

Optical spectroscopy of lanthanide ions in ZnO–TeO₂ glasses[☆]

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Abstract

Zinc tellurite glasses of compositions 19ZnO–80TeO₂–1Ln₂O₃ with Ln = Eu, Er, Nd and Tm were prepared by melt quenching. The absorption spectra were measured and from the experimental oscillator strengths of the $f \rightarrow f$ transitions the Judd–Ofelt parameters Ω_λ were obtained. The values of the Ω_λ parameters are in the range usually observed for oxide glasses. For Nd³⁺ and Er³⁺, luminescence spectra in the near infrared were measured and the stimulated emission cross sections σ_p were evaluated for some laser transitions. The high values of σ_p , especially for Nd³⁺, make them possible candidates for optical applications. Fluorescence line narrowing (FLN) spectra of the Eu³⁺ doped glass were measured at 20 K, and the energies of the Stark components of the ⁷F₁ and ⁷F₂ states were obtained. A crystal field analysis was carried out assuming a C_{2v} site symmetry. The behaviour of the crystal field ratios B_{22}/B_{20} and B_{44}/B_{40} agrees reasonably well with the values calculated using the geometric model proposed by Brecher and Riseberg. The crystal field strength at the Eu³⁺ sites appears to be very low compared to other oxide glasses. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent times, glasses containing heavy network formers doped with luminescent lanthanide ions have attracted a considerable interest [1] due to their low vibrational frequencies which cause non-radiative relaxation [2] from the excited states

[☆] Dedicated to Professor Harald P. Fritzer on the occasion of his retirement.

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of the dopant ions to be inefficient. This can lead to interesting applications for the development of optical devices requiring high emission quantum yields, such as solid state lasers and optical amplifiers [3]. On the other hand, glasses containing heavy network formers and/or modifiers, can show interesting non-linear optical properties, and can find applications for second harmonic generation (SHG) after thermal poling [4,5]. In the case of Ln^{3+} doped materials, these properties could lead to the possible development of self-frequency doubling lasers.

Among these materials, particular attention has recently been devoted to the study of tellurite glasses. In fact, TeO_2 -based glasses are characterised by maximum phonon frequencies which are lower than for many common oxide glasses, such as silicates, borates, phosphates and germanates [6]. In addition, tellurite glasses show other favourable properties, such as good mechanical strength and chemical durability, low process temperature and excellent transmission in the visible and near IR up to 4.5 μm . These properties make tellurite glasses good candidates for the development of optical devices [3,7,8].

Zinc tellurite glasses $\text{ZnO}-\text{TeO}_2$ have been extensively investigated using vibrational spectroscopy [9,10] and neutron diffraction [11]. It was found that the building units of these materials are TeO_4 groups, where the four oxygens are located at four vertices of a trigonal bipyramid, TeO_{3+1} groups, which are similar to TeO_4 but with a long Te–O bond, and TeO_3 groups, where the oxygens are arranged at three vertices of a tetrahedron. The relative abundance of these units depends on the composition. Ln^{3+} doped zinc tellurite glasses have been studied for $\text{Ln} = \text{Pr}$ [7] and Nd [12,13], showing promise for technological applications and interesting properties. In particular, a substantial increase of the radiative lifetime of the $^4\text{F}_{3/2}$ state of Nd^{3+} was found in the case of $\text{ZnO}-\text{TeO}_2$ glasses upon partial substitution of ZnO with ZnF_2 [11]. However, no detailed results relative to the $f \rightarrow f$ transition probabilities and the local geometry of the sites accommodating the Ln^{3+} have been published so far. For this reason, we found it interesting to carry out a thorough study of the optical spec-

troscopy of a series of zinc tellurite glasses doped with Ln^{3+} . In this paper we report on the results obtained for a $20\text{ZnO}-80\text{TeO}_2$ glass host doped with Eu^{3+} , used as a structural probe for FLN spectroscopy [14], and with Nd^{3+} , Er^{3+} and Tm^{3+} ions which emit in the NIR region and are used for lasers and optical amplifiers [15].

2. Experimental

Zinc tellurite glasses of molar composition $20\text{ZnO}-80\text{TeO}_2$ and $19\text{ZnO}-80\text{TeO}_2-1\text{Ln}_2\text{O}_3$ with $\text{Ln} = \text{Nd}, \text{Eu}, \text{Er}$ and Tm were prepared by melting 10 g batches composed of analytical grade TeO_2 , ZnO and Ln_2O_3 in an alumina crucible for 40 min at 750°C, followed by quenching in air on a stainless steel plate. Samples were annealed for 17 h at 250°C, and subsequently cut and carefully polished for the optical measurements.

Electronic absorption spectra were measured at room temperature (293 K) in the ultraviolet, visible and near infrared regions using a Cary 05E Double Beam spectrophotometer, with air in the reference beam, a spectral bandwidth of 1 nm in the UV-VIS region and ranging from 3 nm at 850 nm to 1.5 nm at 1500 nm in the NIR region.

Low-resolution excitation and emission spectra were measured at room temperature using a Jasco FP 777 spectrofluorimeter. Decay curves of the luminescence were measured using a Perkin Elmer LS 50 luminescence spectrometer.

The near infrared luminescence spectra were measured at room temperature (293 K) using a custom-made apparatus (Laser Point) equipped with a 25 mW He–Ne laser (NEC), a grating spectrometer with a reciprocal dispersion of 24 $\text{\AA} \text{mm}^{-1}$ (Jobin Yvon HR640) and a liquid nitrogen cooled Ge detector (North Coast EO817L). The spectral bandwidth was 2.4 nm for the whole spectral range.

FLN measurements were obtained by exciting with a dye laser (Coherent CR599) operating with Rhodamine 6G pumped by an Argon laser (Coherent Innova 300). The laser had a typical linewidth (full width at half maximum, FWHM) of 0.8 cm^{-1} over the tuning range 17 210–17 380 cm^{-1} used in this work. The luminescence signal

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