

Lead (II) Luminescent Properties in Different Apatites

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Summary. The incorporation of toxic heavy metals such as lead, into the apatite crystal structure is a potential solution to the problem of storage of this pollutant. The purpose of this work is to examine the Pb²⁺ luminescence in mixed calcium-lead apatites, by laser-induced time-resolved spectroscopy. The method involves recording the intensity in a specific time gate at a given delay after the excitation laser pulse where both the delay and the gate width have to be carefully chosen. An attempt to identify the pure electronic transitions between the ground and the excited levels of Pb²⁺ is made. As a consequence of the two different sites in the apatite, two emission bands due to the $^3P_1 \rightarrow ^1S_0$ (at room temperature) and $^3P_{0,1} \rightarrow ^1S_0$ (at low temperature) transitions of the Pb²⁺ ions, are observed. Correlations between the luminescence results and the structural data are discussed.

Introduction

Because of their biological occurrences and their chemical properties, apatite-type compounds have been widely investigated. The general formula of the apatites is $M_{10}(AO_4)_6X_2$ (M is an alkaline earth metal, lead or a rare earth metal etc., A = P, V, As, ... , and X = OH, halogen). Apatite crystallizes in the hexagonal system (space group P6₃/m), with cations occupying the 4f (Ca I) and 6h (Ca II) sites in the crystal lattice. Many studies have reported the synthesis, structure, thermal stability and physical properties of these compounds⁽¹⁻⁵⁾. Apatites have been extensively studied for their great interest in the fields of phosphors, lasers, bioceramics, catalysts, adsorbents, thermal and radiation damage resistant. Besides, apatite appears to be an outstanding material for storage of heavy metals and nuclear waste conditioning.⁽⁶⁻⁷⁾ Introduction of iodine in the apatitic structure is possible, with respect to the steric bulk and to the chemistry conditions.⁽⁶⁾

The luminescence of compounds containing metal ions with s² configuration like Tl⁺, Bi³⁺ and Pb²⁺ can be used in X-ray imaging devices, low pressure lamps.⁽⁸⁻⁹⁾ The

optical properties of Pb^{2+} have been progressively studied⁽¹⁰⁾. The luminescence properties of the Pb^{2+} ion with $6s^2$ configuration are attributed to the ground state $^1\text{S}_0$ and two excited states of singlet $^1\text{P}_1$ and triplet $^3\text{P}_{0,1,2}$.⁽¹¹⁾ Usually, Pb^{2+} emission is located from UV to visible range whereas Pb^{2+} absorption is located in the UV range only.

This study concerns the research program on lead apatites conducted in our laboratory [1-2, 12-14]. Two families (phosphate and vanadate) of apatites were examined. A comparative study is also carried out on natural analogues.

Our purpose is to put in evidence the possibility of the lead trapping in the apatites by using, essentially the time resolved photoluminescence technique.

2. Experimental Procedure

Samples corresponding to $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6\text{X}_2$ ($\text{X} = \text{OH}, \text{Cl}$) were prepared as described in our previous references [1-2]. Vanadate apatites $\text{Pb}_{10}(\text{VO}_4)_6\text{X}_2$ ($\text{X} = \text{Cl}, \text{I}$) were synthesized as described by Audubert et al. [6]. The purity of the samples was checked by X-ray powder diffraction, chemical analysis, as well as IR, Raman scattering and NMR spectroscopies.

The luminescence spectra were measured under a Nd:YAG laser (Spectra Physics Quanta-Ray, GCR130) which delivers pulses of 10 ns duration and 0.1 cm^{-1} spectral width. The luminescence was analyzed by a f-125 monochromator and detected by an Instaspec ICCD detector enabling time-resolved spectra acquisition. The UV excitation spectra were recorded with a 450 W Xenon lamp associated with a monochromator Gemini 180 from Jobin-Yvon.

3. Results And Discussion

3.1. X-ray diffraction analysis

All the samples reveal the existence of one single phase indexed on the hexagonal $\text{P6}_3/\text{m}$ apatite structure.

3.2. IR and Raman investigations

IR and Raman spectra of lead phosphate apatites are well established and the bands have been assigned in our previous publications [1-2].

In this paper, we will interest to the study of the IR and Raman spectra in different lead vanadate apatites. Our results are summarized in table 1 where assignments have been done using literature data concerning vanadate apatite $\text{Pb}_{10}(\text{VO}_4)_6\text{Cl}_2$ [15]. The IR and Raman spectra of $\text{Pb}_{10}(\text{VO}_4)_6\text{X}_2$ ($\text{X} = \text{Cl, I}$) are similar. In comparison with those of the calcium phosphate apatites, one can observe a shift of the bands to lower wavenumbers.

Table 1. Infrared and Raman band wavenumbers (cm^{-1}) and assignments for $\text{Pb}_{10}(\text{VO}_4)_6\text{X}_2$ ($\text{X} = \text{Cl, I}$)

Sample	Assignment			
	$\nu_s(\text{VO}_4) + \nu_{as}(\text{VO}_4)$		$\delta_s(\text{VO}_4) + \delta_{as}(\text{VO}_4)$	
	IR	Raman	IR	Raman
$\text{Pb}_{10}(\text{VO}_4)_6\text{Cl}_2$	828	826	-	404
	790	798		364
	762	770		290
	719	725		330
$\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$	845	826		370
	783	720	-	320
	775			220
	720			

ν_{as} : antisymmetric stretching mode

ν_s : symmetric stretching mode

δ_{as} : antisymmetric bending mode

δ_s : symmetric bending mode

3.3. NMR study

^{207}Pb MAS (magical angle spinning) NMR spectra of the apatites $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6\text{X}_2$ ($0 \leq x \leq 10$) ($\text{X} = \text{OH, Cl}$) were well established and described in our previous paper [16]. In this paper, we will interest to the study of the ^{207}Pb NMR spectroscopy in different vanadate apatites. ^{207}Pb MAS NMR spectra in synthetic and natural vanadinite $\text{Pb}_{10}(\text{VO}_4)_6\text{Cl}_2$ are similar. They put in evidence two isotropic lines of resonance at isotropic chemical shift of -1622 ppm and -1722 ppm with relative intensities at about 40 and 60 %, respectively.

The line with isotropic chemical shift $\delta_{\text{iso}} = -1722$ ppm is attributed to the Pb(II) in substitution on Ca (II) sites (6h) and the less intensity line with $\delta_{\text{iso}} = -1622$ ppm is ascribed to the Pb(I) site of the apatite structure.

3.4. Pb^{2+} luminescent properties

The emission spectra were measured for different Pb^{2+} contents in calcium-lead apatites $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6\text{X}_2$ ($0 \leq x \leq 10$) ($\text{X} = \text{OH}, \text{Cl}$).

At room temperature, the emission spectrum of 2% Pb^{2+} -doped $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ under 266 nm laser excitation (Figure 1) shows one broad band at about 340 nm and a second more intense one at 430 nm. These two bands are attributed to the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ allowed electronic transition of Pb^{2+} in the two Ca (I) and Ca (II) sites. According to Andres-Verges et al. [4], the blue intense emission (430 nm) is ascribed to Pb^{2+} ions in the Ca (II) site whereas the weak UV emission (340 nm) is related to Pb^{2+} ions in the Ca (I) site.

The overlap of the emission band at 340 nm and the excitation band at 348 nm reveals an energy transfer: the light emitted by Pb (Ca I) sites at 340 nm is partially transferred by both non-radiative and radiative energy transfer to Pb (Ca II) sites. From $x \geq 1$ (10 %), we observed a high quenching of the blue emission.

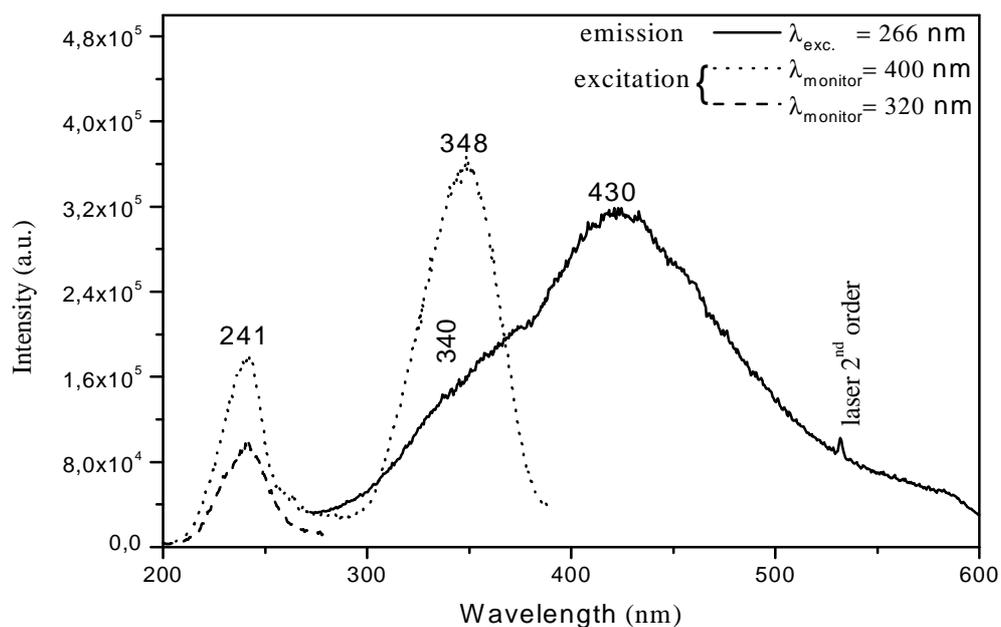


Figure 1. Pb^{2+} excitation (dashed line) and emission (solid line) spectra in 2 % Pb^{2+} - doped $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ at room temperature.

As the temperature decreases the ultraviolet band becomes more intense and shifts towards the higher wavelength as shown by the deconvolution of the spectra (Figure 2). This is in good agreement with that found in the Bi^{3+} -doped Ln_2O_3 oxides [17].

From the obtained results, we consider the excitation process in which the transitions are provided from the $^3\text{P}_1$ level. It is also necessary to take into account the presence of the metastable level $^3\text{P}_0$ located just below $^3\text{P}_1$ level [8].

After excitation in the $^3\text{P}_1$ level, can occur a direct settling to the $^1\text{S}_0$ fundamental level or another settling from the $^3\text{P}_0$ metastable level involving the non radiative transition $^3\text{P}_1 \rightarrow ^3\text{P}_0$. The emission can then occur in two ways:

- either directly by the $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transition with the much weaker probability than that of $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition because of the forbidden transition ($\Delta J = 0$). So until 40 K, the emission is originated from the $^3\text{P}_0$ level;
- or by the $^3\text{P}_0 \rightarrow ^3\text{P}_1$ transition when there is thermal equilibrium. In the temperature range $40 < T < 200$ K, both levels $^3\text{P}_0$ and $^3\text{P}_1$ can emit.

At higher and room temperatures, the $^3\text{P}_1$ level is thermally populated, and due to the mixing of $^1\text{P}_1$ and $^3\text{P}_1$ states the spin selection rule is partially lifted and the decay lifetime of this allowed $^3\text{P}_1 \rightarrow ^1\text{S}_0$ emission is shortened.

As expected, due to the concentration quenching phenomenon, there is no Pb^{2+} emission in concentrated vanadate apatites $\text{Pb}_{10}(\text{VO}_4)_6\text{X}_2$ ($\text{X} = \text{Cl}, \text{I}$).

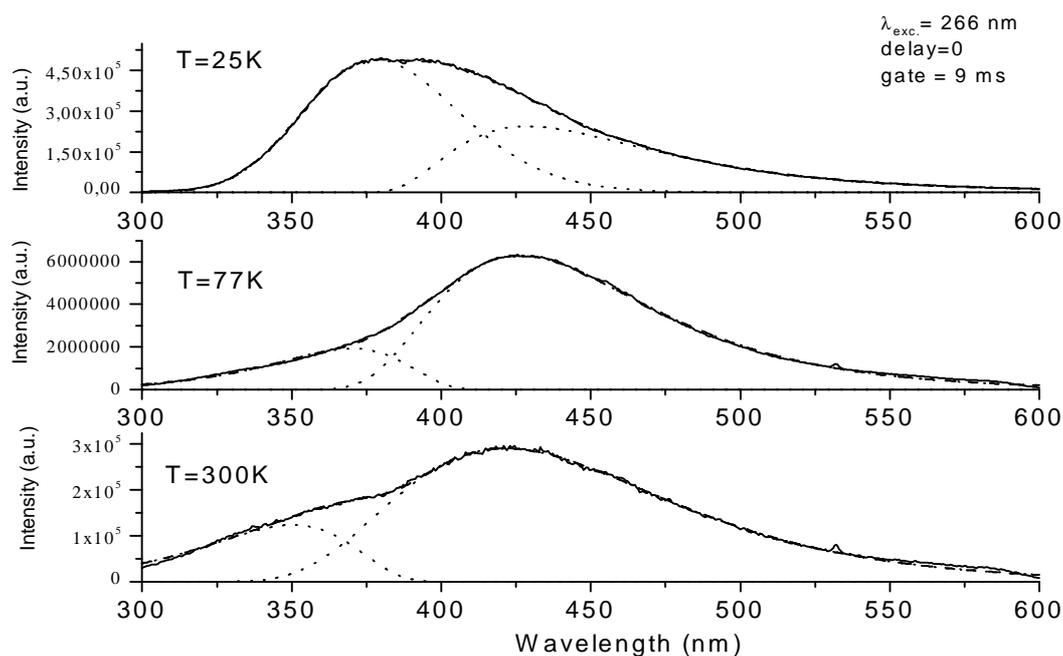


Figure 2. Pb^{2+} emission spectra in 2 % Pb^{2+} -doped $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ under 266nm laser excitation at different temperatures. Deconvolution curves are in dotted line.

4. CONCLUSION

The luminescence of Pb^{2+} -doped calcium apatites is originated from two kinds of sites. This is the consequence of the presence of two crystallographic sites in the apatite structure.

Moreover, the superposition of the emission and excitation bands is connected with an energy transfer phenomenon in these compounds. Experimental results show the possibility to use Pb^{2+} ion luminescent properties to detect very low lead content under UV excitation in synthetic and natural apatitic matrixes. Besides, the intense emission at 430 nm could be potentially used in apatites as blue emitting phosphors.

Revealing the optical properties of lead in apatite structure, it is then possible to detect very low Pb^{2+} ions content by photoluminescence in apatite biomaterials.

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