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Effect of $Li_4P_2O_7$ and $Li_2Cu_2P_6O_{18}$ minor phases on the luminescent properties of Cu^+ doped Li_3PO_4

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ABSTRACT

The $Li_4P_2O_7$ and $Li_2Cu_2P_6O_{18}$ phase formation and its correlation with luminescent properties in Cu^+ doped Li_3PO_4 were studied. The study shows that in air annealed samples minor phase of $Li_4P_2O_7$ along with $Li_2Cu_2P_6O_{18}$ is formed. The amount of $Li_4P_2O_7$ is inversely proportional to the annealing temperature whereas amount of $Li_2Cu_2P_6O_{18}$ increases with annealing temperature. These phases affect luminescence properties of the material significantly. The Cu^+ luminescence decreases with the increase in $Li_2Cu_2P_6O_{18}$ whereas, the TL–OSL sensitivity is found to be a function of amount of $Li_4P_2O_7$ phase present in the sample. Of the sample annealed at various temperatures maximum OSL sensitivity is obtained for the 600 °C annealed sample for which 20% $Li_4P_2O_7$ phase is detected which is maximum among all air heated samples. The minimum sensitivity is observed in case of sample melted in air in which 3% of this phase is detected. Vacuum heated sample also shows minimum sensitivity, in which no $Li_4P_2O_7$ phase is detected.

1. Introduction

Among various orthophosphates, Li_3PO_4 has received lot of attention because of its chemical and physical stability and ability to form solid solutions with various compounds. Li_3PO_4 is known to exist in three different phases α, β and γ which form at normal pressure and are stable at progressively higher temperatures [1–3]. β-Li_3PO_4 has a wurtzite superstructure and is a low temperature phase. This low temperature phase undergoes a phase transition to γ-Li_3PO_4 (high temperature phase) at 500 °C [4]. But this transition is found to be irreversible under normal dry conditions [5]. At ambient temperature, Li_3PO_4 may exist in both polymorphic forms. At 1170 °C, γ-Li_3PO_4 transforms into α-Li_3PO_4 which is stable up to the melting point at 1220 °C [1]. Li_3PO_4 possesses high ionic conductivity in this phase which is suitable for battery applications. The ionic conductivity of alkali orthophosphates is also found to be enhanced significantly when synthesized under humid or hydrogen containing atmosphere [6]. Attempts were also made to dope nitrogen to enhance the ionic conductivity over several orders of magnitude. This led to the development of a new material named as LIPON.

Luminescence of $3d^n$ ions such as Cr^{4+}, Mn^{5+} and Fe is studied in Li_3PO_4 as part of study in tetrahedral configuration for possible applications as NIR laser material. Li_3PO_4:Mn^{5+} is found to be a potential laser material [7]. The spectroscopic properties of this phosphor have also been used for studying the pressure induced phase transitions of Li_3PO_4 [8]. $LiZn_{1-x}PO_4$:Mn_x is another potential phosphor that can be used as a UV radiation-converting phosphor for LEDs [9]. The Z_{eff} of Li_3PO_4 is 10.6 very near to that of tissue (Z_{eff}=7.4) and other routinely used dosimetry phosphor like Al_2O_3:C. Therefore, attempts were made to develop this phosphor for applications in radiation dosimetry. Cu^+ emission in Li_3PO_4 is reported as early as 2001 [10]. Thermoluminescence in Li_3PO_4 is studied by Naranje et al. [11] with the intention to study role of phosphorous 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. [12].

Several luminescence properties of solids such as luminescence efficiency, emission spectra and excited state lifetimes are affected by the phase of the material. Discontinuities have been observed to occur in these luminescence parameters during phase transitions [13]. In our earlier work changes in luminescence spectra of Cu^+ with respect to phase are observed in Na_2SO_4 [14]. Recently, the

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discontinuities in the 110 °C TL peak intensity are reported in bioglass with the hydroxyl apatite formation [15]. In this paper we report the photoluminescence, thermoluminescence, and optically stimulated luminescence in Cu-doped Li_3PO_4 and its correlation to the $Li_4P_2O_7$ and $Li_2Cu_2P_6O_{18}$ phases which are formed during the annealing of the material.

2. Experimental

Cu doped Li_3PO_4 was synthesized using co-precipitation method in which lithium salt is dissolved in double distilled water to which $CuCl_2$ solution in desired amount was added. The phosphorous precursor in stoichiometric proportion was dissolved in double distilled water separately. Both solutions were mixed to get the white precipitate of Li_3PO_4. This precipitate was filtered, washed several times by double distilled water and then dried under drying lamp to get the dried powder of Li_3PO_4. Several samples with varying Cu concentration (0.01 mol% to 0.5 mol%) were prepared however sample with 0.05 mol% Cu impurity concentration yielded maximum photoluminescence. Hence this concentration is referred to as optimized concentration and sample with this concentration was chosen for further study. All the Li_3PO_4 samples discussed hereafter are with 0.05 mol% of Cu concentration. The sample was heated in air in graphite crucible for 30 min in the temperature range 600–800 °C. Part of the sample was melted at 1200 °C in graphite crucible and quenched. Melted sample is labeled as sample B whereas precipitated sample is labeled as sample A. All the samples were synthesized three times and were found to be reproducible within ± 5%. For taking measurements sieved particles in the 90–210 μm were used.

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 per min. All the samples were weight normalized and the measurements were carried out under identical experimental conditions. Photoluminescence studies were carried on Hitachi-4000 Spectrofluorometer. For recording PL, 200 mg powder of the samples having particle size in the range of 90–210 μm was used. Emission spectra were recorded with excitation band pass 5 nm and emission band pass 1.5 nm, while excitation spectra is recorded with excitation band pass 1.5 nm and emission band pass 5 nm. 150 W Xenon lamp with ozone self deozonating housing is used as a light source. Large stigmatic concave grating having 900 lines per mm is used for the excitation and emission side with eagle mounting (F:3). Blaze wavelengths are 300 nm on excitation side and 400 nm on emission side. Photomultiplier Tube (PMT) R 372F with flat spectral response is used for measurements. The spectra are corrected for wavelength response of the instrument in the range 220–600 nm.

Optical stimulated luminescence (OSL) and thermoluminescence was studied on the fabricated set up [16]. The assembly consists of array of blue/green LEDs as a stimulation source with adjustable power from 11 mW/cm^2 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 thermoluminescence 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. The details regarding the uncertainty in the temperature measurement are discussed elsewhere [16]

3. Results and discussions

Fig. 1 shows the X-ray diffraction pattern of various Li_3PO_4 samples. XRD pattern of as-prepared sample A (Fig. 1(a)) shows that the intense diffraction peaks can be assigned to Li_3PO_4 in orthorhombic phase with space group Pmnb(62) and is similar to observed earlier (JCPDS No. 83-0339). No other peaks that can be assigned to different compounds of Lithium and Phosphorous are observed indicating purity of phase. Fig. 1(b) shows the XRD pattern of sample 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. These minor phases are present in all annealed samples and the relative percentage is found to be the function of annealing temperature. This could be judged by comparing the relative ratio of most intense diffraction line of Li_3PO_4 to that of 100% intense line of these phases. Table 1 shows tabulation of the relative percentage of these phases in the sample annealed at different temperature.

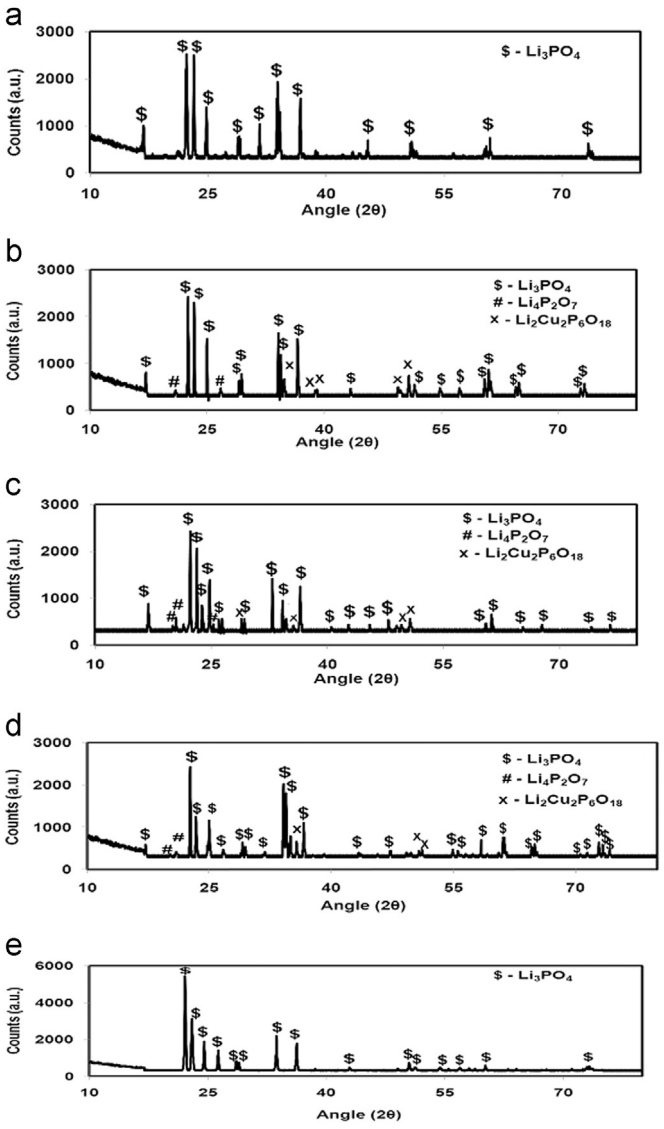

Fig. 1. X-ray diffraction pattern of various Li_3PO_4 samples. (a) X-ray diffraction pattern of as-prepared sample A. (b) X-ray diffraction pattern of sample A heated at 600 °C. (c) X-ray diffraction pattern of sample A heated at 800 °C. (d) X-ray diffraction pattern of sample B. (e) X-ray diffraction pattern of vacuum heated sample.