

Synthesis and optical characterization of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Tb}^{3+}$ and Mn^{2+} phosphor for solid state lighting

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ABSTRACT

In present work we studied the luminescence properties of Tb^{3+} and Mn^{2+} doped $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor synthesized by wet chemical method were studied with extra heat treatment, to understand the mechanism of excitation and the corresponding emission of prepared phosphor. For the green emission, Tb^{3+} ion is used as an activator, the excitation and emission spectra indicate that this phosphor can be effectively excited by 380 nm, to exhibit bright green emission centered at 545 nm corresponding to the $f \rightarrow f$ transition of Tb^{3+} ions. The emission spectrum of Mn^{2+} ion at 405 nm excitation ${}^4\text{T}_1(4\text{G})\text{-}{}^6\text{A}_1(6\text{S})$ gives an emission band at 591 nm (orange-red). The observed photoluminescence (PL) measurements of Tb^{3+} and Mn^{2+} activated prepared phosphor indicates that these are the outstanding green and orange-red emitting potential phosphor, suitable application for the solid state lighting. The synthesized phosphors were analyzed by X-ray diffraction (XRD) for confirmation of phase and purity. The morphology and structure were characterized by scanning electron microscopy. Thus the phosphors in this system may be chosen as the green component for the tri-color lamp and certainly applied in w-UVLEDs. In the view of the excitation band and excellent luminescent properties, $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Tb}^{3+}$ and Mn^{2+} phosphor is expected to be a potential candidate for application in n-UV white LEDs and solid state lighting because of its cost efficient manufacturing, mercury free excitation and eco-friendly characteristics. Copyright © 2015 VBRI Press.

Keywords: Wet chemical method; solid state lighting; photoluminescence; XRD; SEM.

Introduction

Solid-state lighting and phosphor material to produce white light is the recent research focus in the lighting industry. It has lot of advantages over conventional fluorescent lamps for example reduced power consumption, compactness, efficient light output, and longer lifetime. Solid-state lighting will have its impact on reducing the global electricity consumption [1, 2]. White light-emitting diodes (LEDs) can save about 70% of the energy and do not need any harmful ingredient in comparison with the conventional light sources, such as incandescence light bulbs and the luminescent tubes [3]. Therefore white LEDs have a great potential to replace them and are considered as next generation solid state light devices [4, 5]. Rare earth ions are characterized by an incompletely filled 4f shell, which can absorb the excitation energy to be at the excited state and then return to the ground state, resulting in emitting state in the visible region [6, 7]. These feature transitions within the $4f_n$ configuration have been found an important application in lighting and display. The synthesis of

conventional rare earth phosphors primarily focused on the high-temperature solid-state reactions providing agglomerated powders. They can allow to readily altering the structural characteristics of the solid powders [8]. So, in this work we focused on the preparation condition and process of the phosphor with extra heat treatment because many factor affect its structure and luminescent properties. Thus the phosphors in this system may be chosen as the green component for the tri-color lamp and certainly applied in w-UVLEDs. In the view of the excitation band and excellent luminescent properties, $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Tb}^{3+}$ and Mn^{2+} phosphor is expected to be a potential candidate for application in n-UV white LEDs and solid state lighting because of its cost efficient manufacturing, mercury free excitation and eco-friendly characteristics. The Tb^{3+} doped $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor were prepared by using wet chemical method with extra heat treatment and their luminescent properties are discussed in detail, thermal stability, the synthesis processing details and factors those affecting the structure and luminescent properties of phosphor [9] were also studied.

Experimental

Sample preparation

Phosphors with compositions of $\text{Ca}_2\text{PO}_4\text{Cl}$ were prepared by a wet chemical synthesis method with extra heat treatment. The constituent raw materials was all from A.R. grade from merk such as $\text{Ca}(\text{NO}_3)_2$, NH_4Cl and $\text{NH}_4\text{H}_2\text{PO}_4$, Tb_4O_7 and $\text{Mn}(\text{NO}_3)_2$ with purity 99.99 %. Tb_4O_7 is converted in to nitrate form by mixing of appropriate amount of dilute nitric acid. All the mixtures were mixed according to stoichiometric ratio. An appropriate amount of distilled water was taken to dissolve all the compounds. After dissolving all the mixture put it on magnetic stirrer for complete the dissolve process. The resulting solution is then transferred into a hot oven maintained at 100°C for 24 hrs. After the solid compound so formed was taken out of oven and crushed it for 15 to 20 minute and then a homogeneous compound which was further heated at 300°C in case of Tb^{3+} for 8 hrs and with reducing atmosphere of charcoal treatment at 400°C for 12 hr duration in case of Mn^{2+} . The final product obtained is in the powder form, which is used for further investigations. The same amount of sample was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

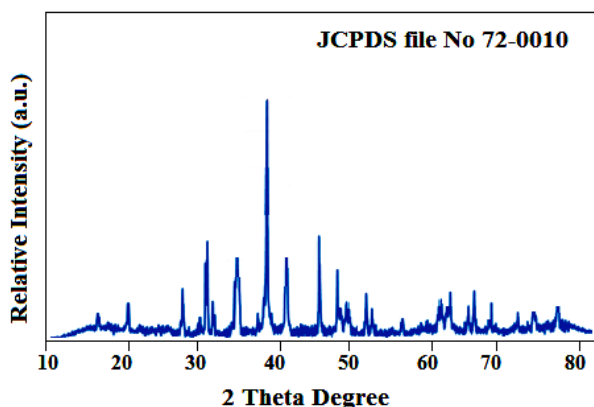


Fig. 1. XRD pattern of $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor.

Results and discussion

XRD phase analysis

In order to explore the crystal phase structure, the XRD phase analysis was adopted. The typical XRD patterns of $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor are shown in Fig. 1. For the obtained phase, it is carefully observed that there are no peaks of raw materials. It is found that the main phase is in good agreement with standard JCPDS data file no.72-0010.

SEM study

The surface morphology and crystalline sizes of the synthesized $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor was observed and shown in Fig. 2. It can be seen that all of the phosphor powders consisted of irregular fine grains with an average size of about micrometer range and have surface morphology of crystalline grains which looks like sharp edge chip. It is seen from the micrographs that the crystallite sizes vary from a few microns to several tens of microns.

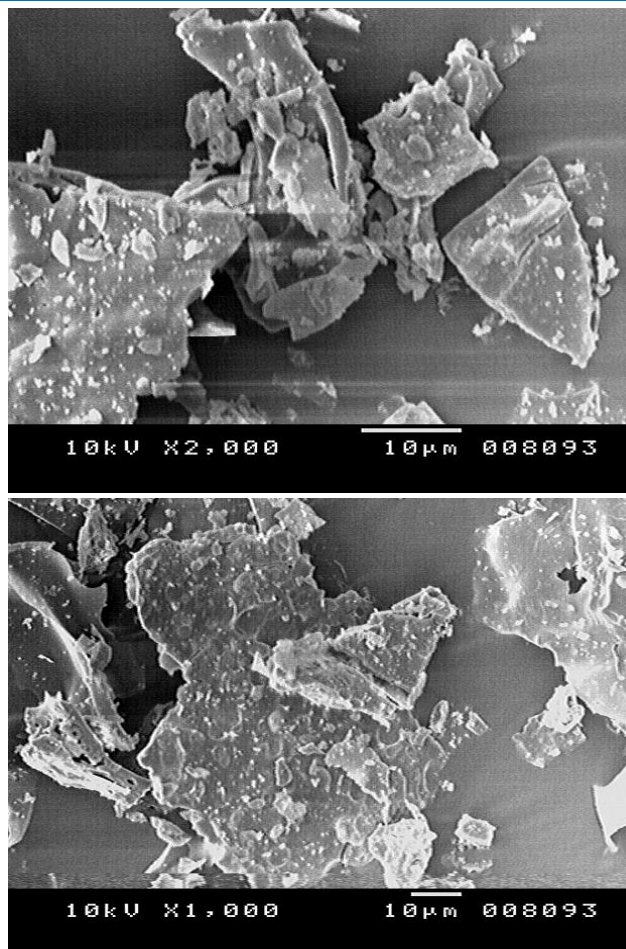


Fig. 2. SEM of $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor.

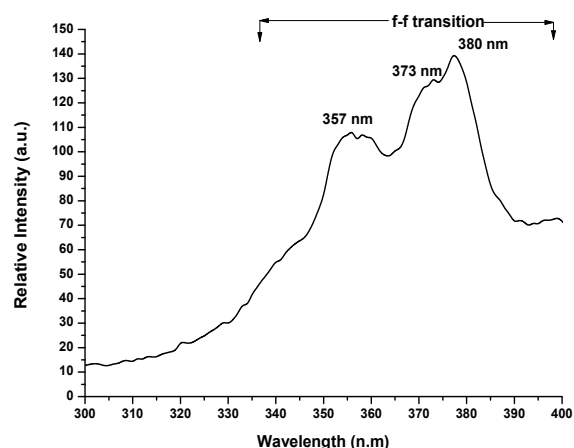


Fig. 3. Excitation spectrum of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Tb}^{3+}$ phosphor, $\lambda_{\text{em}} = 545$ nm.

Photoluminescence measurements

As shown in Fig. 3, the excitation spectrum observed at 545 nm emission wavelength of $\text{Ca}_2\text{PO}_4\text{Cl}$ doped with Tb^{3+} consisting of a broad band as well as some sharp lines. Some peak observed due to f-d interaction while sharp lines are due to f-f transitions. The emission spectrum Fig. 4 has sharp lines on account of f-f transition of Tb^{3+} ions. The emission spectrum usually has major contribution from $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) and peak due to $^5\text{D}_3 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) can

also be seen. The nature of ${}^5D_4 \rightarrow {}^7F_1$ transitions is governed by the selection rule $\Delta J = \pm 1$ for electric dipole and $\Delta J = 0, \pm 2$ for magnetic dipole transitions respectively. The emission intensity of 5D_3 level is very weak and weakens further with increasing Tb^{3+} concentration, followed by the enhancement of the emission from the 5D_4 level, occurs due to non-radiative cross-relaxation via the resonant energy transfer process between 5D_3 and 5D_4 levels. As the concentration of Tb^{3+} is changed, the cross-relaxation effect becomes stronger, which enhances the intensity of green emission at 545 nm. The other reason that has been assigned to weak luminescence from 5D_3 level is the lack of phonon energy of the host. The smaller the phonon energy of the host at diluted concentrations of terbium ions, the lower will be the 5D_3 emission intensity and vice versa [9, 10].

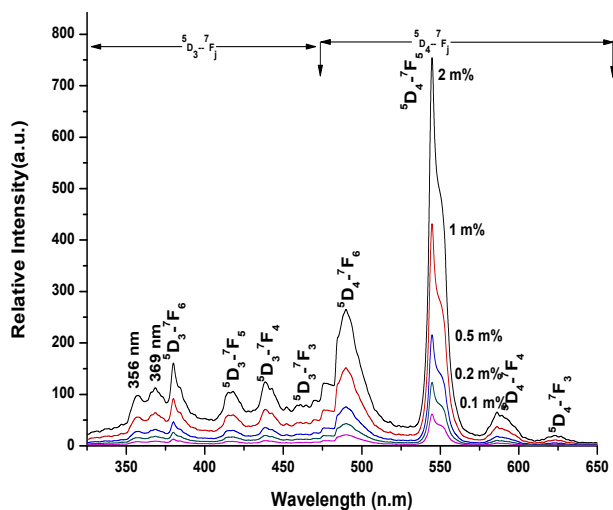


Fig. 4. Emission spectrum of $Ca_2PO_4Cl: Tb^{3+}$ λ_{ex} 380 nm.

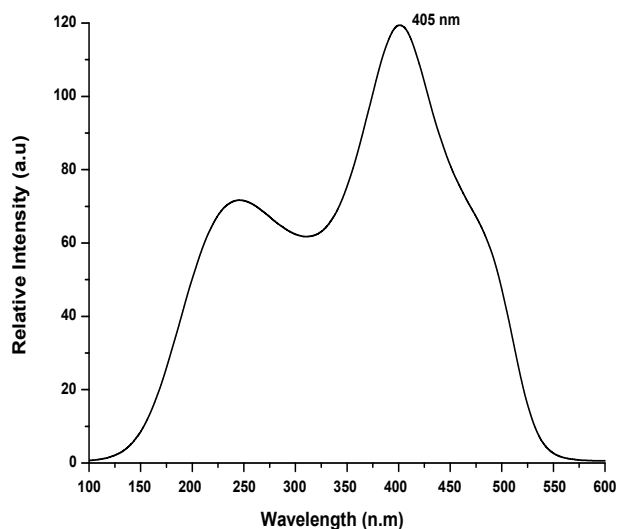


Fig. 5. Excitation spectrum of $Ca_2PO_4Cl: Mn^{2+}$ phosphor, $\lambda_{em} = 591$ nm.

The emission spectra of $Ca_2PO_4Cl: Mn^{2+}$ are shown in the Fig. 5 at different Mn^{2+} concentrations. The emission intensities increased with increasing Mn^{2+} concentration, reaching a maximum at 10 m%, respectively. Fig. 6 shows that $Ca_2PO_4Cl: Mn^{2+}$ had an orange-red emission around 591 nm, ascribed to the spin forbidden ${}^4T_1(4G) \rightarrow {}^6A_1(6S)$

transition of the Mn^{2+} ion. The excitation spectrum of $Ca_2PO_4Cl: Mn^{2+}$ contains a number of bands, and the strongest excitation at 405 nm corresponds to the transition from the ${}^6A_1(6S)$ ground state to the excited states [$4E(4G)$, ${}^4A_1(4G)$] [11-12].

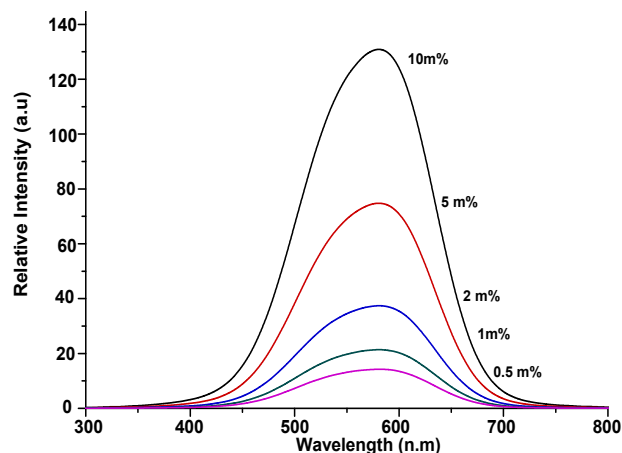


Fig. 6. Emission spectrum of $Ca_2PO_4Cl: Mn^{2+}$ λ_{ex} 405 nm.

Conclusion

Tb^{3+} and Mn^{2+} activated Ca_2PO_4Cl phosphor was prepared successfully by the wet chemical synthesis with extra heat treatment. The SEM indicated that the particle size of the phosphor is in the sub-micron range. The crystal phases of the prepared particles were analyzed by X-ray diffraction (XRD) pattern which exactly matches with standard JCPDS data file. The emission spectrum of $Ca_2PO_4Cl: Tb^{3+}$ (at 380 nm excitation) has intense bands centered at 545 nm and which correspond to the green regions of the visible spectrum, and under the excitation around 405 nm, the $Ca_2PO_4Cl: Mn^{2+}$ phosphors show the orange-red emission from Mn^{2+} . The result indicates that $Ca_2PO_4Cl: Tb^{3+}$ phosphor is a good promising green and orange-red emitting phosphor while Mn^{2+} is the orange-red emitting phosphor for solid state lighting. Thus the phosphors in this system may be chosen as the green component for the tri-color lamp and certainly applied in w-UVLEDs. In the view of the excitation band and excellent luminescent properties, $Ca_2PO_4Cl: Tb^{3+}$ and Mn^{2+} phosphor is expected to be a potential candidate for application in n-UV white LEDs and solid state lighting because of its cost efficient manufacturing, mercury free excitation and eco-friendly characteristics.

Reference

- Panse, V. R.; Kokode, N.S.; Dhoble, S.J.; *Adv. Mat. Lett.* **2014**, *5*(10), 604.
DOI: [10.5185/amlett.2014.amwc432](https://doi.org/10.5185/amlett.2014.amwc432)
- Nagpure, I.M.; Pawade, V.B.; Dhoble, S.J.; *J. Lumin.* **2010**, *25*, 9.
DOI: [10.1002/bio.1132](https://doi.org/10.1002/bio.1132)
- Karabulut, Y.; Canimoglu, A.; Kotan, Z.; Akyuz, O.; Ekdal, E.; *J. Alloys Compd.* **2014**, *583*, 91.
DOI: [10.1016/j.jallcom.2013.08.172](https://doi.org/10.1016/j.jallcom.2013.08.172)
- Hoppe, H.A.; *Angew. Chem. Int. Ed.*, **2009**, *48* (20), 3572.
DOI: [10.1039/c1jm15084g.824](https://doi.org/10.1039/c1jm15084g.824)
- Chan, T.S.; Liu, R.S.; Ivan, B.; *Chem. Mater.* **2008**, *20*(4), 1215.
DOI: [10.1021/cm7028867](https://doi.org/10.1021/cm7028867).
- Shaik, N.P.; Rao, N.V. P.; Murthy, K.V.R.; *Adv. Mat. Lett.* **2014**, *12*(5), 722.

- DOI: [10.1021/cr00025a002](https://doi.org/10.1021/cr00025a002)
7. Tuan, D.C.; Olazcuaga, R.; Guillen, F.; Garcia, A.; Moine, B.; Fouassier, C.; *J. Phys. IV, France*, **2005**, 123, 259.
DOI: [10.1051/jp4:2005123047](https://doi.org/10.1051/jp4:2005123047)
8. Panse, V.R.; Kokode, N.S.; Dhoble, S.J.; *J. Chem. Bio. Phy. Sci.* **2014**, 4(4), 3736.
DOI: www.jcbosc.org/admin/get_fileph.php?id=274
9. Nag, A.; Kutty, T.R.N.; *J. Mater. Chem. Phys.* **2005**, 91, 524.
DOI: [10.1016/j.matchemphys.2004.12.020](https://doi.org/10.1016/j.matchemphys.2004.12.020)
10. Chang, Y.S.; Lin, H.J.; Li, Y.C.; Chai, Y.L.; Tsai, Y.Y.; *J. Sol. State Chem.* **2007**, 180, 3076.
DOI: [10.1016/j.jssc.2009.08.022](https://doi.org/10.1016/j.jssc.2009.08.022)
11. Huang, C.H.; Chen, T.M.; Liu, W.-R.; Chiu, Y.-C.; Yeh, Y.-T.; Jang, S.-M.; *ACS Appl. Mater. Interfaces* **2010**, 2, 259.
DOI: [10.1021/am900668r](https://doi.org/10.1021/am900668r)
12. Liu, W.R.; Huang, C.-H.; Yeh, C.W.; Chiu, Y.-C.; Yeh, Y. T.; Liu, R.-S.; *RSC Adv.* **2013**, 3, 9023.
DOI: [10.1039/C3RA40471D](https://doi.org/10.1039/C3RA40471D)

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