Review

# Fano's antiresonance and crystal-field study of $Cr^{3+}$ in metaphosphate glasses

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## ARTICLE INFO

## ABSTRACT

This work is devoted in first part to a study of the features observed on the $^4T_{2g}$ ($^4F$) absorption band of phosphate glasses containing $Cr^{3+}$. These features results from interaction of the $^2E_g$ ($^2G$) and $^2T_{1g}$ ($^2G$) sharp levels with the vibrationally broadened $^4T_{2g}$ ($^4F$) quasi-continuum via spin–orbit coupling and have been analyzed in the frame of the Fano's antiresonance model. In second part, the electronic structure of $Cr^{3+}$ ion occupying Oh site symmetry in the phosphate glasses is determined by the crystal-field ana-lysis. The influence of the different oxides ($Na_2O$, $PbO$, $ZnO$) on the spectroscopic properties of $Cr^{3+}$ is evaluated. In metaphosphate glasses, we found that $Na_2O$ and $PbO$ oxides act as glass modifiers while $ZnO$ enters the glass forming network.

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## 1. Introduction

Phosphate glasses have several advantages due to their super-ior physical properties: high thermal expansion coefficient, low melting and softening temperatures, high electrical conductivity and high ultraviolet and far-infrared transmissions [1–5]. There are widely used in fast ion conducting materials [6,7], laser hosts, glass-to-metal seals, IR transmission components, energy storage devices and solid state batteries. More recently, their potential use as bio-materials has been studied [8–10]. Phosphate glasses doped

with transition metal ions attract much attention because of their interesting applications in solid state lasers [11], luminescent solar energy concentrators [12] and optical fibers for communication devices [13]. Many studies have been carried out on the phosphate glasses containing $Cr^{3+}$ [14,15].

The oxide glasses doped with $Cr^{3+}$ are of great interest due to their high nonlinear optical parameters. Actually the $Cr^{3+}$ ions lead to the enhancement of the second harmonic generation SHG and the Racah parameters play crucial role. The change of valence states of $Cr^{3+}$ ions is responsible of the formation of the local charge density which is characteristic of the SHG [16].

The investigated phosphate glasses in this study are namely sodium metaphosphate ($Na_2O–P_2O_5$ called NaP), lead metaphosphate

(PbO–$P_2O_5$ called PbP) and zinc metaphosphate (ZnO–$P_2O_5$ called ZnP). $P_2O_5$ is a glass former oxide and the divalent oxides (PbO and ZnO) have a different role than the one of $Na_2O$. These two divalent oxides are accepted by most glass scientists to behave in a dual role, partly as modifier and partly as glass former within the glass network while $Na_2O$ exhibits only the role of modifier [17,18]. The optical visible absorption spectra of $Cr^{3+}$ doped phosphate glasses of the three varieties were measured by Marzouk et al. [14] at room temperature. These spectra consist of broad absorption bands with the presence of features which are attributed to the d–d transitions of the active center $Cr^{3+}$ with $3d^3$ configuration.

In this work, we firstly focus the study on the features observed in the low absorption bands of $Cr^{3+}$ ions in the phosphate glasses using the Fano's antiresonances model. These spectra consist of broad absorption bands attributed to spin-allowed d–d transitions of center $Cr^{3+}$ with the presence of features related to spin-forbidden d–d transitions. In many published works on $Cr^{3+}$-doped glasses [14,19–24] the interpretation of the additional features is incorrect in view of the Fano's antiresonances model [25]. The features have been regarded as peaks while they are in fact dips, leading to wrong energies values. In a second step, we present a detailed crystal-field analysis of electronic energy levels of $Cr^{3+}$ in the phosphate glasses. This analytical study is based on the Racah tensor algebraic method and was carried out for the $Cr^{3+}$ with an $O_h$ site symmetry. For the electronic structure study with crystal-field theory, we have added a corrective term in the Hamiltonian ($H_{Trees}$) in order to improve the precision of the theoretical calculations. Moreover, we have taken into account the splitting of the Stark levels under the spin–orbit interaction. The majority of the published works do not consider this interaction because of the unavailability of spin–orbit coupling constant.

We choose to study metaphosphate glasses with different cations ($Na^+$, $Pb^{2+}$ and $Zn^{2+}$) to evaluate the variation of Racah $B$, $C$ parameters and crystal-field Dq parameters and to understand the role of each cation on the spectroscopic properties of $Cr^{3+}$.

## 2. Experimental support

The theoretical analysis realized in this work is based on the experimental spectroscopic data obtained by Marzouk et al. [14]. The optical absorption spectra of 0.1 wt% $Cr^{3+}$-doped phosphate glasses $Na_2O–P_2O_5$ and $XO–P_2O_5$ (X=Pb and Zn) are presented in Fig. 1. In the spectra, two quartet broad bands are attributed to the spin-allowed d–d transitions in $O_h$ symmetry: $^4A_{2g}$ ($^4F$)→$^4T_{2g}$ ($^4F$) and $^4A_{2g}$ ($^4F$)→$^4T_{1g}$ ($^4F$). In addition, features are also observed on
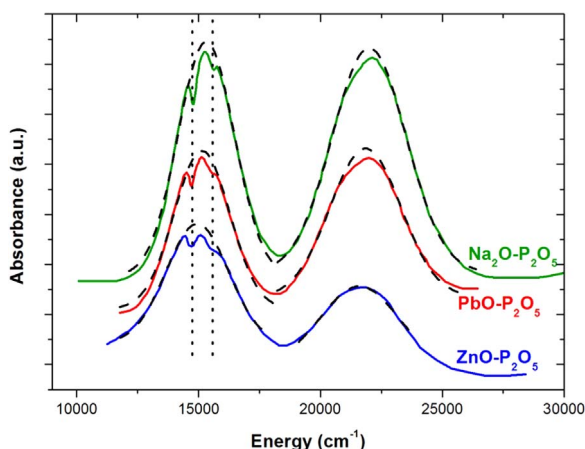


**Fig. 1.** Optical absorption spectra of $Cr^{3+}$ doped phosphate glasses (solid line) at room temperature [14] and Gaussian adjustments (dashed line).

**Table 1**
The energy values of the different transitions ($cm^{-1}$) for $Cr^{3+}$ in phosphate glasses [14].

| transitions | $Na_2O–P_2O_5$ | $PbO–P_2O_5$ | $ZnO–P_2O_5$ |
| --- | --- | --- | --- |
| $^4A_{2g}(^4F)→^2E_g(^2G)$ | 14,598 | 14,493 | 14,598 |
| $^4A_{2g}(^4F)→^4T_{2g}(^4F)$ | 15,151 | 15,151 | 15,038 |
| $^4A_{2g}(^4F)→^2T_{1g}(^2G)$ | 15,873 | 15,723 | 15,625 |
| $^4A_{2g}(^4F)→^4T_{1g}(^4F)$ | 22,727 | 21,834 | 21,739 |

the $^4T_{2g}$ ($^4F$) absorption band of each phosphate glass in the vicinity of the sharps levels attributed to the spin-forbidden transitions from the quartet ground state $^4A_{2g}$ ($^4F$) to the doublet excited states $^2E_g$ ($^2G$) and $^2T_{1g}$ ($^2G$). The energies of all the above transitions given by Marzouk et al. [14] are listed in Table 1.

## 3. Theoretical background

The features observed on the $^4T_{2g}$ ($^4F$) absorption band of $Cr^{3+}$ in the vicinity of the sharps levels attributed to the transition from ground state $^4A_{2g}$ ($^4F$) to the excited state $^2E_g$ ($^2G$) and $^2T_{1g}$ ($^2G$) will be analyzed by the Fano's antiresonance model [25].

On the following section we remember briefly the Fano's antiresonance and crystal-field theories. Also, we discuss the structural aspect of glass.

### 3.1. Fano's antiresonance method

Antiresonances features are analyzed by means of the Fano's profile function $R(\omega)$. This function is obtained from the ratio of the experimental absorption spectrum to the background spectrum, the latter being obtained by fitting the wings of the experimental absorption spectrum with a Gaussian function. In the notation of Sturge et al. [26], the theoretical profile $R(\omega)$ is given by:

$$R(\omega) = 1 + \sum_i \rho_i^2 \frac{q_i^2 + 2q_i\xi_i - 1}{1 + \xi_i^2} \qquad (1)$$

where:

$$\xi_i = \frac{\omega - \omega_{ri}}{\gamma_i}, \quad q_i = \frac{\langle \phi_i | z | \psi_0 \rangle}{\sqrt{\pi}\gamma_i \rho_i \langle \psi_{E_i}^{(d)} | z | \psi_0 \rangle}$$

$$\gamma_i = \pi \left| \langle \psi_{E_i}^{(a)} | H_i | \varphi_i \rangle \right|, \quad \rho_i = \langle \psi_{E_i}^{(a)} | \psi_{E_i}^{(d)} \rangle$$

The index $i$ ranges over the number of sharp levels (two in our case, $i=1$ for $^2E_g$ ($^2G$) and $i=2$ for $^2T_{1g}$ ($^2G$)). Interactions between these sharp levels and the vibrationally broadened $^4T_{2g}$ ($^4F$) are neglected. $\varphi_i$ is the wave function of the sharp level in the absence of the interaction $H_i$ with the continuum (spin–orbit in our case). $\Phi_i$ represents a modification of $\varphi_i$ by the continuum and $\psi_0$ the ground state. $z$ is the optical operator (electric or magnetic dipole). $\psi_{E_i}^{(a)}$ and $\psi_{E_i}^{(d)}$ arise, respectively, by auto-ionization state of $\varphi_i$ and by direct transition from ground state $\psi_0$.

The four parameters $\rho_i^2$, $\gamma_i$, $q_i$ and $\omega_{ri}$ are to be fitted. is the overlap integral of and; this parameter gives the fraction of the band states that take part in the interference process and thus quantifies the relative intensity of the dip. $\gamma_i$ indicates the spectral width of the auto-ionized state $\varphi_i$. $q_i$ is a numerical index which characterizes the line profile: $|q_i| \sim 0$ the line shape is a though (antiresonance), $|q_i| = \infty$ the line shape is a peak . Finally $\omega_{ri}$ is the resonance energy which is slightly shifted due to the interaction with the continuum, compared to the resonance energy for the unperturbed sharp absorption line.