



Original research article

Electron-vibrational interaction in the 3d states of Cu⁺ ions activated in Na₅Ca₄(PO₄)₄F

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ABSTRACT

Cu⁺-doped Na₅Ca₄(PO₄)₄F fluorophosphate was synthesized by wet-chemical method. This blue-emitting phosphor was characterized by XRD, FTIR and photoluminescence measurements. Rietveld refinement method was employed to analyse the phase formation of the as-prepared phosphor. The electron-vibrational interaction (EVI) parameters were calculated by the spectrum-fitting method. Na₂Ca₄(PO₄)₃F:Cu⁺ phosphor demonstrated blue emission under near-UV excitation and its CIE coordinates were found at (0.151, 0.037).

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1. Introduction

The LED phosphor market is, currently, being dominated by rare-earth activated phosphors. However, the expenses arising from the use of rare-earth ions makes it a costly affair. In this viewpoint, alternatives like transition metal ions are considered as dopants for phosphor materials [1,2]. Among them, copper ions are capable of producing excellent luminescence. On doping, Cu ions can exist in monovalent or divalent charge state and both of them are capable of producing luminescence. Unfortunately, it is a matter of concern to obtain a favourable host environment for the Cu⁺ ions to luminesce. Subsequently, very few number of materials are reported to exhibit Cu⁺ luminescence [3–6]. Cu⁺ ions have generally produced luminescence in the NUV or blue region [3,7]. Hence, Cu⁺-doped phosphors can be best replacements for highly expensive Ce³⁺ or Eu²⁺ doped blue-emitting phosphors.

In this context, we have developed a new blue-emitting Na₂Ca₄(PO₄)₃F halophosphate phosphor activated with Cu⁺ ions. The luminescence spectra were analysed theoretically to find the electron-vibrational interaction parameters.

2. Experimental

Na₂Ca₄(PO₄)₃F:Cu phosphor was prepared by a facile wet-chemical synthesis technique. Highly pure, analytical grade NaNO₃, Ca(NO₃)₂, NH₄H₂PO₄ and NH₄F were taken in a stoichiometric ratio. Separate solutions of each precursor in double distilled de-ionized water were prepared and then each of them was added in a teflon beaker with continuous stirring. Thereafter, water soluble salt of Cu(NO₃)₂·3H₂O was added to these solution. It was confirmed that all the salts had completely dissolved in water and no residual constituents were left behind. The resultant solution was kept for mild heating along

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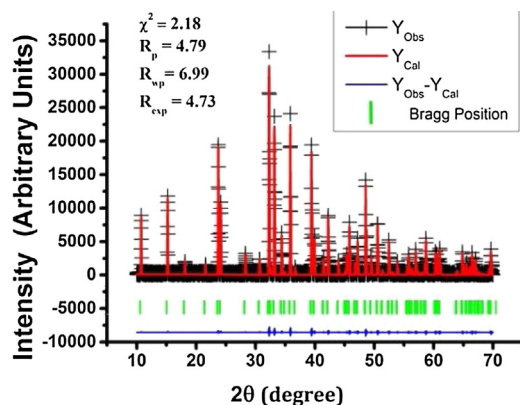


Fig. 1. Rietveld Refinement of the XRD pattern of $\text{Na}_5\text{Ca}_4(\text{PO}_4)_4\text{F}:0.001\text{Cu}^+$ phosphor.

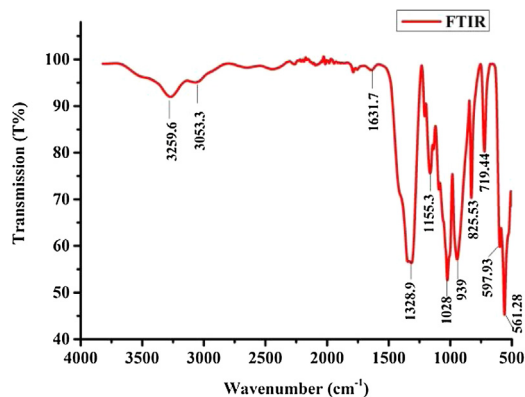


Fig. 2. FTIR spectrum of $\text{Na}_5\text{Ca}_4(\text{PO}_4)_4\text{F}:0.001\text{Cu}^+$ phosphor.

with stirring. The transparent solutions were then evaporated at 80°C in a hot air oven until the samples became dry. The powders were further heated at 600°C for 4 h in a muffle furnace to improve the crystallinity of the powders and to remove maximum possible water molecules from the powder. The dried samples were then slowly cooled at room temperature. The resultant powders were crushed to fine particles in a mortar pestle and were used for further characterization.

3. Results and discussion

Fig. 1 shows the Rietveld refinement analysis of the XRD pattern of $\text{Na}_5\text{Ca}_4(\text{PO}_4)_4\text{F}:0.001\text{Cu}^+$ phosphor using FullProf Suite program 2.05 [8]. The refinement was performed until the reliability factors converged to $\chi^2 = 2.18$, $R_p = 4.79$, $R_{wp} = 6.99$, $R_{exp} = 4.73$. The structure is found to crystallize into a tetragonal phase with space group $I\bar{4}$ (No. 82). All the peaks in the XRD pattern can be indexed as per the JCPDS data card No. 73–0074. Obviously, no peak corresponding to impurity phases or residual precursors were detected and the doping of Cu^+ ions did not produce any noticeable changes in the XRD pattern. Following refinement, the crystallographic parameters were found to be $a = b = 11.644$, $c = 5.396$, $\alpha = \beta = \gamma = 90^\circ$ and $V = 731.604$. Fig. 2 shows the FTIR spectrum of $\text{Na}_5\text{Ca}_4(\text{PO}_4)_4\text{F}:0.001\text{Cu}^+$ phosphor. Some very strong absorption peaks can be perceived from 500 to 800 cm^{-1} corresponding to the bending vibrations of PO_4^{3-} species. The O–P–O symmetric and asymmetric bending vibrations of PO_4^{3-} species has given rise to the absorption peaks at 561.28 cm^{-1} , 597.93 cm^{-1} and 714.44 cm^{-1} [9–11]. The strong absorption peaks at 825.53 cm^{-1} and 939 cm^{-1} can be attributed to the symmetric stretching vibrations of P–O, whereas the absorption peaks at 1028 cm^{-1} and 1153.3 cm^{-1} can be assigned to the asymmetric stretching vibrations of P–O [12,13]. The peak observed at 1328.29 cm^{-1} is attributed to the stretching mode of P=O bond. The peak at 1631.7 cm^{-1} corresponds to the hydrogen bonding, thus, indicating the presence of water molecules [14]. The absorption bands observed at 3053.3 cm^{-1} and 3259.6 cm^{-1} can be assigned to the fundamental stretching vibrations of O–H bond [15]. The presence of water molecules is generally observed for wet chemical synthesis methods. Even prolonged heat treatments of the samples are unable to remove the water molecules that occupy deeper inter-molecular positions of a material.

Fig. 3(a) and (b) shows the photoluminescence (PL) excitation and emission spectra of $\text{Na}_5\text{Ca}_4(\text{PO}_4)_4\text{F}:0.001\text{Cu}^+$ phosphor recorded at room temperature. The excitation spectrum was recorded by monitoring the emission wavelength at 435 nm (22988.5 cm^{-1}); it consists of a dominant peak at 405 nm (24691.35 cm^{-1}) and a shoulder peak at 382 nm (26178.55 cm^{-1}). The emission spectrum shows two distinct peaks at 435 nm (22988.5 cm^{-1}) and 463 nm (21598.27 cm^{-1}). The emission

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