

# Mn<sup>2+</sup> doped Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> phosphors: Irreversible thermochromic materials useful as thermal sensors



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## ABSTRACT

Mn<sup>2+</sup> doped Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> phosphate exhibits a rich thermal history with numerous events. Following the dehydration of Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O hopeite at temperatures up to  $T = 400$  °C, various allotropic forms  $\alpha/\delta \rightarrow \gamma \rightarrow \beta$  can be stabilized with irreversible transitions for a  $600$  °C  $\leq T \leq 1000$  °C temperature range. Furthermore, in these different networks, a transition metal can occupy distorted tetrahedral ( $\alpha/\delta$  forms) and pentahedral sites as well as octahedral sites for the high-temperature  $\gamma$  and  $\beta$  forms that correspond to non-centrosymmetric environments. Depending on the thermal history of the samples, two different types of emission spectra were obtained. By increasing the annealing temperature, the green emission associated with Mn<sup>2+</sup> in a Td environment progressively disappears in favor of the red one that corresponds to Mn<sup>2+</sup> stabilized in fivefold and sixfold coordination sites. There is also a dependence of the emission color on the excitation wavelength arising from the differences in the excitation spectra of Mn<sup>2+</sup> in these two types of sites. Excitations in the oxygen-manganese charge transfer band at 250 nm or in the 3d–3d absorption region at 420 nm give rise to the red or green emission at 420 nm, the green one being enhanced for an excitation at 420 nm. The  $\alpha/\delta \rightarrow \gamma$  transition at  $600$  °C  $\leq T \leq 900$  °C can easily be monitored in the emission spectra obtained after an excitation at 250 nm with a rather good chromatic contrast. The  $\gamma \rightarrow \beta$  high-temperature transition at  $900$  °C  $\leq T \leq 1000$  °C can be more easily followed by in the emission spectra obtained after an excitation at 420 nm. By taking into account both these emission spectra, various trichromatic coordinates can be calculated and allow subsequent phase transitions. The chromaticity of Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>: Mn<sup>2+</sup> will strongly change for  $600$  °C  $\leq T \leq 1000$  °C, and one can consider this phosphate as an interesting thermal sensor.

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## 1. Introduction

Over the past few decades, research on phosphor-based thermometric systems has become increasingly important, and these systems have been the subject of international reviews in different fields such as aeronautic engineering [1–3], and the nanosciences [4,5].

The temperature dependence of the thermographic phosphors can be evaluated by different measurement techniques. In such systems, a change in temperature can induce a spectral and/or a temporal modification of the luminescence emission [1,2,6]. Thus, the temperature of exposure of a compound could be extracted from the emission decay time; more specifically, the temperature is extracted from modifications in the spectral distribution, for instance from changes in the intensity ratio between two or several emission lines or bands or from wavelength shifts of the main emission lines [6–8].

The choice of the measuring technique also depends on the reversible or irreversible character of the thermochromic properties required for a given application. Hence, reversible thermochromic modifications that require in-situ measurements are generally based on temporal modifications because the incandescence phenomenon prohibits the characterization of a variation in an emission spectrum at high temperature. Conversely, the irreversible character of the emission spectrum as a function of the thermal history, phase transformation, phase transition and crystallographic site distribution is largely investigated.

Among the different thermometric phosphors, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> doped with a luminescent center can be used as an irreversible thermographic sensor. Indeed, this compound can exhibit significant modifications in its emission spectrum based on its thermal history in a wide temperature range [9].

These zinc phosphate phosphors consisting of non-polluting elements [10], present a wide band gap in the UV domain (reported in literature equal to 3.8 eV [11]) and a high melting point allowing its use as thermal sensor to about 1000 °C. Two allotropic forms,

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named hopeites, can be obtained at ambient conditions by soft chemistry and form similar networks that differ only by the positions of atomic hydrogens [12]. The anhydrous compound obtained by successive dehydration procedures exists in three monoclinic forms referred to as  $\alpha$ ,  $\beta$  and  $\gamma$ . The stable phase obtained at low temperature after dehydration is the  $\alpha$ -phase [13]. In this phase, the  $\text{Zn}^{2+}$  ions are located in two non-equivalent distorted tetrahedral sites (Fig. 1) [11]. It has to be noted that zinc phosphates doped with transition metals can also exhibit the low temperature  $\delta$ -modification as shown in our previous studies [12]. From a structural point of view, this network is close to the  $\alpha$ -form. Actually, the  $\delta$ -modification was shown to slightly diverge from the  $\alpha$ -phase only in the organization of the zinc and phosphate tetrahedral sites [12]. The  $\beta$  and  $\gamma$  phases are the two high-temperature forms. In these forms, the  $\text{Zn}^{2+}$  ions are located in distorted octahedral and fivefold coordination sites (Fig. 1) [14].  $\text{Zn}_3(\text{PO}_4)_2$  is a suitable host for the incorporation of  $\text{Mn}^{2+}$  dopant because of the similar ionic radius and electronegativity of  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  ions.

$\text{Mn}^{2+}$  ions possess a  $d^5$  electronic configuration. The main emission of this luminescent dopant corresponds to a  ${}^4T_1 \rightarrow {}^6A_1$  transition, which is strongly dependent on the ligand field and the coordination number. In agreement with the ionic-covalence theory, i.e., the  $\text{Mn}^{2+}-\text{O}^{2-}$  bond strength, the  $\text{Mn}^{2+}$  ions in inorganic oxides can be generally inserted in fourfold and sixfold coordination sites. They are inserted here in the  $\alpha$ -form and in the  $\beta$ - and  $\gamma$ -forms, in four and fivefold or sixfold coordination spheres, respectively [9,11,14,15]. Hence, the phase transition from the  $\alpha$ -form to the  $\gamma$ - or  $\beta$ -form results in a strong modification of the ligand field around the  $\text{Mn}^{2+}$  ions. This increase in the coordination number of the  $\text{Mn}^{2+}$  ions leads to a shift in the  $\text{Mn}^{2+}$  luminescence emission from green to red [9].

In this paper, the irreversible modification of the emission properties of the 2 mol% Mn-doped  $\text{Zn}_3(\text{PO}_4)_2$  with a thermal treatment under air up to  $T = 1000^\circ\text{C}$  was accurately investigated. The dehydration of Mn<sup>2+</sup>-doped hopeite was characterized by thermo-gravimetric analysis. The relationship between the annealing temperature and the luminescence due to the modification of the crystal field of the  $\text{Mn}^{2+}$  ions in the network was established by combining X-ray diffraction and luminescence spectroscopy. The evolution of the compound chromaticity versus its thermal

history was fully interpreted and then evaluated in terms of the potential of this compound as a thermographic phosphor.

## 2. Material and methods

### 2.1. Samples synthesis

Powder samples were synthesized by an aqueous co-precipitation method [12]. Appropriate amounts of  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$  were previously dissolved in aqueous medium and added dropwise in an equimolar solution of  $(\text{NH}_4)_2\text{HPO}_4$ . The reaction is performed under vigorous stirring at room temperature with three hours of ripening. Then, the as-prepared precipitate is allowed to dry at ambient temperature.

### 2.2. Characterization techniques

X-ray diffraction patterns were recorded on a Philips X'Pert MPD apparatus equipped with a copper  $K_{\alpha 1}$  anticathode (40 kV, 40 mA). Diffraction patterns were collected from  $8^\circ$  to  $80^\circ$  in  $2\theta$  with a  $0.017^\circ$ -step scan and a counting time of 59 s. Thermogravimetric (TG) and differential thermal-gravimetric analyses (DTG) were carried out on a Setaram MTB 10-8 microbalance. The experiments were performed in air with a heating rate of  $10\text{ K min}^{-1}$  from room temperature to 1000 K. Excitation and emission spectra were recorded with a SPEX Fluorolog FL212 spectrofluorometer. The excitation spectra were corrected for the variation in the incident flux and the emission spectra were corrected for the transmission of the monochromator and the response of the photomultiplier. The  $x$  and  $y$  chromatic coordinates were directly determined from the emission spectra.

## 3. Results

The dehydration of the 2% manganese doped hopeite was followed by TGA under atmospheric pressure and the resulting curve is reported in Fig. 2. A first noticeable change in mass was observed in the  $78\text{--}120^\circ\text{C}$  temperature range. The associated mass loss of 7.23% corresponds to two molecules of water per unit formula, i.e., half of the hydration water molecules are lost during this first step. In a second stage, three successive DTG peaks with increasing intensity are detected. The first one is associated with a small mass variation (0.78%) approximately  $110^\circ\text{C}$  and corresponds to approximately 0.2 water molecule. The second and third peaks roughly correspond to one molecule of water each. Approximately  $370^\circ\text{C}$ , all of the constitutive water molecules of the compound have disappeared. According to the literature [12,13], the X-ray pattern

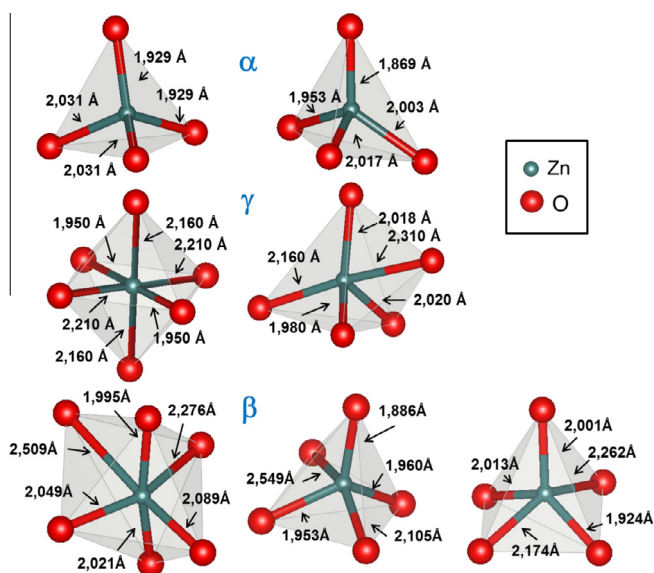


Fig. 1. Representation of the various cationic sites in the different  $\alpha$ ,  $\gamma$ , and  $\beta$  allotropic forms of  $\text{Zn}_3(\text{PO}_4)_2$  from the literature [11,14].

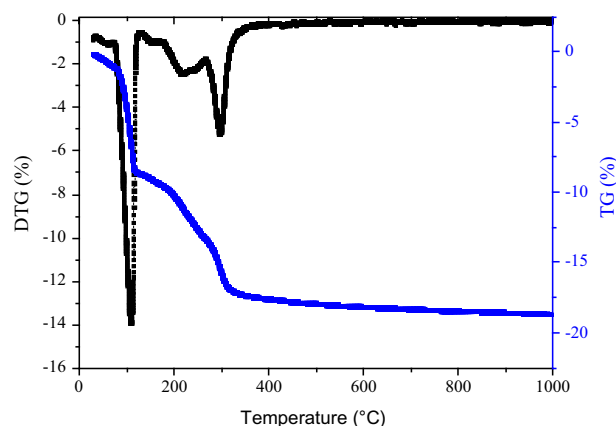


Fig. 2. TG curve of the 2% Mn-doped hopeite.

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