas barium glasses are more ionic.

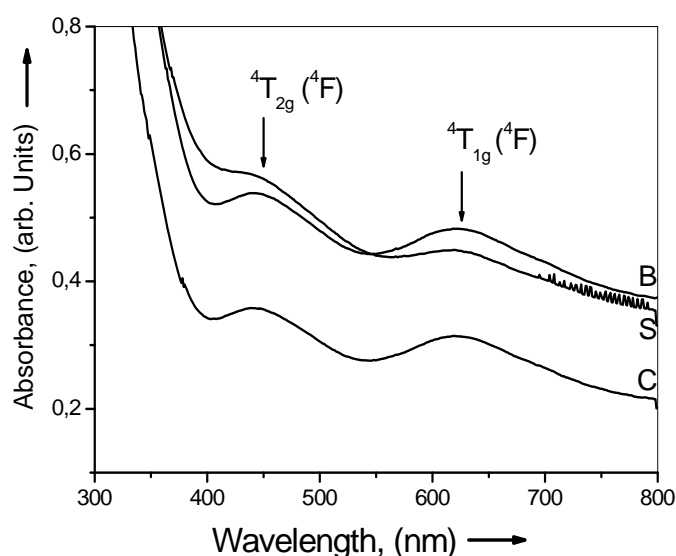


Fig. 2. Optical absorption spectra of  $30\text{AlF}_3\text{-}10\text{YF}_3\text{-}30\text{PbF}_2\text{-}10\text{MF}_2\text{-}20\text{MgF}_2\text{:} 0.2\text{CrF}_3$  glasses

The values observed for the ratio  $Dq/B$  confirm that these glasses provide low-field sites for  $Cr^{3+}$  ions in which the energy of the  ${}^4T_{2g}$  level is lower than that of the  ${}^2E_{2g}$  level for all studied glasses (Table 1). The comparison between the two series of samples at 0.2 and 0.3 %  $Cr^{3+}$  emphasizes a significant influence of chromium content: the 50 % relative increase in  $Cr^{3+}$  concentration leads to the decrease of both  $B$  (Racah parameter) and  $Dq$  (crystal field parameter). This may be attributed to the decrease of the covalency in the  $Cr^{3+} - F^-$  bonding, and possibly to the clustering of the  $Cr^{3+}$  ions.

Table 2.

configuration	Level	Energies according to $Dq$ , $B$ and $C$
$d^3$	${}^4A_{2g} ({}^4F)$	$-12Dq$
	${}^2E_{2g} ({}^4F)$	$-12Dq + 9B + 3C - 50B^2/10Dq$
	${}^2T_{1g} ({}^4F)$	$-12Dq + 9B + 3C - 24B^2/10Dq$
	${}^4T_{1g} ({}^4P)$	$7.5B + 3Dq + \frac{1}{2}(225B^2 + 100Dq^2 - 180 DqB)^{1/2}$

Fluoride glass structure may be viewed as a random packing of large ions, namely fluoride anions and large cations: earth alkali elements, lead and Yttrium. In this random packing numerous octahedral sites are available for insertion of  $Al^{3+}$  and  $Cr^{3+}$  ions, under the conditions octahedron is made only from fluorine anions. We may assume that glass structure is the same for the three glasses of the  $AlF_3$ - $YF_3$ - $PbF_2$ - $MF_2$ - $MgF_2$  ( $M = Ca, Sr$  and  $Ba$ ) systems. Then, replacing  $Ca^{2+}$  cations by larger  $Sr^{2+}$  or  $Ba^{2+}$  ions induces some stretching stress over the vitreous network constructed from the  $AlF_6$  and  $CrF_6$  octahedra. This mechanism could account for the evolution of the  $10 Dq$  and  $B$  parameters.

## 6. Conclusion

The study of the optical properties of  $Cr^{3+}$  cations in fluoroaluminate glasses with different earth alkali cations  $M$  ( $M = Ca, Sr$  and  $Ba$ ) confirms their octahedral coordination. Absorption spectra and energy levels have been reported. The evolution of the ligand field parameters emphasizes changes in  $Cr-F$  bond length and ionicity. These parameters are also sensitive to chromium concentration.

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