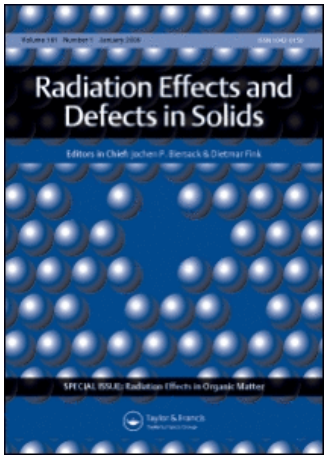

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Optical properties of $Zr_5Ti_7O_{24}:Eu^{3+}$ prepared by the sol–gel technique

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Thermal processes can lead to the creation of photoluminescence centers in sol–gel derived $Zr_5Ti_7O_{24}:Eu^{3+}$ (ZT:Eu^{3+}) systems. Photosensitivity starts with heat treatments at 700 °C in air. The photoluminescence excitation occurs in the 225–550 nm range. The emission spectra covers the 550–700 nm range and consist of several sharp lines associated with transitions between the stark components of the excited states of the $4f^6$ configuration to the ^7F_j states of the Eu^{3+} ion. The crystalline structure of the compound was obtained by X-ray diffraction techniques and is associated with a space group *Pbcn*. The thermal treatments in the 700–960 °C range have corresponding effects on both, the crystalline parameters and the optical properties of the europium ions. Time-resolved experiments were performed and the results are presented and discussed in order to get a better understanding of the effects of the thermal treatments on the Eu^{3+} transition lifetimes.

Keywords: Zirconium titanate; Sol–gel; Luminescence; Europium

PACS: 78.47.+p; 78.55.-m; 81.40.Tv

1. Introduction

Zirconium titanate-based ceramics have long been used in electronic applications where low-loss, temperature stable dielectric materials are required [1]. However, there are few works intended for explaining the optical properties of zirconium titanate ceramics [2, 3] and there are not reports, to the best of our knowledge, on doped zirconium titanate ceramics. On the other hand, it is known that the incorporation of rare earth ions in different solid state systems modify their optical properties. This allows producing new materials with novel optical properties to be considered in technological applications. In order to make a contribution in this field, we incorporate Eu^{3+} ions in the orthorhombic $Zr_5Ti_7O_{24}$ [4] crystalline lattice. The samples were prepared by the sol–gel technique. This method permits to reduce

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the annealing temperature as compared to the conventional solid state reaction synthesis. The samples obtained show a continuous change in their crystalline parameters as function of thermal treatment, in the room temperature (RT) to 960 °C temperature range. The first set of experimental data concerning structural and optical properties are presented and discussed in this paper.

2. Experiment

The $Zr_5Ti_7O_{24}$:Eu^{3+} (ZT: Eu^{3+}) samples prepared by the sol–gel technique were obtained from a solution consisting of a mixture of zirconium propoxide (70% in 1-propanol Fluka) and titanium isopropoxide (99.999% Aldrich) dissolved in acetic acid (99.8% Aldrich). Europium was incorporated to the solution as $Eu(NO_3)_3 \cdot 5H_2O$ (99.9% Aldrich) and finally water was added. The concentration was 2×10^{-2} Eu^{3+} ion/(Zr + Ti) mole. Heat treatments of the solid were performed at 100 and 200 °C during 12 h, to produce gel powders, which then were calcinated at different temperatures in the range 300–960 °C, with 0.5 h as dwell time in air. The Continuous Wave (CW) and time resolved photoluminescence spectra were obtained by using a Fluorolog (SPEX) spectrofluorometer FL111, fitted with a 450 W xenon lamp. The time resolved spectra and the lifetime measurements were acquired with the same apparatus but attaching the phosphorimeter 1934 D and a pulse xenon lamp with 40 μs pulse width pulses. The excitation and emission wavelengths were selected by two 0.34 Spex spectrometers. The signal detection was performed with a R-928 PMT. The spectrum deconvolutions were done with the PeakFit v4 software. In order to establish the crystalline structure of our samples, the diffractograms were obtained in a D-8 Advanced Bruker Instruments diffractometer. The angle step and the integration time were 0.05° in 2θ and 1 s, respectively. The potential and the current were 40 kV and 35 mA, respectively. The Rietveld refinement to obtain cell parameters was done on diffractograms recorded at different X-ray acquisition conditions, in order to improve the counting statistics: step 0.02° in 2θ and 9 s of integration time; the operating conditions on the X-ray tube were as previously indicated.

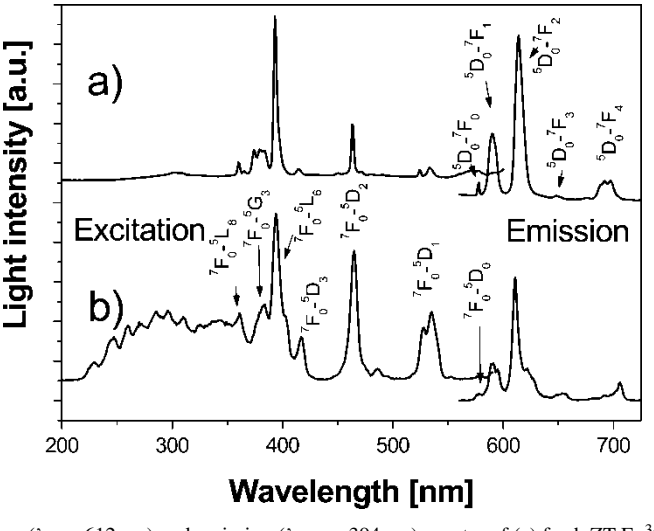

Figure 1. Excitation ($\lambda_0 = 612$ nm) and emission ($\lambda_{exc} = 394$ nm) spectra of (a) fresh ZT:Eu^{3+} and (b) annealed ZT:Eu^{3+} during 30 min at 960 °C samples.

3. Results and discussion

In figure 1, the RT characteristic emission and excitation spectra of our $Zr_5Ti_7O_{24}$:Eu^{3+} (ZT:Eu^{3+}) samples are shown. The spectra portrayed in figure 1(a) correspond to those observed in our fresh ZT: Eu^{3+} sample that has not been treated thermally just after its preparation by the sol–gel technique. On the other hand, figure 1(b) shows the spectra of a ZT:Eu^{3+} sample that has been treated at 960 °C for 30 min. In figure 1(b) the excitation spectrum shows a wide structured band in the range 215–390 nm with a maximum at around 295 nm. Currently experiments are being performed in our laboratory in order to identify the origin of this band.

Figure 2(a) portrays the Eu^{3+} emission and excitation spectra of our samples as a function of the annealing temperature of the sample in the RT-960°C range. In Figure 2 (b), we also present the results of the X-ray diffraction experiments performed in our samples in order to

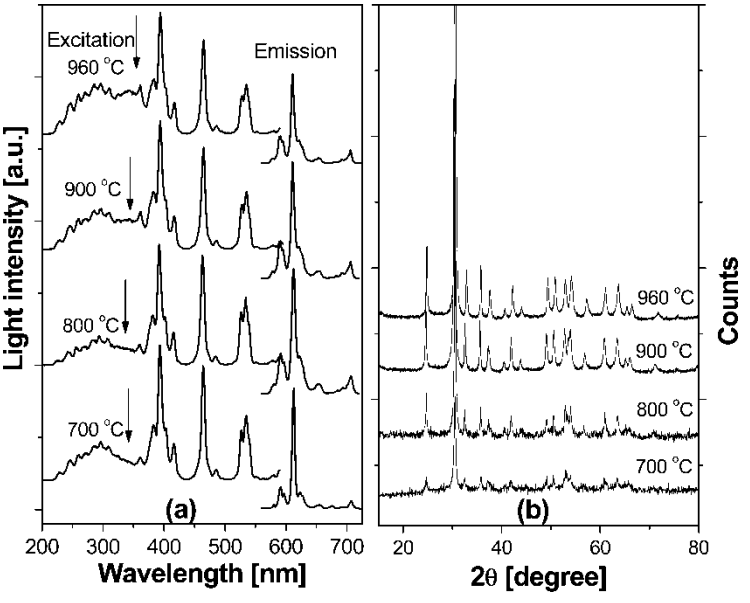

Figure 2. Sequential behavior of luminescence and structural evolution of the ZT:Eu^{3+} compound.

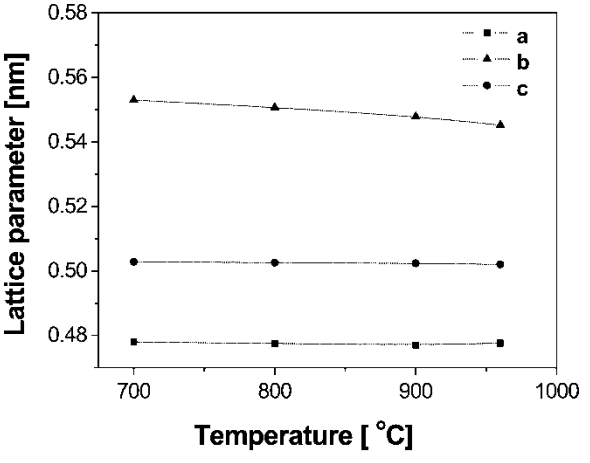

Figure 3. Temperature dependence of the cell a, b and c parameters of the orthorhombic ZT:Eu^{3+}.

Table 1. Lifetime measurements from transitions $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_1$ as a function of the annealing temperature of the ZT:Eu^{3+} samples.

	Decay constant (μs) [$^5D_0 \rightarrow {}^7F_2$]				Decay constant (μs) [$^5D_0 \rightarrow {}^7F_1$]			
Temperature °C	$\lambda_{exc} = 265$ nm	$\lambda_{exc} = 325$ nm	$\lambda_{exc} = 365$ nm	$\lambda_{exc} = 394$ nm	$\lambda_{exc} = 265$ nm	$\lambda_{exc} = 325$ nm	$\lambda_{exc} = 365$ nm	$\lambda_{exc} = 394$ nm
700	1042(5)†	1008(4)†	893(3)†	1163(9)†	850(13)†	811(7)†	739(6)†	936(4)†
800	1129(4)†	1044(4)†	943(4)†	1301(13)†	889(13)†	849(4)†	779(5)†	1083(6)†
900	1213(5)†	1083(4)‡	1029(3)‡	1268(10)†	986(11)†	890(4)†	844(4)†	1102(6)‡
960	1356(4)†	1150(5)‡	1137(6)‡	1205(8)†	1139(10)†	965(4)†	958(3)†	1100(6)‡

†non-exponential decay ‡exponential decay. Standard deviations, which show the last figure variation of a number, are given in parentheses.

make evident the structural changes originated by the thermal annealing treatment. A good correlation occurs between the improvement of the crystalline quality ZT:Eu^{3+} system and the observation of the characteristic emission and excitation bands of the europium ions in our samples, as a function of the thermal treatment.

From this figure, it is shown that the thermal treatment-induced changes in the crystalline parameters characteristic of the orthorhombic ZT:Eu^{3+}. This fact is also evident from the data portrayed in figure 3. Even when the main crystalline phase can be identified from the data obtained from the X-ray diffraction experiments, whenever the annealing temperature of the sample is higher than 700 °C, the crystalline cell parameter **b** shows a temperature dependence and an effective decrement in its value.

On the other hand, from the data portrayed in table 1, an increment in the characteristic lifetime of either, the forced dipolar electric transition $^5D_0$–$^7F_2$ and the dipolar magnetic $^5D_0$–$^7F_1$ emission bands, follows the crystalline transformation of the system. There is an systematic behavior of the lifetimes between the $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_1$, no matter what is the excitation wavelength: $\tau[^5D_0 \rightarrow {}^7F_2] > \tau[^5D_0 \rightarrow {}^7F_1]$. Time resolved experiments were also performed. In table 1 the temperature dependence of the characteristic decay constants is shown, they are associated with the relaxation curves of the Eu^{3+} luminescence from the $^5D_0$ excited state to the ground levels ^7F_j. It was found that the decay constants are sensitive to the crystalline structure of the sample as a function on the thermal treatment described above, an increment of the lifetime of the Eu^{3+} emission is observed at higher temperature. Such behavior is still an open question and extended experiments are currently conducted in our laboratory, in order to get a better understanding of such kind of behavior.

Additionally, a stronger ion-lattice interaction is also observed from the data shown in figure 2 (a) (indicated by arrows). From this figure, a relative increment in the intensity of the host lattice is evident as a result of the structural modifications observed in our system.

4. Conclusions

We have obtained the orthorhombic crystalline phase of the ZrO_2-TiO_2 solid solution doped with Eu^{3+} by sol–gel method.

From the spectroscopic data, a good correlation has been observed between the optical properties and the structural changes induced by the thermal treatment of our samples.

Currently experiments are being conducted in our laboratory in order to get a better understanding of the nature of the host-ion optical interactions responsible for the modifications in (a) the lifetimes constants, (b) the emission and (c) the excitation spectra produced by the thermal treatment of our samples.

Acknowledgements

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