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Optical coefficients and microstructure of fluoroborate glasses doped with europium and silver

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Abstract In this work we have prepared fluoroborate glasses doped with Eu^{3+} containing small silver particles and characterized by X-ray diffraction and electron microscopy. The optical properties of these samples were studied by measuring the reflectance between 460-4000 cm^{-1} and the absorbance in the far infrared, visible and ultraviolet. Electron microscopy investigation, together with Electron Diffraction have shown two main features: a) heterogeneity in the concentration of silver particles and b) a highly inhomogeneous size distribution of particles, with an average diameter of 3.4nm.

1. Introduction

Search for new efficient luminophors, laser and optical-fiber materials has stimulated the production of new fluorine-contaíning glasses. Among these, a class of glasses based on fluorides of alkali-earth metals and boron oxide is particularly important[1-3].

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Recently, it has been observed that the emission yield of Eu^{3+} ions in fluoroborate glasses can be substantially enhanced if the glasses contain very small silver particles[4]. In connection with the Surface Enhanced Raman Scattering (SERS) phenomenon[5], this effect can be explained through the interaction between the plasmons, localized on the metallic particles, and the emitting ions[4]. It happens that the efficiency of this process, and more generally the optical properties of these materials, depend strongly on the particle concentration, size distribution and structure. Further, these parameters are necessary to characterize these glasses as host media in which multiphoton and/or energy transfer processes occur[6].

This work is primarily concerned with the study of some opticai coefficients and microstructure of these composite media in order to provide informations for a detailed forthcoming work on the quantum yield of the Eu^{3+} emission in these glasses. We present, in the next sections, these results.

2. Experimental Procedure

The glass samples' preparation was the same as already described elsewhere[4]. Host composition was such that the weight of glass forming B_2O_3 and CaF_2 was $(B_2O_3 + CaF_2)/CaF_2 = 1.43$ and the dopping concentrations, by weight, were 3% Eu_2O_3 and 3% Ag.

To record the reflectance and absorption spectra in the region of small absorption a polished parallel-flat plate with a diameter of $\approx$ 13mm and a thickness of 3.55mm was used. For the transmission spectrum in the region of high absorption, a small part of the sample was melted in a platinum crucible at 1200^0 C and fine layers of 3.5μm thickness were blown.

The reflectance spectrum in the region 460 - 4000 cm^{-1} was recorded with a Jasko DS - 301 spectrophotorneter. The absorption spectra in the visible and ultraviolet were recorded with a Hitachi-EPS-3T spectrophotometer while in the far infrared a Hitachi-FIS-3 spectrophotometer was used.

3. Results of the optical study

Numerical values of the absorption coefficient $K(cm^{-1})$ in the long wavelength edge of the transparency region are given in table 1. The reflection spectrum, in the infrared, is presented in fig. 1.

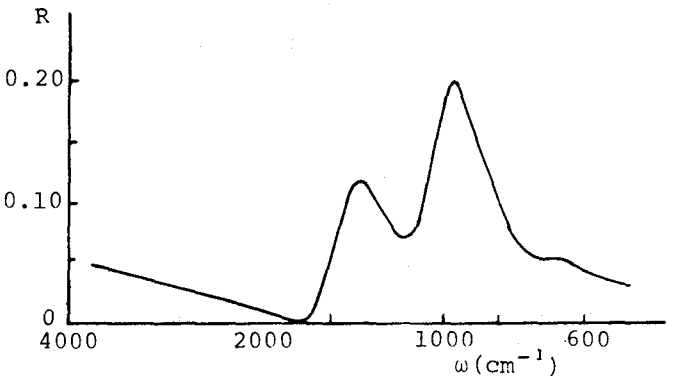

Fig.1 - Reflectance spectrum for the B_2O_3-CaF_2 glass.

Table 1 - Values of absorption coefficient K for the long wave edge of the transparency region.

$\omega[cm^{-1}]$	4000	3800	3600	3500-3240	3200	3100	3000
K $[cm^{-1}]$	1.6	2.05	4.1	5.7	6.7	8.5	11

Using samples of very thin glass layers, with a sufficient homogeneity by depth, allowed us to determine the dispersion of the refraction index, $n(\lambda)$, in the u.v. and visible, by an analysis of a well-resolved interference pattern having 12 sharp maxima (0.624, 0.580, 0.547, 0.525, 0.488, 0.462, 0.441, 0.422, 0.404, 0.386, 0.371, 0.358μm). The value of the refraction index necessary to decipher the interference pattern was obtained by using the data on reflection for a high-frequency slope of

the minimum of the reflectivity R. This procedure turned out to be possible due to the use of a DS-301 spectrophotometer with a double monochromator and with an intermediate slit that permits one to get rid of the diffused light that leads to erros in the photometric measurements in the regioon of small reflection. As an etalon an optical wedge made of CaF_2, for which the dispersion is well known, has been used.

Knowing the values of the reflectivity at three points of the slope, we found three values of the refraction coefficient which allowed us to determined the dispersion constants n_0^2, A_0 and λ_0 in the equation

$$n^2 = n_0^2 + \frac{a_0}{1 - \left(\frac{\lambda_0}{\lambda}\right)^2} \tag{1}$$

In this case $n_0^2 = 2.347$, $A_0 = 0.435$, $\lambda_0 = 7.40\mu$m.

For the interference bands from a film the following relation has been used

$$m\lambda_m = n(\lambda_m)d \tag{2}$$

where m is the interference order of the band and d is the film thickness. Assuming that $n(\lambda)$ is nearly constant in the interval $\lambda_m - A_{+1}$, we have

$$\frac{\lambda_m}{\lambda_{m+1}} = \frac{m+1}{m} \tag{3}$$

Using the values $A = 0.624\mu$m and $\lambda_{m+1} = 0.580\mu$m we obtain m = 13. Now taking the values of $\lambda_{13} = 0.624\mu$m and $n(\lambda_{13})$ determined from eq.(1) we restored a dependence of $n(\lambda)$ for the range 0.624-0.358μm by using a relation that could be derived from eq.(2).

$$n(\lambda_k) = \frac{m\ \lambda_m}{k\ \lambda_k} n(\lambda_m) \tag{4}$$

A set of $n(\lambda_k)$ obtained in this way and the dependence of the refraction index in the infrared as given by eq.(1) can be well described by the united dispersion relation

$$n^2(\lambda) = 1.857 + \frac{0.49}{1 - \frac{0.06}{\lambda^2}} + \frac{0.435}{1 - \frac{54.7}{\lambda^2}} \tag{5}$$

which is valid for transparency range of the glass.

Using the advantage that the obtained glass films are not only homogeneous by depth but they also have a sufficient square dimension, we recorded the absorption spectrum (which gives the values of Kd) in the ***1600-30*** cm^{-1} region including all strong absorption bands. To find out the dependence of K with $\omega(\omega \quad \lambda^{-1})$ it is, initially, necessary to know the value of K for a given frequency. The reflectivity R at normal angle of incidence is determined by the well known expression

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{6}$$

where $k = K/4\pi\omega$. In the reflection minimum $n = 1$, i.e. $K = 8\pi\omega_{min.}R_{min}^{1/2}$. From the reflection spectrum $\omega_{min.} = 1562cm^{-1}$, $R_{min.} = 0.001$ and therefore $K(1562\ cm^{-1}) = 1241\ cm^{-1}$. From this value, together with the absorption spectrum, we could establish the dependence of K with *w*. This is shows in fig.2.

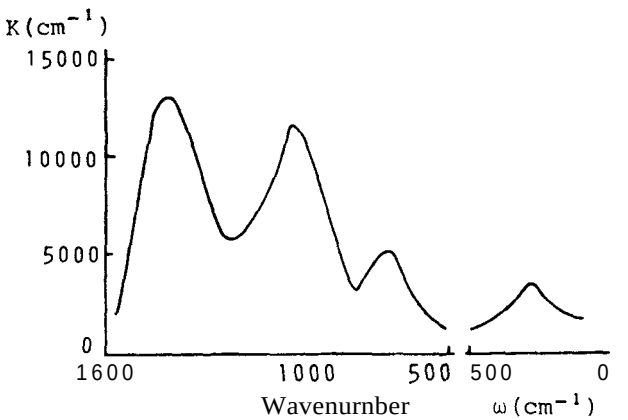

Fig.2 - Absorption spectrum for the B_2O_3-CaF_2 glass.

Expanding, according to an additive scheme, the function given graphically in fig. 2 we have determined the integrated intensities. A,, of the individual absorption bands. The results are given in table 2. A comparison of these data with those derived from eq.(5) shows that in the **3200** cm^{-1} > w > 1562 cm−1 range a term that gives an effectivecontribution to the dispersion, caused by bands in the infrared, can be written as a sum of only two terms corresponding to bands 1 and 2. It appears that an effective value of the frequency $\omega_{eff} = 1352$ cm^{-1} in eq.(4) is close to ω_1, and for $A_{eff} = 0.435$ (A_0 in eq.(1)), only a contribution from band 2 is important. As to bands 3 and 4, in this range, their influence may be neglected.

Table 2 – Characteristics of the infrared absorption bands.

number of band (i)	1	2	3	4
ω_i [cm^{-1}]	1385	990	704	230
A_i	0.27	0.39	0.343	4.32
localization of vibrations [7]	[BO_3]	[BO_4]	[BO_3]*	[CaF_2]

* Oxygen atoms are partially substituted by fluorine atoms.

4. Electron microscopy and diffraction structural investigation

To prepare the electron microscopy (EM) specimen the glass was cut by a wire saw in small strips of 100μm thickness. With a conducting adhesive the strips were glued together. A mechanical thinning, from both sides in the direction perpendicular to the glued surfaces until 70μm, was made. After that, the specimens were thinned by argon-ion (Ar+) bombardment until a hole appeared. The ion energy was 5kV, and the angle of incidence was 12-15'.

To prevent the specimens from static charge during EM-investigation, a carbon film 2nm thick was surface-sputtered. The areas suitable for EM-investigation were near a conducting adhesive layer.

Transmission electron microscopy was carried out by using a Philips EM-400 at an operating voltage of 100kV in dark-field mode with a beam inclination of 11 m rad and an objective aperture of 30 μm. Due to low image intensity, an exposition of up to 90s was used.

The EM micrographs (fig.3) reveal images of fine particles with dimensions 2-150nm. Estimated from 60 particles, the average size is 3.4nm. The particle concentration on the micrographs is 5 x 10^{12} cm^{-2}. Taking into account that the specimen thickness is 5-10nm, the particle concentration was estimated to be 5 x 10^{17} – 1 x 10^{18} cm^{-3}.

Electron diffraction investigation shows (fig.3a, inset) that the particles are randomly oriented Ag precipitates. This is confirmed by the micrographs. At severa1 high-resolution pictures of particles (fig. 3b), lattice images with a 0.24nm periodicity were revealed.This is in good agreement with Ag interplanar distance 0.236nm for [111] strong reflection.

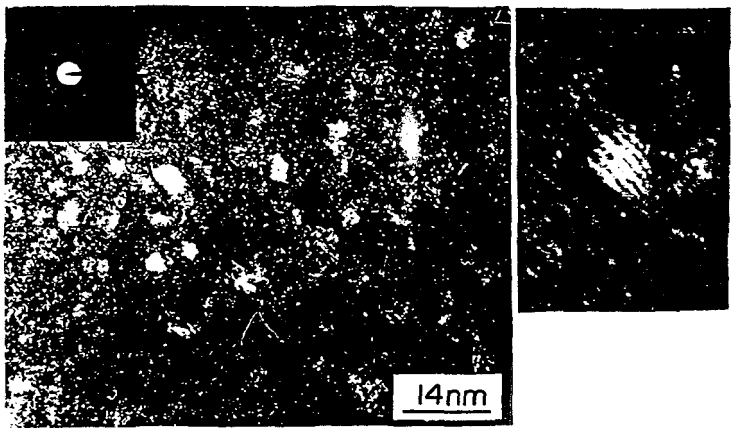

Fig.3 - (a) Dark-field image of sample. Selected area electron diffractogram is in inset. (b) Dark-field image of the particle with interplanar distance 0.24nm.

At the same time, for some particles on the high-resolntion images (fig.4) and optical diffractograms (fig. 4a, inset) two periodicities can be seen: 0.38

and 0.48nm. These values can be attributed to a binary compound as Ag_5Eu which crystallises into a hexagonal lattice (cell parameters: $a = 0.56201$nm, $c = 0.4639$nm, space group P6/mmm)[8].

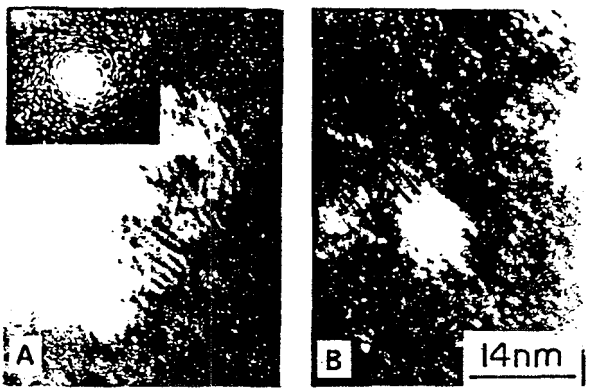

Fig.4 - High-resolution dark-field irnages of Ag_5Eu particles. Optical diffractogram frorn *the* particle *is in* inset.

These results are very preliminar and are obtained from first structural attempts. As the size, shape and concentration of the metallic particles are quite dependent on the preparation conditions, many different samples must be observed in order to draw stronger conclusions. As mentioned in the introduction, these structural features have a direct influence on the fluorescence enhancement effect since the complex dielectric function of the composite medium depends directly on them.

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Resumo

Neste trabalho foram preparados vidros fluoroboratos, dopados com Eu^{3}+, contendo pequenas partículas metálicas e caracterizados por difração de raios-X e microscopia eletrônica. As propriedades óticas dessas amostras foram estudadas medindo-se os espectros de reflectância entre **460** e **4000** cm^{-1} e absorbância no infravermelho longínquo, visível e ultravioleta. Os principais resultados observados a partir da miscroscopia eletrônica e difração de elétrons foram: a) heterogeneidade na concentração de partículas de prata e b) uma acentuada heterogeneidade na distribuição de tamanho dessas partículas, com um diâmetro mkdio de **3.4** nm.