

Spectroscopic Properties of pigment $\text{Li}_{2-x}\text{Zn}_{1-x}\text{Pr}_x\text{Ti}_3\text{O}_8$

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Inorganic compounds doped with rare earths (Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Tm^{3+}) have been used in various applications including light-emitting devices such as fluorescent lamps, cathode ray tubes, lasers and inorganic pigments. In this study, Pr^{3+} is doped in spinel $\text{Li}_2\text{ZnTi}_3\text{O}_8$ system and synthesized by the polymeric precursor method, which is based on the process developed by the Pechini, and characterized by X-ray diffraction, UV-visible and CIE-L colorimetric measures * a * b *, in order to study the effect of doping and thermal treatment on its colorimetric properties. With three different samples of Pr^{3+} doping (0.01; 0.05 and 0.1 mol%) were prepared and calcined at 500°C, 600°C, 700°C, 800°C and 900°C for 4 h. The analysis of X-ray diffraction confirmed the formation of pure phases with spinel structure and average crystallite size of less than 46 nm. It was found that the colorimetric properties ranging from green to red, in accordance with the increase in the concentration of Pr^{3+} and thermal processing temperature.

Keywords: Ceramics, inorganic compounds, nanostructures, chemical synthesis, X-ray diffraction

1. Introduction

Inorganic compounds doped with trivalent rare earth (RE) ions (Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Tm^{3+}) have been used in many different applications, including luminescent devices such as fluorescent lamps, cathode ray tubes and lasers. In these applications are particularly preferred ions displaying $4f^n$ transitions^{1,2}. Among the rare earth ions, trivalent praseodymium shows a particular feature due to close energy separation between the low edge of the $4f5d$ configuration and the 1S_0 level of the $4f^2$ configuration. The radiative de-excitation between these two configurations gives rise a broad band emissions between 220 and 450 nm approximately, depending on the host lattice³. Moreover, emitting species can be excited, either directly or by two-step excitation processes related to the 3P_0 or 1D_2 metastable intermediate levels, located in the blue or orange spectral domains, respectively. The two-steps excitation of the $4f5d$ states of Pr^{3+} ions has been demonstrated in $\text{YAlO}_3:\text{Pr}^{3+}$ crystals, as well as in fluoride crystals such as $\text{KY}_3\text{F}_{10}:\text{Pr}^{3+}$, $\text{BaY}_2\text{F}_8:\text{Pr}^{3+}$, $\text{LiYF}_4:\text{Pr}^{3+}$ and $\text{LiLuF}_4:\text{Pr}^{3+}$.

The Pr^{3+} emission spectra strongly depend on the crystalline field which the ion is allocated. For instance, while $\text{Gd}_2\text{O}_3:\text{Pr}^{3+}$ emits green color due to the $^3P_0 \rightarrow ^3H_4$ transition, $\text{LiYF}_4:\text{Pr}^{3+}$ displays a red color associated to

the $^3P_0 \rightarrow ^3H_6, ^3F_2$ transitions³. The chromatic properties of rare earth sesquisulfides Ln_2S_3 and Aln_2S_4 ($A = \text{Ca}, \text{Sr}$) have been recently investigated. These compounds exhibit pronounced color, ranging from yellow to red depending on the rare earth. The color of these compounds has been related to various energetic parameters, such as ionization energies, crystal field splitting or nephelauxetic effect, the positions of the energy levels at the valence and the conduction bands, which are a function of the crystal structure⁵. Metal oxides have been extensively used as host matrices due to their much better chemical stability than conventional sulfide compounds. The spinel structure is an interesting class of oxides with general formula AB_2O_4 which can act as a host matrix for rare earth ions. A refers to cations in tetrahedral sites and B represents the cations in the octahedral positions. It is a cubic structure with space group symmetry $Fd\bar{3}m$ ⁶. This elaborate crystallographic structure, which can accommodate significant cation disorder, has a unique perspective for studies of substitutions and their relations with the chemical and physical properties^{7,8}. Spinel crystal structures can be divided into two types: normal (or direct) and inverse spinel. In the normal spinels, the A^{2+} ions are contained in the tetrahedral holes, and the B^{3+} in the octahedral holes. In the inverse spinels, on the other hand, the A^{2+} ions and half the B^{3+} ions are in octahedral holes, and the remaining B^{3+} ions are

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in tetrahedral holes⁹⁻¹². In fact, very few *spinel*s have exactly the normal or *inverse* structure, and these are sometimes called *mixed spinels*. $\text{Li}_2\text{ZnTi}_3\text{O}_8$ presents a *derived spinel structure* with $\text{P4}_3\text{2}$ space group, in which the octahedral 12d and 4b sites are occupied by Ti and Li respectively, and the tetrahedral 8c sites are shared by Zn and Li, suggesting an intermediary spinel structure¹³⁻¹⁵.

The present paper presents an optical properties study of the $\text{Li}_{2-x}\text{Zn}_{1-x}\text{Pr}_x\text{Ti}_3\text{O}_8$ spinels, where $x = 0.01; 0.05$ and 0.1 mol%, synthesized by the Pechini method¹⁴. This study was based on analyses of diffuse reflectance and colorimetric coordinates and focused in the energy levels of the Pr^{3+} ions. It should be emphasized that no publication was found in the literature about the energy levels of the Pr^{3+} ions in the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ host lattice.

2. Experimental Procedure

The polymeric precursor solution was prepared by the Pechini method¹⁶, which has been used to synthesize polycationic powders. The process is based on the metallic citrate polymerization using ethylene glycol in order to promote polymerization of the metallic citrate. Due to the formation of high viscosity polyester, the segregation of the cations during thermal decomposition is minimal¹⁷. A hydrocarboxylic acid, such as citric acid, is used to chelate cations in an aqueous solution. The addition of a glycol such as ethylene glycol leads to the formation of an organic ester. Polymerization, promoted by heating the mixture, results in a homogeneous resin in which

metal ions are uniformly distributed throughout the organic matrix.

The polymeric precursor aqueous solution was prepared using the 3:1 molar ratio between citric acid and metallic cations. First, a citric acid solution was kept under stirring for 5 min at 70°C , then lithium carbonate (Li_2CO_3 , Merck), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, Aldrich) and praseodymium carbonate ($\text{Pr}_2(\text{CO}_3)_3$, Nuclemon) were added to the solution and kept under stirring until their complete dissolution. Subsequently, ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, Merck) was added in a ratio of 2:3 in relation to the citric acid and stirred vigorously for 10 min at 100°C to promote polyesterification reactions and water evaporation, which lead to formation of a polymeric resin. The resin was heat treated at 300°C for 3 h, and then the obtained powder was ground in a mortar and calcined in air at 500, 600, 700, 800 and 900°C for 4 h.

The produced powders were characterized by XRD using a Siemens D5000 equipment operating with Cu K α radiation. The data were collected in the range $5\text{--}100^\circ$ (2θ), step size of 0.02° and count time of 10 s per step. UV-vis-NIR spectroscopy (diffuse reflectance) of the samples was performed with a Varian 5G spectrophotometer. In addition, the L^* , a^* and b^* color parameters and diffuse reflectance were measured by a Gretac Macbeth Color-eye spectrophotometer 2180/2180 UV, in the 300-800 nm range, using the D65 illumination. The CIE- $L^*a^*b^*$ colorimetric method, recommended by the CIE was followed. In this method, L^* is the lightness axis [black (0) \rightarrow white (100)], b^* is the blue (-) \rightarrow yellow (+) axis, and a^* is the green (-) \rightarrow red (+) axis, and ΔE is the hue variation.

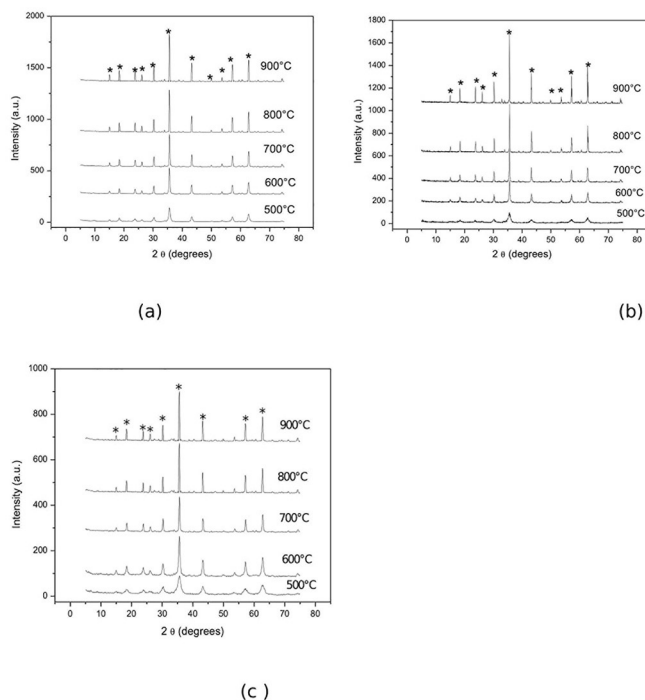


Figure 1: XRD patterns of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ spinel doped with: (a) 0.01% mol % of Pr^{3+} , (b) 0.05 mol% of Pr^{3+} , (c) 0.1 mol % in Pr^{3+} .

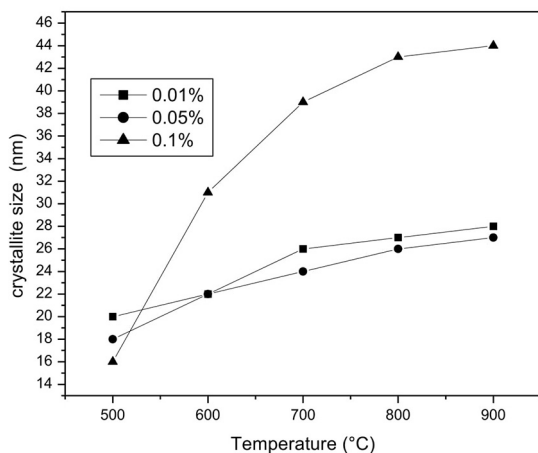


Figure 2: Effect of the calcinations temperature on the crystallite size of the spinel phase.

3. Results and discussion

The X-ray diffraction patterns confirmed the presence of a single pure phase with spinel-type structure, $\text{Li}_2\text{ZnTi}_3\text{O}_8$, for all samples treated at the 500-900°C temperature range, independently of the Pr^{3+} ions concentration (Figure 1). These results suggest that Pechini method is able to produce oxide powders with a high crystallinity and nanometric size crystallites. It was also observed crystallite size increases when the heat-treatment temperature increases (Figure 2).

Figure 3 presents the diffuse reflectance of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ doped with 0.01, 0.05 and 0.1 mol% of Pr^{3+} ions and calcined at 500, 600, 700, 800 and 900°C. It can be seen by the spectra that the spinel phase presents absorption bands at the spectral domains ranging from blue to yellow. The CIE- $L^*a^*b^*$ chromatic coordinates are depicted in Figure 4. It is noticed that the color of the spinel phase is more intense, toward the direction of the green, when the Pr^{3+} ions concentration increases. On the other hand, the color becomes darker when the calcination temperature raises and the compounds become more crystalline (Figure 4a).

Figure 5 illustrates the diffuse reflectance of the spinel calcined at 800°C for different concentrations of dopant. The spectra obtained at room temperature showed the $4f^2$ Stark levels characteristic of Pr^{3+} ions which are presented in Table 1. It is noticed for all samples the characteristic spectral lines of Pr^{3+} ions in the range from 1.75 to 3 eV, attributed to intercon figurational transitions of RE $4f^{n-1}5d \rightarrow 4f^n$ ions, due to the strong coupling between the 5d electrons of the active ion and the host lattice⁹. It is well known that Pr^{3+} ion energy levels are shifted toward lower energies when in the presence of a crystalline field. Usually, the difference between the energy levels of the rare earth ion when isolated and into a crystalline field (ΔE) is higher than 500 cm^{-1} . It was found (Table 1) that Pr^{3+} ions presents greater ΔE when placed into a spinel-type host lattice than into LiYF_4 and LiLuF_4 compounds, however, smaller than into a LuAlO_3 compound. All these results lead to the energy level scheme presented in Figure 6.

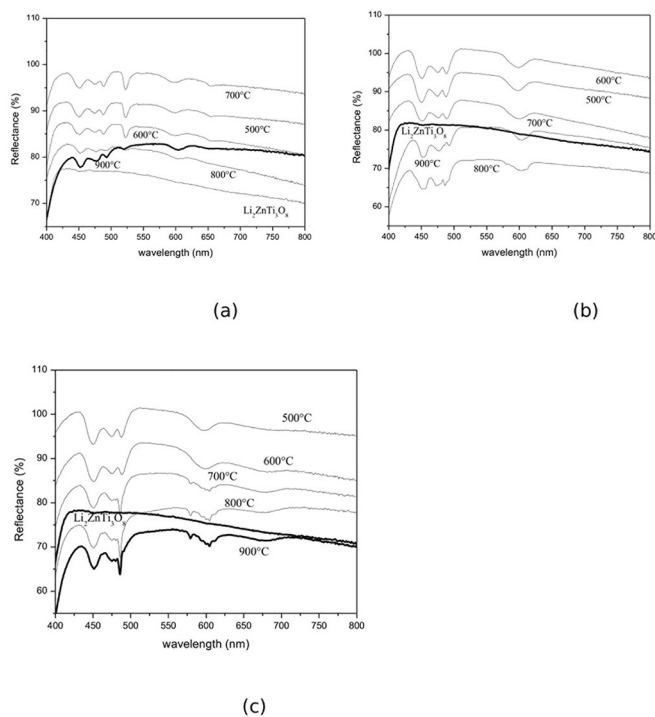


Figure 3: Diffuse reflectance of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ spinel, calcined at the 500-900°C temperature range, and doped with Pr^{3+} (a) 0.01mol%, (b)0.05mol% and (c) 0.1mol%.

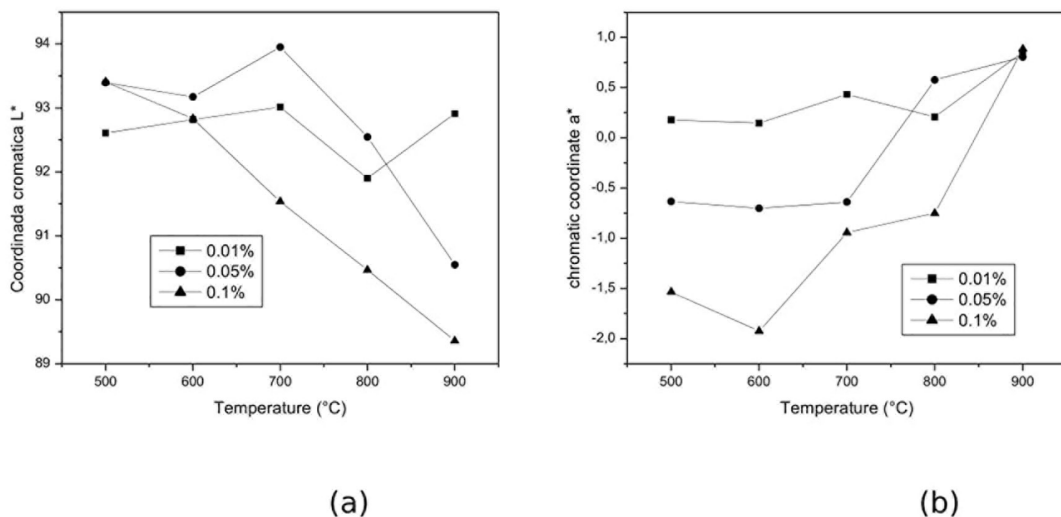


Figure 4: Chromatic coordinates of the of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ spinel doped with Pr^{3+} (a) “L*” and (b) a*.

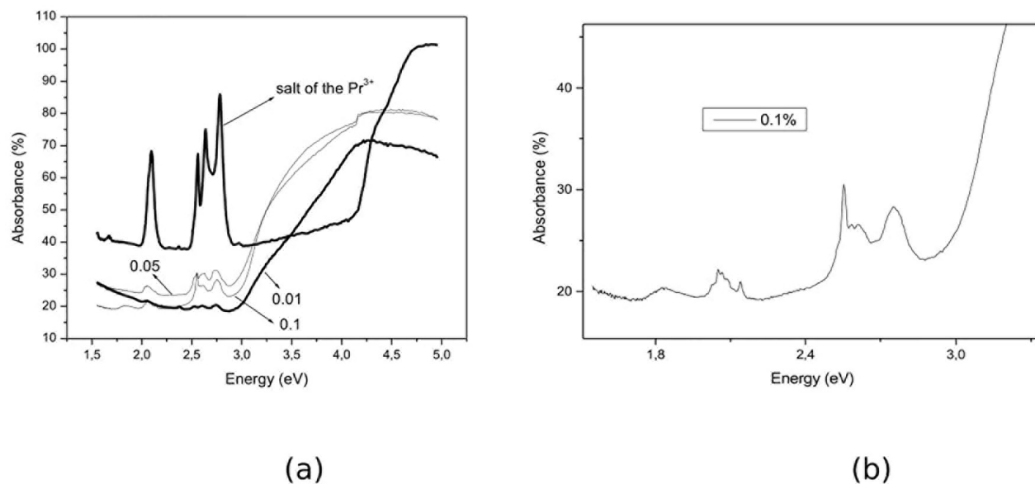


Figure 5: Diffuse reflectance of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ spinel doped with Pr^{3+} (a) 0.01, 0.05 and 0.1 mol% (b) amplification of the 0.1% curve, calcined at 800°C.

Table 1: Crystal field splitting of the $2s+1L_j$ manifolds of Pr^{3+} ion in $\text{Li}_2\text{ZnTi}_3\text{O}_8$, LiYF_4 , LiLuF_4 and LuAlO_3 .

sL_j	$V(\text{cm}^{-1}) \text{Pr}^{3+}$	$V(\text{cm}^{-1}) \text{Li}_2\text{ZnTi}_3\text{O}_8$	$V(\text{cm}^{-1}) \text{LiYF}_4$	$V(\text{cm}^{-1}) \text{LiLuF}_4$	$V(\text{cm}^{-1}) \text{LuAlO}_3$
1G_4		14806 (c) 16570 (a) 16619 (c) 16554 (c) 16724 (c)			
1D_2	17334	17314 (c) 17331 (c) 16619 (b) ΔE (515)	16740 ΔE (594)	16812 ΔE (522)	16337 ΔE (997)
3P_0	21390	19240 (a) 20656 (b) 20640 (c) ΔE (1241)	20860 ΔE (530)	20864 ΔE (526)	20361 ΔE (1029)
3P_1	22007	20430 (a) 21222 (b) 20890 (c) ΔE (1159)	21414 ΔE (593)	20471 ΔE (1536)
1I_6	22212	21069 (a) 22169 (b) 21093 (c) ΔE (769)	21825 ΔE (387)	21105 ΔE (1107)
3P_2	23161	22258 (a) 22250 (c) ΔE (907)	22498 ΔE (663)	22521 ΔE (640)	21935 ΔE (1216)

a = 0.01% Pr^{3+} , b = 0.05% Pr^{3+} , c = 0.1% Pr^{3+}

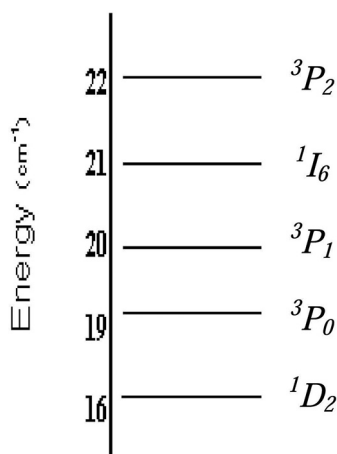


Figure 6: Energy level diagram of Pr^{3+} in $\text{Li}_2\text{ZnTi}_3\text{O}_8$, obtained from absorption spectra.

4. Conclusions

We have demonstrated that $\text{Li}_{2-x}\text{Zn}_{1-x}\text{Pr}_x\text{Ti}_3\text{O}_8$ nanocrystalline powders can be successfully synthesized by a polymer precursor method. These compounds showed a green color directly related to the Pr^{3+} ion concentration. By using a simple technique of diffuse reflectance it was possible to determinate the positions of the Stark $4f^2$ levels of the Pr^{3+} ion in the $\text{Li}_{2-x}\text{Zn}_{1-x}\text{Pr}_x\text{Ti}_3\text{O}_8$ host lattice. It was found that the spinel $\text{Li}_{2-x}\text{Zn}_{1-x}\text{Pr}_x\text{Ti}_3\text{O}_8$ is a promising material to be used as fluorescent material and/or a pigment.

5. Acknowledgements

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6. References

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