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Magneto-optical investigations of rare earth doped sol–gel derived silicate xerogels

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ABSTRACT

Rare-earth doped xerogels (Eu^{3+}, Sm^{3+}, Ho^{3+}, Pr^{3+}) were prepared by using the sol–gel method and their magneto-optical and optical properties have been studied. The Magnetic Circular Dichroism (MCD) spectra are quite similar to those recorded in the RE-doped fluorozirconate glasses; the fine structures shown by the MCD spectra are better resolved compared to the optical absorption spectra. The MCD technique has been correlated with optical measurements in order to investigate the site symmetry in the particular case of Eu^{3+}-doped xerogel and oxyfluoride glasses. In the xerogel, coordination symmetry around the Eu^{3+} ions is close to $\underline{D}_{3h}$ and is lower in the oxyfluoride glass.

1. Introduction

There is considerable interest in sol–gel technology with regard to rare-earth (RE) luminescent materials for various applications in luminescent solar concentrators, tunable lasers, active waveguide sensors for environmental and biological impurities, waveguides and materials for non-linear optics ([1] and references therein). The sol–gel method has several advantages over conventional "melt-quenching" glass preparation methods such as the wide range of compositions achievable, lower processing temperature, easier composition control and better chemical homogeneity of the product.

Optical spectroscopy methods such as absorption and photoluminescence (PL) are well known and used for the study of the optical properties associated with the RE dopant ions. The absorption spectra are due to superposition of different electric-dipole (ED) and magnetic-dipole (MD) transitions of the RE ions [2]. Additional effects due to the multiplets degeneracies, inhomogeneous broadening and crystal field splittings make the analysis difficult. Magnetic Circular Dichroism (MCD) is a very useful method for the detection of the overlapping transitions in the absorption spectra [3]. Compared with the optical absorption the MCD spectrum contains more information since in addition to the intensity the MCD signal is characterized by its sign (positive or negative), which is related to the symmetry of the RE environment [3]. The usefulness of the MCD technique has been proved in the particular case of RE^{3+}-doped fluorozirconate (ZBLAN) glasses and aqueous solution [4–10].

In this paper, we report MCD and optical absorption investigations on RE^{3+}-doped xerogels. The MCD and photoluminescence measurements have been used to investigate the site symmetry in the particular case of Eu^{3+}-doped xerogel and oxyfluoride glasses.

2. Experimental

2.1. Samples preparation

Transparent bulk silicate xerogels doped with (1%) RE=Eu^{3+}, Sm^{3+}, Ho^{3+} and Pr^{3+} were prepared by the sol–gel method according to the methods described in Ref. [11]; concentration of the RE ions diluted in the xerogel was 0.291 mol l^{-1} [12]. Tetraethyl orthosilicate (> 99%), $Si(OC_2H_5)_4$ (Aldrich), trifluoroacetic acid (> 99%), CF_3COOH (Aldrich), barium acetate (> 99%), $(Ba(CH_3COO)_2$ (Aldrich) and rare-earth (III) acetate hydrate $Eu(CH_3COO)_3 \cdot xH_2O$) (> 99%; Aldrich) were used as starting materials.

In the first step TEOS diluted with equal volume of ethyl alcohol was hydrolyzed with water under constant stirring and a TEOS solution was obtained. The volume ratio of TEOS:H_2O:CH_3COOH was 7:2:1. Glacial acetic acid was used here as the catalyst. Required amounts of barium acetate and rare-earth (III) acetate hydrate were disolved in TFA with molar ratio of 1:10 and a small amount of water was added; a TFA solution was obtained.

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Then the TFA solution was added dropwise to the TEOS solution, followed by stirring for 30 min at room temperature. The mixed solution was then poured into the culture vessel and covered to form the gel, which was aged for 2 weeks at room temperature and then dried at 120 °C within 7 days to form the xerogel.

A glass with the composition of $62SiO_2$–$17ZnF_2$–$20BaF_2$–$1EuF_3$ (mol%) has been prepared from the reagents and materials by the melt-quenching technique. The constituent chemicals were melted in a corundum crucible at 1400 °C in open atmosphere for 45 min, poured on a preheated copper plate, where it was kept to relinquish the inner stress, and then cooled naturally to room temperature.

2.2. Optical measurements

The MCD measurements have been recorded in the 300–650 nm range using a Jasco J-815 CD spectro-polarimeter with a static magnet of 1.4 T; the resolution was set to 1 nm. For the CD calibration we used (1S)-(+)-10-camphorsulfonic acid salt and ammonium salt (ACS).

Optical absorption spectra have been recorded in the UV–vis region 200–800 nm, using a Cary spectrophotometer. For the photoluminescence (PL) spectra we used a Horiba Jobin Yvon spectrophotometer. PL lifetime measurements have been performed using a chopped 10 mW laser diode centered at 402 nm; the luminescence signal has been detected with a photomultiplier and scanned with a box-car integrator.

A Fourier transform infrared spectrometer (FTIR; Model Spectrum BX, Perkin Elmer Instruments) was used for the FTIR measurements. A mixture of the gel powder and KBr powder was used for infrared spectroscopy studies.

3. Theoretical details

The MCD signal gives the difference between the left and right circularly polarized light, more precisely between the optical densities or absorbances of the polarized components of light. The difference between the optical densities of left and right circularly polarized lights for an absorption band can be written as [13]

$$\Delta D = \left(A\frac{\partial f(E)}{\partial E} + \left(B + \frac{C}{kT}\right)f(E)\right)H \quad (1)$$

where $f(E)$ is the shape function of the absorption band and H is the applied magnetic field. These three terms are connected with the lifting of degeneracy of the ground state and excited states, in the particular case of the RE ions with changes of the populations via new Boltzman distributions or mixing of the electronic levels. The first A term is connected to the diamagnetic properties of the ions due to the Zeeman splitting of the electronic levels in the magnetic field. The B term is connected to the mixing of the electronic levels in the magnetic field and the C term is temperature dependent, being responsible for the paramagnetic properties of the RE ions. If the B term is negligible, i.e. when the electronic levels are shifted energetically enough such that the magnetic field cannot mix the levels, the line-shape of the MCD signal is similar to the first derivative of the absorption band and changes its sign at the absorption maximum.

4. Results

4.1. FTIR spectroscopy

The FTIR spectra of Eu^{3+}-doped xerogel and oxyfluoride glass samples in the spectral region 400–1400 cm^{-1} are shown in Fig. 1; the spectra for the other RE^{3+}-doped xerogels are essentially the same. In the xerogel sample the bands at 455, 800, 1085, 1150 and 1200 cm^{-1} are attributed to the Si–O–Si bonds; the band at 950 cm^{-1} was assigned to the Si–O stretching mode vibration [14] and a small peak at 725 cm^{-1} is due to absorbed CO_2. The shoulder at around 550–600 cm^{-1} was observed in un-doped xerogel too (not shown) and is due to Ba–O bond vibrations [15]. The spectrum recorded in the oxyfluoride glass sample is relatively similar to the one recorded in the xerogel (except a broadening of the maxima). The fraction of the non-bridging oxygen (NBO) is higher because of the network modifiers (Ba^{2+} and Zn^{2+}) and therefore the spectrum shows a strong peak at about 970 cm^{-1} due to the stretching mode Si–O with one non-bridging oxygen per SiO_4 tetrahedron (Si–O–NBO) [14].

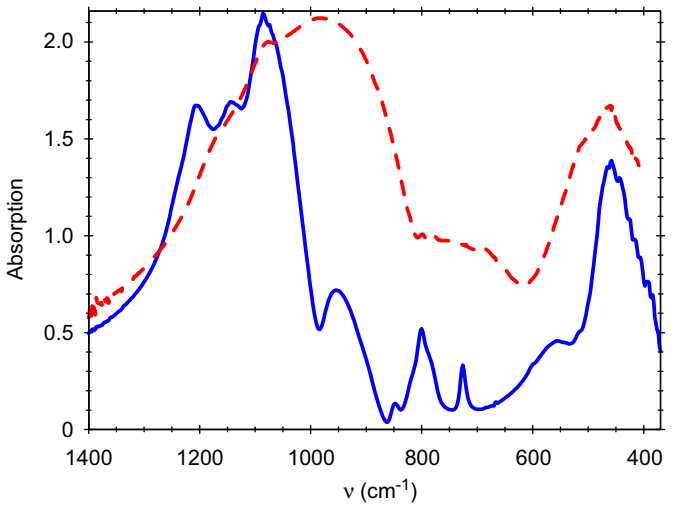

Fig. 1. FTIR spectra recorded of Eu^{3+}-doped xerogel (solid curve) and oxyfluoride glass (dashed curve).

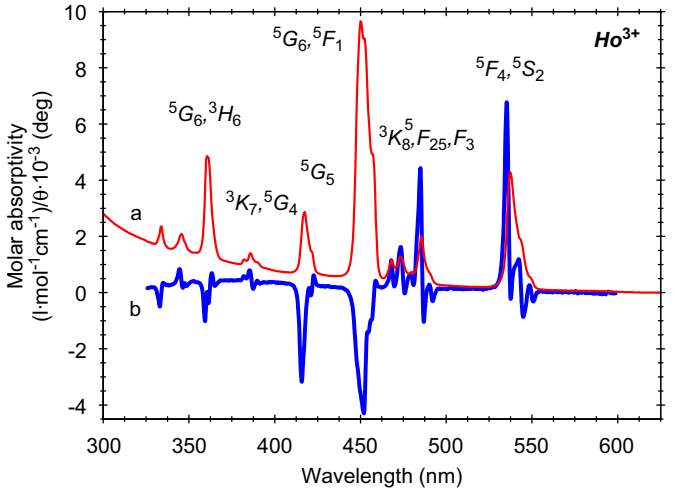

Fig. 2. Optical absorption (curve a) and MCD spectra (curve b) recorded of Ho^{3+}-doped xerogels; the transitions from the ground state to the various excited states [2] are indicated.

4.2. Optical absorption and MCD spectroscopy

The optical absorption and MCD spectra recorded on RE^{3+}-doped xerogels are depicted in Figs. 2–5. The spectra show complex and composed curves due to superposition between different magnetic-dipole (MD) and electric-dipole (ED) transitions of the RE ions. These are due to transitions of the RE^{3+} ions