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Optically stimulated luminescence in Cu^+ doped lithium orthophosphate

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ABSTRACT

Optically stimulated luminescence (OSL) in Cu^+ doped Li_3PO_4 synthesized by co-precipitation technique using different phosphorus precursors was studied. Changes in the luminescent properties were observed with change in the phosphorus precursors. All the synthesized phosphors showed intense fading but the OSL sensitivity was comparable to that of the commercially available Al_2O_3:C (Landauer Inc.). In general, BSL (blue stimulated luminescence) decay was very fast but the GSL (green stimulated luminescence) decay was comparable to that of Al_2O_3:C phosphor. Phosphors with fast decay, good sensitivity and intense fading are suitable for real-time dosimetry. Therefore, Cu-doped Li_3PO_4 could be developed for real-time dosimetry using a fiber optic based OSL reader system.

1. Introduction

In the recent years, optical stimulated luminescence (OSL) technique is being widely used in almost all the dosimetric applications. In OSL the localized defects act as traps and capture electrons or holes generated by the ionizing radiation. These traps are stimulated by the light in the visible/IR region, which results in release of charge carriers of one sign, which then are able to recombine with charge carriers of the opposite sign, leading to the emission of light. OSL was first used in archeological dating [1] and later, with the development of Al_2O_3:C, proposed for personnel and environmental monitoring [2]. The general requirement for a material to be a good OSL phosphor is that the emission should be between 350 and 425 nm and the defects should have a high photoionization cross-section in blue-green region (450–550 nm) or IR region (650–800 nm). This limit on the wavelength is due to the availability of suitable filters, stimulation sources as well as sensitive PM tubes in this range, and most importantly the requirement of separation of stimulating wavelength from the emission wavelength which ensures better signal-to-noise ratio.

Over nearly 20 years, Al_2O_3:C has been used for various dosimetric applications, using OSL technique, due to its excellent dosimetric properties. Several efforts have been made towards development of different phosphors for dosimetric applications but it is mainly centered on natural/synthetic quartz, feldspars, oxides, fluorides, chlorides, etc. [3–7]. More recently, OSL of cerium, europium, samarium and copper ions doped into borate and silicate glasses has been reported [8–12]. Attempts were also made to develop/characterize materials like MgO:Tb [13], $NaMgF_3$:Eu [14], BeO [15], $LiMgPO_4$:Tb,B [16], Cu-doped alkali fluorosilicates [17], etc. But except for BeO, they still remain in development stage as far as their use in routine radiation dosimetry is concerned. Cu-doped Li_3PO_4 could be another candidate as an OSL phosphor. Cu^+ emission in Li_3PO_4 has been reported as early as 2001 [18]. In Li_3PO_4:Cu the emission is observed around 367 nm and thus it satisfies one of the important criteria for a material to be a good OSL phosphor. Earlier, thermoluminescence (TL) in Li_3PO_4 was studied by Naranje et al. [19] with the intention to the study role of phosphorus in LiF:Mg, Cu, P. This study led to the development of new Li_3PO_4 based phosphor for TL dosimetry. Detailed characterization of this phosphor was later done by Bhatt et al. [20]. Aghalte et al. [21] reported OSL in Li_3PO_4:Cu but the detailed study of this phosphor is not yet done. In the recent past we have studied the effect of micro phases of lithium phosphate on the OSL sensitivity in Cu-doped Li_3PO_4 [22].

In this paper we report the OSL properties of this phosphor synthesized using different precursors and their effect on TL/OSL properties. This study may lead to the development of highly sensitive Cu-doped Li_3PO_4 OSL phosphor for radiation dosimetry.

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2. Experimental

Cu-doped Li_3PO_4 was synthesized using co-precipitation method by reacting an analytical grade lithium chloride and the phosphorus precursor. $CuCl_2$ solution in desired proportion (500 ppm) was added in lithium chloride solution before the reaction. The obtained precipitate was filtered, washed several times by double distilled water and then dried under a drying lamp to get the dried powder of doped Li_3PO_4. Some lithium and phosphorus precursor combinations did not yield precipitate. In such cases, the solution was evaporated to dryness to get the white powder. This powder was then washed several times to remove the unwanted byproducts/un-reacted salts and yield Li_3PO_4. All the powders were heated in air in graphite crucible for 25 min at 600 °C. Various synthesized samples were labeled as

Sample A: from the reaction

$3LiCl + Na_2HPO_4 \rightarrow Li_3PO_4 + 2NaCl + HCl$

Sample B: from the reaction

$3LiCl + H_3PO_4 \rightarrow Li_3PO_4 + 3HCl$

Sample C: from the reaction

$3LiCl + NaH_2PO_4 \rightarrow Li_3PO_4 + NaCl + 2HCl$

For studying the TL/OSL response, all the samples were exposed to a test dose of 100 mGy using $^{90}Sr/^{90}Y$ beta source with the dose rate of 20 mGy/min. All the samples were normalized with respect to weight and dose and the measurements were carried out under identical conditions. Photoluminescence studies were carried on Hitachi-4000 Spectrofluorometer. OSL and TL measurements were taken on the locally fabricated set-up [23]. The assembly consists of array of blue/green LEDs as a stimulation source with power adjustable from 11 to 48 mW/cm^2. Two optical filters viz. UG-1 (across PMT), to prevent stimulation signal from reaching PMT (9111B, 25 mm diameter end window PMT) and GG-435 (across LEDs), to cut-off the stimulation wavelengths below 435 nm, were used in the assembly. All the operations in the assembly are controlled by the suitable software.

During all the OSL measurements the LED power was kept at 11 mW/cm^2 and signal was recorded for 200 s with the acquisition time 0.1 s. All the TL measurements were taken at the heating rate 4 °C/s. The TL was recorded in air atmosphere with HA-3 filter used on PMT side.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the X-ray diffraction patterns of various Li_3PO_4 samples. Fig. 1a shows the XRD pattern of sample A heated at 600 °C. In this pattern along with major phase of Li_3PO_4, minor phase of $Li_4P_2O_7$ (JCPDS no.: 77-1045) along with $Li_2Cu_2P_6O_{18}$ (JCPDS no.: 27-1232) is detected. The relative percentage of these phases can be found out by comparing the relative ratio of the most intense diffraction line of Li_3PO_4 to that of the 100% intense lines of these phases. When the relative ratios were compared, percentages of $Li_4P_2O_7$ and $Li_2Cu_2P_6O_{18}$ in this sample were found to be 20% and 2.2%, respectively. Similar features were observed for samples B (Fig. 1c) and C (Fig. 1b) with different relative percentages of the minor phases and are summarized in Table 1. From the table it could be seen that the relative percentage of $Li_4P_2O_7$ is highest in sample A, whereas relatively high percentage of $Li_2Cu_2P_6O_{18}$ was observed in sample B.

3.2. Photoluminescence properties

Fig. 2 shows the photoluminescence spectra of Cu-doped phosphor synthesized using different phosphorus precursors. As-prepared and un-doped samples do not exhibit any Cu fluorescence. Cu-doped sample A heated at 600 °C shows emission around 365 nm (Fig. 2c) with excitation at 254 nm (Fig. 2a). Cu-

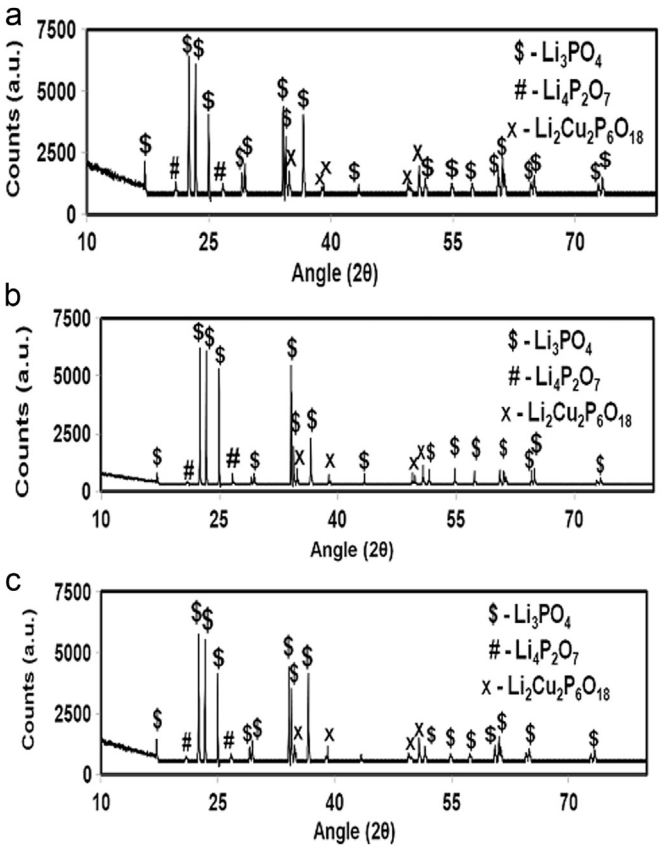

Fig. 1. X-ray diffraction patterns of various Li_3PO_4 samples heated at 600 °C. (a) Sample A, (b) sample C and (c) sample B.

Table 1
Relative intensity of 100% line of $Li_4P_2O_7$ and $Li_2Cu_2P_6O_{18}$ phases with the most intense diffraction line of Li_3PO_4 in the three synthesized samples.

Li_3PO_4 sample	$Li_4P_2O_7$	$Li_2Cu_2P_6O_{18}$
Sample A (%)	20	2.2
Sample C (%)	12	3.5
Sample B (%)	4	5.7

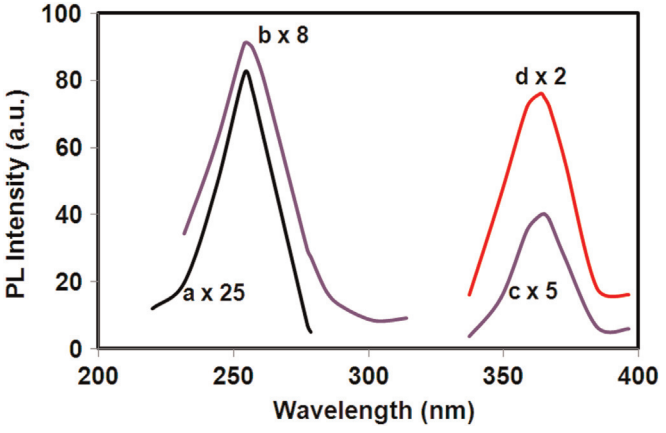

Fig. 2. Photoluminescence spectra of Cu-doped phosphor synthesized using different phosphorus precursors and heated at 600 °C. (a) Excitation curve of sample A, (b) excitation curve of sample C, (c) emission curve of sample A and (d) emission curve of sample C.