

STUDY ON OPTICAL SPECTRA OF  $\text{Cr}^{3+}$  IONS IN PHOSPHATE, FLUOROPHOSPHATE AND FLUORIDE GLASSES

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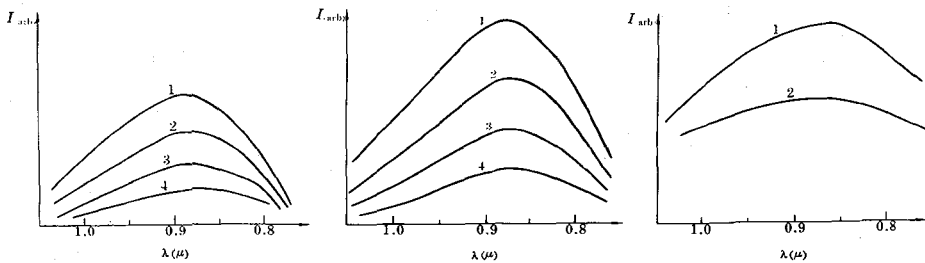
Résumé. - On mesure l'absorption, la fluorescence et la durée de vie des ions  $\text{Cr}^{3+}$ ,  $\text{Mo}^{3+}$  dans trois espèces de verres en base, analyse et calcule des données de spectre basées sur la théorie du champ coordinateur. En outre, on étudie l'excitation du laser et le spectre d'émission de résolution dans le temps, discute la caractéristique spectrale et la structure de site dans le réseau d'ion  $\text{Cr}^{3+}$  dans des verres.

Abstract. - Absorption, fluorescence and lifetime measurements of  $\text{Cr}^{3+}$ ,  $\text{Mo}^{3+}$  ions in three kinds of glass bases have been performed. Analysis and calculation of the spectral data based on the ligand field theory have been carried out. Furthermore, laser excited and time resolved emission spectra have been studied, spectral characteristics and site structure of  $\text{Cr}^{3+}$  ion in glasses are also discussed.

Recently, a great attention has been paid to the transition element ion doped glasses for the development of tunable solid state laser, among them  $\text{Cr}^{3+}(3d^3)$  ion is the most important one. The absorption spectra of  $\text{Cr}^{3+}$  has been studied extensively in many glass systems<sup>[1-3]</sup>, but a few work has been done for fluorescence and relaxation spectra, there is still an argument about the fluorescent transition of  $\text{Cr}^{3+}$  in glasses<sup>[4,5]</sup>. We have investigated the spectroscopic characteristics of  $\text{Cr}^{3+}$  in phosphate, fluorophosphate and fluoride glasses<sup>[6]</sup>. The measured and calculated peak wavelengths of absorption bands, their optical transitions, Racah parameter B and ligand field strength Dq of  $\text{Cr}^{3+}$  ion in glasses are listed in Tab.1. The calculated results based on the ligand field theory are consistent with those obtained from the experiments. The temperature dependence of fluorescence spectra and lifetime of  $\text{Cr}^{3+}$  doped glasses are shown in Fig.1 and 2. The peak wavelengths of fluorescence of  $\text{Cr}^{3+}$  in phosphate, fluorophosphate and fluoride glasses are  $11290\text{cm}^{-1}$ ,  $11520\text{cm}^{-1}$  and  $11680\text{cm}^{-1}$  respectively. It can be found that in order of phosphate--fluorophosphate--fluoride glasses, the ionic contribution of the chemical bond between the central activated ions and ligands increases gradually with the increase of Racah parameters B. The corresponding peak positions of absorption spectra, as well as those of fluorescence spectra shift to the shorter wavelengths.

Tab.1 Measured and Calculated Absorption Peak Position, Correspondent Transition and Parameters B, Dq of Cr<sup>3+</sup> and Mo<sup>3+</sup> in Glasses

Ions	Glass	${}^4A_{2g} - {}^4T_{1g}(P)$		${}^4A_{2g} - {}^4T_{1g}(F)$		${}^4A_{2g} - {}^4T_{2g}$	${}^4A_{2g} - {}^2E(G)$	10Dq	B
		Meas. cm <sup>-1</sup>	Cal. cm <sup>-1</sup>	Meas. cm <sup>-1</sup>	Cal. cm <sup>-1</sup>	Meas. cm <sup>-1</sup>	Meas. cm <sup>-1</sup>		
Cr <sup>3+</sup>	Phosphate	33400	33700	21900	21600	15100	14500	15100	667
	Fluoro-phosphate	34200	34590	22600	22200	15400	14700	15400	706
Mo <sup>3+</sup>	Phosphate	-	-	27900	27910	22400	15800	22400	500



a. Phosphate glasses  
 1) 80K 2) 109K  
 3) 153K 4) 204K  
 b. Fluorophosphate glasses  
 1) 91-124K 2) 156K  
 3) 189K 4) 237K  
 c. Fluoride  
 1) 85K  
 2) 176K

Fig.1 Temperature Dependence of Fluorescence Spectra of Cr<sup>3+</sup> in Glasses

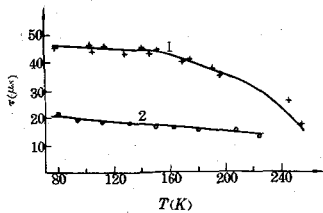


Fig.2 Temperature Dependence of Fluorescent Lifetime of Cr<sup>3+</sup> in Glasses  
 1) Fluorophosphate glasses  
 2) Phosphate glasses

The experimental results also show that the increase of fluorescence intensity, lifetime and weakening of temperature quenching effect of glasses from phosphate to fluorophosphate can be considered as the decrease of non-radiative transition probability. As a comparison absorption and fluorescence spectra of Mo<sup>3+</sup>(4d<sup>3</sup>) in phosphate glass have also been studied. The experimental results are shown in Tab.1 and Fig.3.

There is an argument about the fluorescent transition of Cr<sup>3+</sup> in glasses, because the upper energy levels  ${}^4T_{2g}$  and  ${}^2E_g$  are very close to each other. Compared with the fluorescence spectra of Mo<sup>3+</sup>, the emission from Cr<sup>3+</sup> doped glasses is characterized by its wider bandwidth (2500-3000cm<sup>-1</sup>) and shorter lifetime (~50ns), it belongs to the spin-allowed transition. So we consider that the ligand field strength Dq of Mo<sup>3+</sup>

in glasses is larger in comparison with that of  $\text{Cr}^{3+}$ , the near infrared emission is correlated with  ${}^4\text{T}_{2g} - {}^4\text{A}_{2g}$  for  $\text{Cr}^{3+}$  and  ${}^2\text{E}_g - {}^4\text{A}_{2g}$  for  $\text{Mo}^{3+}$ .

Furthermore, laser excited fluorescence of  $\text{Cr}^{3+}$  ion in glasses has been investigated. We used different laser wavelengths for excitation, such as  $0.5106\mu$  and  $0.5782\mu$  (copper vapor laser),  $0.57\text{--}0.62\mu$  (flash lamp pumped dye laser) and  $0.6328\mu$  (He-Ne laser). The laser excited emission spectra of  $\text{Cr}^{3+}$  in fluorophosphate glasses are shown in Fig.4. Only small variation in  ${}^4\text{T}_{2g} - {}^4\text{A}_{2g}$  fluorescence could be noticed. This agrees with the results measured by Brawer and White<sup>[7]</sup>. It is evident that site to site variation is not sensitive to laser excitation due to the phonon-photon coupling assisted energy level broadening and the dependence of energy gap between excited and ground states on Dq value.

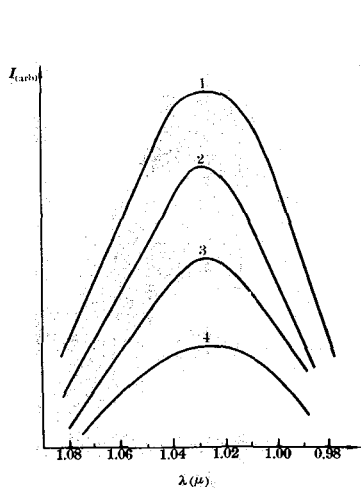


Fig.3 Temperature Dependence of Fluorescence Spectra of  $\text{Mo}^{3+}$  in Phosphate Glasses

- |         |         |
|---------|---------|
| 1) 92K  | 2) 110K |
| 3) 173K | 4) 249K |

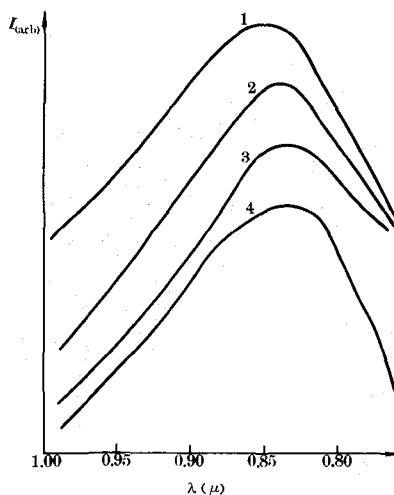


Fig.4 The Dependence of Fluorescence Spectra of  $\text{Cr}^{3+}$  in Fluorophosphate Glasses on the Excited Laser Wavelength

- |                      |                               |                                  |
|----------------------|-------------------------------|----------------------------------|
| 1) broad band        | $\lambda_E = 0.85\mu\text{m}$ | $\Delta\lambda_L = 192\text{nm}$ |
| 2) 5106A Cu laser    | 0.84                          | 176                              |
| 3) 5782A Cu laser    | 0.836                         | 173                              |
| 4) 6328A He-Ne laser | 0.834                         | 185                              |

Then we put more emphasis on the measurement of time resolved and laser excited emission spectra. After laser excitation a group of  $\text{Cr}^{3+}$  ions absorbed laser light and statistically distributed at the excited state. In the period of relaxation some  $\text{Cr}^{3+}$  ion sites with larger energy gap between  ${}^4\text{T}_{2g} - {}^4\text{A}_{2g}$  states or with larger Dq value possess longer lifetime, so that they emit late and their fluorescence

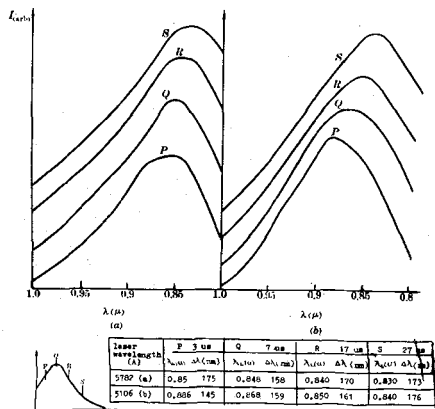


Fig.5 Time Resolved Spectra of Cr<sup>3+</sup> in Fluorophosphate Glasses (Cr<sub>2</sub>O<sub>3</sub> 0.5% wt, room temperature)

spectra shift to shorter wavelength region. Fig.5 shows the time resolved and laser excited emission spectra of Cr<sup>3+</sup> ions in fluorophosphate glasses taken at different decay time. The fluorescence line narrowing and peak wavelength shifting can be clearly observed. The emission spectra move to shorter wavelength region with longer decay time after excitation. Cr<sup>3+</sup> ion sites excited by 5106A laser line (located at the longer wavelength side of <sup>4</sup>T<sub>1g</sub> absorption band) possess smaller Dq value and exhibit more obvious line narrowing and shifting effect than those excited by 5782A laser line (located at shorter wavelength side of <sup>4</sup>T<sub>2g</sub> absorption band) which possess larger Dq value. Laser

line of 6328A is at the central part of <sup>4</sup>T<sub>2g</sub> absorption band, its excited emission spectra is similar to those of broad band excitation due to overlapping transition of different Cr<sup>3+</sup> sites. So that the laser excited and time resolved fluorescence line narrowing is a useful tool for studying the site structure of transition element ions in glasses.

References

[1] BAMFORD C.R., Phys. Chem. Glass., 3(1962) 189.  
 [2] BATES T., "Modern Aspects of the Vitreous State" Edit MACKENZIE J.D., 1962, 2, chap.5, Butterworthes, London.  
 [3] GAN FUXI, J. Chinese Silicate Soc., 6(1978) 41.  
 [4] KARAPETYAN G.O., KOVALYOV V.P., LUNTER S.G., Opt. & Spect. 19(1965) 951, (Russian).  
 [5] SHARP E.J., MILLER J.E., Phys. Lett., 30A(1966) 142.  
 [6] GAN FUXI, LIU HUIMING, Acta Optica Sinica, 2(1982)  
 [7] BRAWER S.A., WHITE W.B., J. Chem. Phys., 67(1977) 2043.