LUMINESCENT AND OPTICAL PROPERTIES OF THE $LI_2ZnTI_3O_8$:Pr SPINEL

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1. INTRODUCTION

Compounds doped with Pr^{3+} have demonstrated efficient photoluminescence or laser action in the visible region, since they contain various metastable multiplets ($^3P_0$, $^2D_1$, $^1G_4$). Pr^{3+} ions have also been used in glasses as activators, demonstrating luminescent properties. In Pr^{3+} doped zinc borate glass, luminescence is due to the $^3P_0$ and $^1D_2$ states of praseodymium. Several rare earth ions are coloured, and the appearance of colour is due to the "f-f" transitions. The $CaTiO_3$:Pr compound displays photoluminescence in blue ($^3P_0 \rightarrow {}^3H_4$) and red ($^1D_2 \rightarrow {}^3H_4$). The Pr^{3+} ion emits photoluminescence in blue or red, depending on crystalline field, concentration and synthesis conditions.

In this work we have evaluated the optical and photoluminescent properties at ambient temperature of the $Li_2ZnTi_3O_8$:Pr spinel, synthesized by the polymer precursor method, as a function of heat treatment and rare earth ion concentration.

2. RESULTS AND DISCUSSION

The optical properties of the compound are depicted in Figure 1, which shows that the presence of the rare earth ion Pr^{3+} in the $Li_2ZnTi_3O_8$ spinel (white coloration) causes a green-yellow coloration, and the tone of this colouring becomes more intense as calcination temperature and praseodymium concentration increase (Figures 1a-b).

With increasing temperature, mean particle size rises (observed by the increase in mean crystallite size, Figure 2b), reducing surface area and surface defects, thus intensifying the tone of the green-yellow colour.

This intensification can also be attributed to greater ordering of the spinel structure, caused by the increase in heat treatment temperature (Figure 2a). The presence of the Pr^{3+} ion in the $Li_2ZnTi_3O_8$ spinel network creates new states; the gap diminishes originating bands in the visible region (Figure 3). All these factors are responsible for the colour of the synthesized spinel.

The photoluminescent behaviour of the powders treated at 300°C for 20, 40 and 60 h is shown in Figure 3. It can be observed that photoluminescence intensity decreases as the compound becomes more ordered (Figure 3b and a).

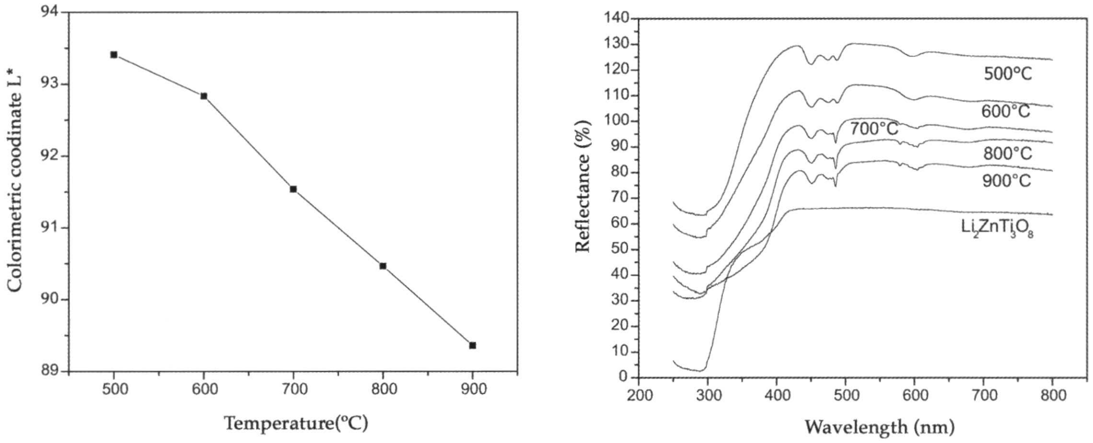
If the photoluminescence spectrum of the $Li_2ZnTi_3O_8$:Pr compound (40 h) is compared with that of the $Li_2ZnTi_3O_8$ compound (40h) (Figure 3c), it can be appreciated that the former displays the same band in the red region observed in the latter (613 nm), in addition to other bands (533.573 662 nm) in the blue and red region.

According to Leite et al. [1], the quantitative analyses of XANES in amorphous titanates showed that the titanium atoms are not only arrayed in octahedra of the TiO_6 type, but also in distorted octahedral structures of the TiO_5 type. With this, titanium adopts the Ti^{4+} and Ti^{3+} oxidation states that causes defects like vacant oxygens, which would cause photoluminescence in the amorphous titanates at ambient temperature.

It is suggested that the band at 613 nm in the red region is characteristic of the photoluminescence of disordered $Li_2ZnTi_3O_8$ titanate (see Figure 3a).

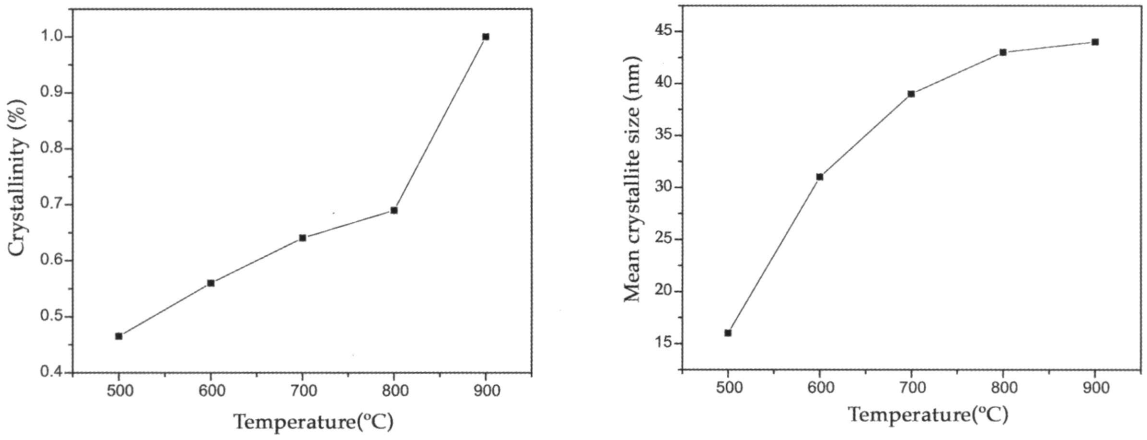
The bands in the 533 region (18823cm^{-1}), 573 (17509cm^{-1}) and 662 nm (15155cm^{-1}) present in the $Li_2ZnTi_3O_8$:Pr spinel are characteristic of the Pr^{3+} ion, and according to Sinha [2] correspond to the electronic transition $^1D_2 \rightarrow {}^3H_4$ of praseodymium that lies in the region 16 – 20,000cm^{-1}.

The presence of the Pr^{3+} ion in the $Li_2ZnTi_3O_8$ spinel lattice increased the intensity of the photoluminescence, and the spinel, which previously emitted hardly any photoluminescence in the red region, also displayed photoluminescence in the blue region.



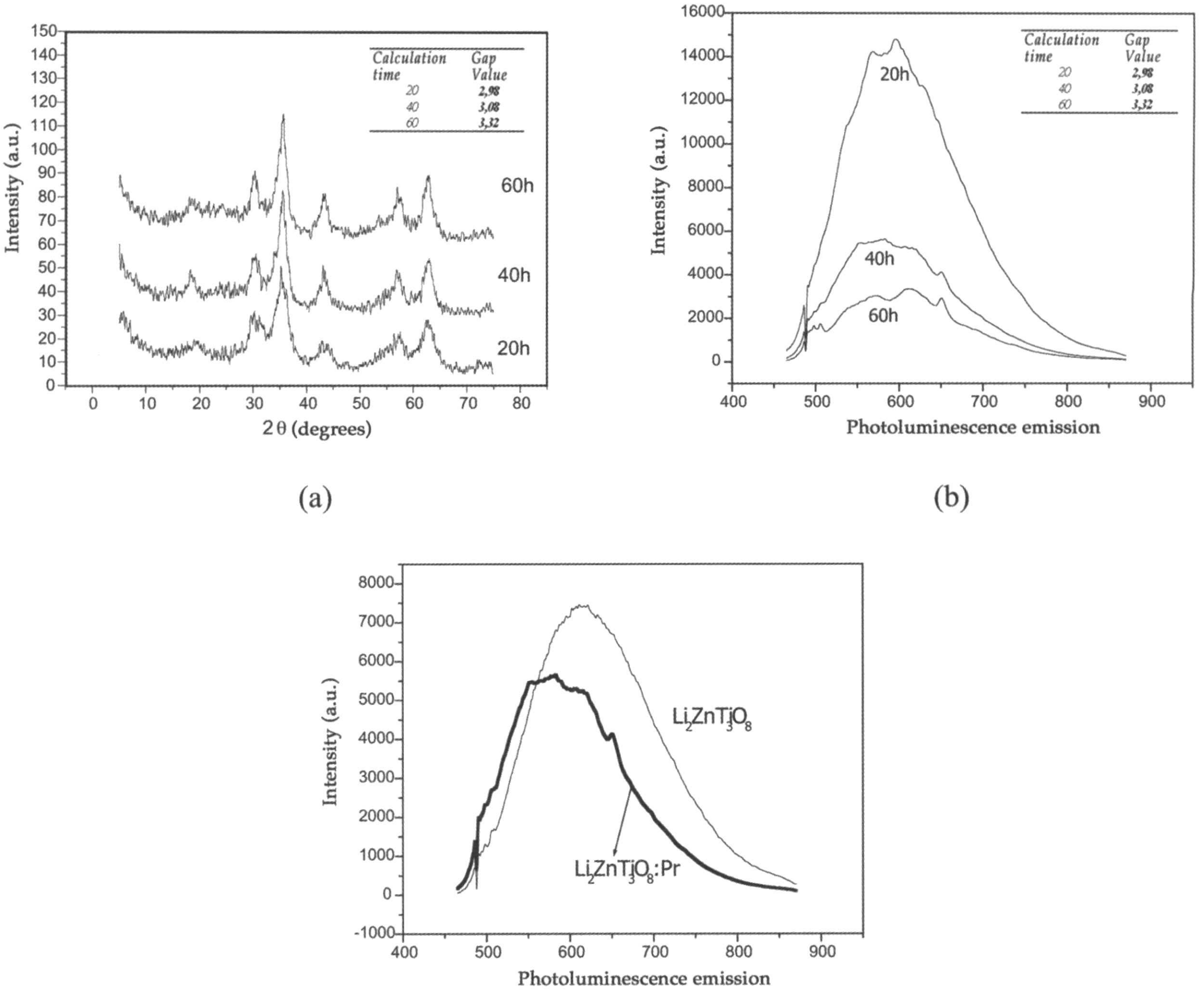
(a) (b)

Figure 1. Evaluation of the colorimetric coordinates of the synthesized spinel (a) L and (b) spectra in the UV-visible region of the compound $Li_2ZnTi_3O_8$:Pr doped with 0.1 Pr^{3+} by mole.*



(a) (b)

Figure 2. Evaluation of the crystallinity of the synthesized spinel (a) and (b) of the mean size of the crystallite of the synthesized spinel.



(a) (b)

Figure 3. X-ray diffractograms of (a) the doped spinel with 0.1% Pr^{3+} by mole calcined at 300°C for 20, 40 and 60 h and (b) photoluminescence spectra at ambient temperature of the $Li_2ZnTi_3O_8$:Pr compound calcined at 300°C for 20, 40 and 60h and (c) of the $Li_2ZnTi_3O_8$ and $Li_2ZnTi_3O_8$:Pr compounds calcined at 300°C for 40h.

REFERENCES

[1] F.M. Pontes, E. Longo, E. R. Leite. Mat. Chem. And Phys. 77 (2002) 598.

[2] S. P. Sinhá, Systematics and the Properties of the Lanthanides, D. Reidel Publishing Company, Boston, 1983