Recent progress in phosphate based luminescent materials: A case study

Toshi S Dhapodkar¹, Abhijeet R Kadam¹, Arati Duragkar²*, N S Dhoble² and S J Dhoble¹

Department of Physics, R. T. M. Nagpur University, Nagpur – 440033, India
Department of Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur-440015, India

*Corresponding author: amduragkar@gmail.com

Abstract. The uses of phosphate based luminescent materials are presented in this study in different fields of luminescence. There are different types of luminescent phosphors are available in the field of luminescence such as borates, sulphates, fluorides, sulphides, phosphates etc. From all these phosphors, phosphate-based phosphors shows their potential in almost every field of luminescence in last few years and it becomes a key material in the luminescence especially in photoluminescence, thermoluminescence and mechanoluminescence. These rare earths activated phosphate-based luminescence materials are synthesized with different techniques by means of wet chemical method, combustion technique, sol gel analysis and solid-state diffusion technique etc. which are described in the present article. Consequently, this article chiefly dealing the overview of different phosphate based luminescent materials and modern development and progression in the field of luminescence.

Keywords: phosphates; luminescent materials; chemical synthesis; dosimetry; photoluminescence.

1. Introduction

Luminescence phenomenon is essentially known for the emission of cold light from the different energy sources which take places at the comparatively low temperatures[1]. Some energy source transferred to an electron from ground to excited state, and then the energy releases by the electron in the form of light so it can fall back to its ground state in luminescence phenomenon. Luminescent material is also called ‘phosphors’. Phosphors are consisting of a host lattice and a luminescent center frequently known as an “Activator”. The activators absorb the exciting radiations and are elevated to an excited state. The excited state proceeds for the ground state by release of radiation. The activator does not absorb the excitation radiation in several materials although the erstwhile ion might absorb the exciting radiation and then move it to the activator. In such studies the absorbing ion is known to be a sensitizer[2]. In various cases the host lattice transmits the excitation energy to the activator, thus the host lattice function as a “Sensitizer”. The host lattice is comprises of as a minimum one sort of oxide certained from the sulphide[3], aluminate[4,5], alumino silicate[6], silicate[7], titanate[8], niobate[9], phosphate[10], halophosphate[1], Borate[11], tungstate[12] etc.

Above all the materials, phosphate plays a significant role in environmental systems and utilize a wide range of functions in consequence of their outstanding simplicity, low viscosity, high ultraviolet(UV) transmission, high-quality mechanical, thermal constancy, isotropic refractive index and simple
In past few years, phosphate compounds encompass attentive important interest as plasma display panels (PDPs) materials owing to the information that phosphate-based phosphors are significant luminescent host and have their tough absorption in VUV region (100–200 nm), and also have a high chemical stability and cheap price[15]. There are different types of rare earth activated phosphate materials were reported in recent times for the use it in the field of light emitting diodes (LEDs). From these materials, mineral based phosphate materials have attracted main attention as photoluminescent materials. Phosphate-based phosphors are well-known materials for solid-state lighting applications. Phosphate is appropriate for hosting w-LEDs since it has medium tone energy, high damage threshold, high thermal and chemical stability, inexpensive raw materials, and gentle preparation conditions, etc. The tetrahedral \((\text{PO}_4)^{3-}\) ions in the phosphate lattice contain four oxygen atoms, which coordinate well to the transition / internal transition metal ions to form a highly crystalline structure. Typically, phosphate minerals are mostly found in the form of apatite’s, mainly in the form of apatites of calcium. It is found as \(\text{Cas(PO}_4)_3\cdot Z\) where \(Z\) is an ion such as \(\text{OH}^-, \text{Cl}^-\), and \(\text{F}^-\). So far, many phosphate minerals have been published according to various applications[16], some of them we are discussing here. \(\text{K}_2\text{BaCa(PO}_4)_2\cdot \text{Eu}^{2+}, \text{Mn}^{2+}\) phosphors for high excellence white LED appliance is reported by the scientists[17]. In the proposed study, researchers have reported \(\text{K}_2\text{BaCa(PO}_4)_2\cdot \text{Eu}^{2+}, \text{Mn}^{2+}\) phosphors prepared via solid state diffusion method. XRD pattern of synthesized phosphors are well matched with standard available data. The synthesized \(\text{K}_2\text{BaCa(PO}_4)_2\) (KBCP) phosphors revealed tetragonal crystal structure with \(\text{P}_4\text{m}(164)\) space group. In this crystal structure, it was expected that rare earth ions \(\text{Eu}^{2+}\) and \(\text{Mn}^{2+}\) occupy the \(\text{K}^+\) sites[17]. DFT calculation was also done for study of electronic structure of the KBCP:0.03 mol % \(\text{Eu}^{2+}\),0.05 mol % \(\text{Mn}^{2+}\) phosphors. Researchers also reported luminescence properties of synthesized \(\text{K}_2\text{BaCa(PO}_4)_2\cdot \text{Eu}^{2+}\), \(\text{Mn}^{2+}\) phosphors. The PL emission spectra shows broad emission band centeret at 470nm, these emission spectra observed under 330 nm excitation wavelength. \(\text{Mn}^{2+}\) concentration dependent PL spectra of KBCP:0.03 mol % \(\text{Eu}^{2+}\),y mol % \(\text{Mn}^{2+}\) phosphors also observed under 330nm excitation. The concentration dependent PL spectra revealed energy transfer mechanism between \(\text{Eu}^{2+}\), \(\text{Mn}^{2+}\) PL spectra revealed red-shift after doping of \(\text{Mn}^{2+}\) ions at various concentration, it also revealed when the concentration of \(\text{Mn}^{2+}\) ions increased. KBCP:0.03mol % \(\text{Eu}^{2+}\),0.05mol % \(\text{Mn}^{2+}\) phosphors show maximum emission intensity. The CIE chromaticity coordinate of KBCP:0.03mol % \(\text{Eu}^{2+}\),0.05mol % \(\text{Mn}^{2+}\) phosphor have (0.301, 0.386) and CCT value of 6664K. Quantum efficiency (QE) of KBCP: \(\text{Eu}^{2+}\), \(\text{Mn}^{2+}\) phosphor is higher than 70%. The synthesized phosphor was fabricated in w-LEDs with 365nm UV chip. The Fabricated WLEDs exhibits good Ra (74.4) and CCT (6787 K) with outstanding current constancy at 300mA. These outcomes present that KBCP: \(\text{Eu}^{2+}\), \(\text{Mn}^{2+}\) have immense quality for employ in LEDs as a appropriate white light emitting phosphor[17].

2. Methodology
There are different types of synthesis methods were reported till date for the synthesis of phosphate-based materials. Details of each method were described below;

2.1 Melt quenching technique
Melt quenching method one amongst the oldest technique of methodology for producing phosphors which also contains phosphate-based phosphors for the preparation of glass or w-LEDs. During this technique, starting materials and minerals were mixed meticulously and melted this solution by keeping it in furnace. This melt solution is then poured on the brass plate then it's pressed instantly with another plate to form a thin transparent glass. This obtained glass shows color depending on the starting material and therefore the dopant we tend to use throughout the preparation process. The rate of quenching is another factor that affects glass formation, the quicker the rate of melt quenching, the better the glass formation[18,19].
2.2 Wet Chemical method

Wet chemical method is chemical based method which requires materials in the form of nitrates usually because they are easily dissolvable in water. Wet chemical method is also a method for material synthesis but under this name “Wet Chemical” there are few more methods are added like sol-gel method, co-precipitation method, combustion method etc. combustion method contains more sub methods therefore we describe this method separately in the end of this section. So, here we explain sol gel method, main wet chemical method separately[20].

2.2.1 Sol – Gel Method

In this method, all water dissolvable materials were used for the synthesis of phosphor. All starting materials were dissolved in the beaker while keeping it on constant stirring at 800 OC. After dissolving all the reagents citric acid and polyethylene glycol (PEG) were added in the solution drop wise with the interval of 30 min. here citric acid is used as chilling agent and PEG is used as cross linking agent in the synthesis process. The ratio of citric acid and PEG is to be maintained 1:1 in the synthesis process. After mixing all the reagents, kept this solution on constant stirring with 800 OC temperature of hotplate. After some time, a gel type solution is formed. This solution is then kept in oven for drying at 100 OC. After drying a black fluffy ash type sol was obtained. This black powder is due to chilling agent. This black powder is then annealed at above 500 OC. After annealing a white fine powder is obtained this is further used for characterizations[21,22].

2.2.2 Main wet chemical method

In this method we don’t need any type of fuel for synthesis like we used before in sol-gel technique. Here we require starting materials which can dissolve in minimum amount of water. Take all starting materials in stochiometric ratio and dissolve them separately in beaker in minimum amount of water with constant stirring on hotplate keeping it at 80 OC. After dissolving it completely, add them in one beaker one by one with constant stirring in one beaker and keep it on hotplate. After this, a white precipitate was found keep this precipitate for drying in hot air oven for over the night at 90 OC. after that collect the dried sample and annealed it for 2 hours for removing an impurity. By cooling it at room temperature collect the final product for further characterizations[23].

2.2.3 Co-precipitation method

This is another wet chemical-based synthesis method which also required water dissolvable salts for synthesis. In this process, all the salts are dissolved into double distilled water solution and rare earths are also dissolved into water solution in the occurrence of ethanol. Ethanol is usually used as a surfactant to: evade agglomeration, organize size of the particles, and sustain consistency in the particle size. The co-precipitation method in the nonappearance of ethanol causes particles to go through aggregation by this means consequential in the non-uniformity and enlarge in particle size. All solutions are mixed in the presence of ethanol. After mixing, the precipitate is then collected by centrifuging it. After getting final precipitate, wash it several times by distilled water in order to remove impurity. This washed precipitate is then dried in oven at 100OC for 24 hrs. This dried sample is then calcinated for 2 hours and a final product is obtained after cooling it at room temperature[24,25].

2.2.4 Combustion synthesis

Combustion synthesis is one of the main types of wet chemical-based synthesis and further divided into two categories i.e., Simple combustion synthesis method and solution combustion synthesis method. In combustion synthesis method, type of synthesis technique is also differing by the fuel we are using for the synthesis. Different fuels are used for the preparation material by both solution and simple combustion
methods like urea, citric acid, glycine, ethanol, DFH etc. Method for preparation of sample by both the methods are explained in subsequent part of this article[26].

2.2.4.1 Simple combustion method
In simple combustion method, all the starting materials was weighed in stoichiometric ratio and fuel which is used can be used in particular ratio and dissolve all the materials in a mortar pestle using distilled water. After dissolving all the samples in distilled water, transfer this solution in the china dish and fired this sample in open furnace at 500 to 550°C. An enormous flame was analysed in the open furnace during the sample is burning. Once this sample is burned completely flame will damped in five minutes. Then takeout this sample from the oven and cooled it at room temperature. After cooling this sample can crushed for five minutes and keep it in furnace for annealing for 24 hrs in purpose of removing impurity. The sample is then cooled down at room temperature after 24 hrs and uses this sample for further studies[27].

2.2.4.2 Solution combustion method
Solution combustion technique is another type of combustion technique using fuel. Same types of fuels were used in this method also like used in simple combustion technique. In this technique, all the starting materials were dissolved in a beaker by keeping it on constant stirring at constant temperature on magnetic stirrer. Once the starting materials and fuel get dissolved, transfer this solution into the china dish and repeat the same procedure as described in simple combustion method. It is to be noted that when citric acid is used as fuel, the sample turns black after firing it in the open furnace in both the methods. Once it keeps for annealing, it turns into white powder and useful for the studies. All above described synthesis techniques are very useful in preparation of phosphate based phosphors for luminescence study[28].

3. Phosphates in different field of luminescence
3.1 Phosphate in photoluminescence
Phosphate based luminescent materials has been widely investigated in the past few year because of its excellent spectroscopic properties and crystalline nature. In few recent studies Lanthanides (Ln)-activated RE phosphate stands out as an interesting and corresponding however applicable optical fluorescent probe in consequence of its inimitable luminescent behaviour in the occurrence of appropriate activators (such as, Ce3+, Tb3+, Eu3+, Gd3+, etc), therefore stand-in as an proficient substitute to the conventional semiconductor QDs enclosing cadmium. Additionally, Ln-activated large band gap nanocrystals furthermore endow with rigorous crystal surroundings for the dopant ions, resultant in a higher photoluminescence (PL) quantum yield (QY). There are numerous phosphate based phosphors are available but LaPO₄ (LAP) also increase supreme significance in numerous fields for example laser materials, catalysts, heat-resistant materials, proton conductors, versatile biological labels, and photon upconversion materials[29].

Until now, frequent techniques for example hydrothermal, microwave heating, and solid-state diffusion have been engaged for the production of LaPO₄:RE³⁺; nevertheless, these syntheses need ruthless environment of high heat and/or high pressure. These drawbacks also bound the potential functions of these phosphors. Thus, low-temperature synthesis, particularly room-temperature growth of RE nanocrystals, has drawn incredible interest in investigate attention because it offers abundant striking rewards over the normally used processes. Moreover Kadam et al. reported Eu³⁺ activated Na₂Sr₂Al₂PO₄Cl₉ phosphors[30] which show very good photoluminescent behaviour in phosphate based materials. Moreover, on replacing phosphate group with doubly and triply ionized ions, the photoluminescent intensity of the phosphor get enhanced by particular amount which shows that the high temperature synthesis methods are not suitable for the PL behaviour as well as optical properties of the phosphors. Figure 1 (a) and figure 1 (b) displays the variation in the PL intensity on replacing PO₄ ion in the phosphor with other doubly and triply ionized ion.
Figure 1 (a). Photoluminescence emission of Eu$^{3+}$ activated Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ phosphor synthesized by solid state reaction method (Reprinted with the permission from ref.[30] © Elsevier publication).

Figure 1 (b). Photoluminescence emission of 1 mol % Eu$^{3+}$ activated Na$_2$Sr$_2$Al$_2$(PO$_4$)$_x$(VO$_4$)$_x$Cl$_6$F$_3$ phosphor synthesized by solid state reaction method (Reprinted with the permission from ref. [30]© Elsevier publication).
4. Concluding remark
In the proposed review article, current progresses of phosphate-based materials in the different field of luminescence have been reviewed. Different synthesis methods for the preparation of phosphate-based phosphor materials such as wet chemical method; combustion method; sol gel method has been described in detail. It is researched that the improvement of PL phosphate phosphors needs the materials whose properties are appropriate for the solid-state lighting. Those phosphors can be utilized for work force, clinical and natural dosimetry and so on especially the quest for extremely low portion dosimetry phosphors necessitates that the materials should be exceptionally touchy toward the ionizing radiations. Above detailed phosphors by and large contain absconds which go about as color centers and are responsible for their alluring optical and photoluminescence properties too. At present specialists, including our gathering are making endeavors to look and grow new phosphate-based materials with upgraded radiance properties.

5. References
[1] Gupta K K, Kadam R M, Dhoble N S, Lochab S P, Singh V and Dhoble S J 2016 Photoluminescence, thermoluminescence and evaluation of some parameters of Dy$^{3+}$ activated Sr$_5$(PO$_4$)$_3$F phosphor synthesized by sol-gel method. J. Alloys Compd. 688 982–93
[2] Lingeshwar Reddy K, Balaji R, Kumar A and Krishnan V 2018 Lanthanide Doped Near Infrared Active Upconversion Nanophosphors: Fundamentals, Synthesis Strategies, and Technological Applications Small 14 1–27
[3] Lu Y, Yang Y, Guan L, Wang D, Zhao J, Yang J, Wei Z, Wang F, Yang Z and Li X 2020 Luminescent modulation of zinc sulphide nano-particles by thermal injection method. J. Lumin. 226
[4] Deopa N and Rao A S 2017 Spectroscopic studies of Sm$^{3+}$ ions activated lithium lead alumino borate glasses for visible luminescent device applications. Opt. Mater. (Amst.) 72 31–9
[5] Kadam A R and Dhoble S J 2019 Synthesis and luminescence study of Eu$^{3+}$-doped SrYAl$_3$O$_7$ phosphor. Luminescence 34 846–53
[6] Ovhal D A, Chopra V, Dhoble N S and Dhoble S J 2021 Thermoluminescence study of sodium aluminosilicate phosphors. J. Mol. Struct. 1225
[7] Zhang L, Wang G, Lu Y, Zhang F, Jia G and Zhang C 2019 Novel bismuth silicate based upconversion phosphors: Facile synthesis, structure, luminescence properties, and applications. J. Lumin. 216 116718
[8] Kadam A R, Mishra G C and Dhoble S J 2021 Thermoluminescence study and evaluation of trapping parameters CaTiO$_3$: RE (RE=Eu$^{3+}$, Dy$^{3+}$) phosphor for TLD applications. J. Mol. Struct. 1225 129129
[9] Baran M, Kissabezkova A, Krasnikov A, Lushchik A, Suchocki A, Tsiuniar V, Vasylicheko L, Zazubovich S and Zhydacheskky Y 2020 Exciton-like luminescence of Bi$^{3+}$-doped yttrium niobate. Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 463 7–15
[10] Kadam A R, Mishra G C and Dhoble S J 2020 Thermoluminescence study of Eu$^{3+}$-doped Na$_2$Sr$_2$Al$_3$PO$_4$C$_9$ phosphor via doping of singly, doubly and triply ionized ions. Ceram. Int. 46 132–55
[11] Kindrat I I and Padyak B V. 2018 Luminescence properties and quantum efficiency of the Eu$^{3+}$-doped borate glasses Opt. Mater. (Amst.) 77 93–103
[12] Pawade V B, Birmod R, Waghmare A, Dabre K V and Dhoble S J 2017 UV–visible downshifting in CdWO$_4$:Ce$^{3+}$ nanosized phosphor Mater. Discov. 10 15–8
[13] Saad M, Stamboul W, Mohamed S A and Elhouichet H 2017 Ag nanoparticles induced luminescence enhancement of Eu$^{3+}$-doped phosphate glasses. J. Alloys Compd. 705 550–8
[14] Phalak G, Patil D, Patil A and Mhaske S 2019 Synthesis of acrylated cardanol diphenyl phosphate for UV curable flame-retardant coating application. Eur. Polym. J. 121 109320
[15] Mukhopadhyay L and Rai V K 2020 Thermally stable red emitting xenotime phosphate nanophosphors for displays. Mater. Res. Bull. 121 110628
[16] Salman S M, Salama S N, Darwish H and Abo-Mosallam H A 2009 In vitro bioactivity of glass-ceramics of the CaMgSi$_2$O$_6$-F-Na$_2$SiO$_3$ system with TiO$_2$ or ZnO additives. Ceram. Int. 35 1083–93
[17] Zhang X, Zhu Z, Guo Z, Sun Z, Yang Z, Zhang T, Zhang J, Wu Z C and Wang Z 2019 Dopant preferential site occupation and high efficiency white emission in K$_2$BaCa(PO$_4$)$_2$:Eu$^{2+}$, Mn$^{2+}$ phosphors for high quality white LED applications Inorg. Chem. Front. 6 1289–98
[18] Kaewkhao J, Wantana N, Kaewjaeng S, Koathan S and Kim H J 2016 Luminescence characteristics of Dy$^{3+}$ doped Gd$_2$O$_3$:CaO-SiO$_2$-B$_2$O$_3$ scintillating glasses. J. Rare Earths 34 583–9
[19] Ullah I, Khan I, Shah S K, Khattak S A, Shoaib M, Kaewkhao J, Ahmad T, Ahmed E, Rooh G and Khan A 2021 Luminescence properties of Sm$^{3+}$ doped Na$_2$B$_4$O$_7$ glasses for lighting application J. Lumin. 230 117700
[20] Ozguz K F, Ekdal E, Aslani M A A, Canimoglu A, Garcia Guinea J, Can N and Karali T 2016 Study of luminescence of Mn-

International Conference on Research Frontiers in Sciences (ICRFS 2021) IOP Publishing
Journal of Physics: Conference Series 1913 (2021) 012024 doi:10.1088/1742-6596/1913/1/012024
doped CaB$_4$O$_7$ prepared by wet chemical method. *J. Alloys Compd.* **683** 76–85

[21] Du P, Huang X and Yu J S 2021 Yb$^{3+}$-Concentration dependent upconversion luminescence and temperature sensing behavior in Yb$^{3+}$/Er$^{3+}$ codoped Gd$_2$MoO$_6$ nanocrystals prepared by a facile citric-Assisted sol-gel method *Inorg. Chem. Front.* **4** 1987–95

[22] Singh V, Prasad A, Rao A S, Jung S W, Singh N and Irfan M 2021 Luminescence and EPR studies of UVB emitting YPO$_4$ doped with Gd$^{3+}$ ions. *Optik* (Stuttgart). **225** 165804

[23] Zhou Q, Dolgov L, Srivastava A M, Zhou L, Wang Z, Shi J, Dramičanin M D, Brik M G and Wu M 2018 Mn$^{2+}$ and Mn$^{4+}$ red phosphors: Synthesis, luminescence and applications in WLEDs. A review *J. Mater. Chem. C* **6** 2652–71

[24] Rivera-Enriquez C E, Fernández-Osorio A and Chávez-Fernández J 2016 Luminescence properties of α- and β-Zn$_2$SiO$_4$Mn nanoparticles prepared by a co-precipitation method. *J. Alloys Compd.* **688** 775–82

[25] Thambidurai S, Gowthaman P, Venkatachalam M, Suresh S and Kandasamy M 2021 Morphology dependent photovoltaic performance of zinc oxide-cobalt oxide nanoparticle/nanorod composites synthesized by simple chemical co-precipitation method. *J. Alloys Compd.* **852** 156997

[26] Khan A, Shkir M, Ashraf I M, El-Toni A M, Aldalbahi A and AlFaify S 2020 One-step straightforward synthesis of Tb-doped NiO nanocomposites using flash combustion method: Structural, optical, luminescent, and electrical switching properties. *Ceram. Int.* **46** 10678–90

[27] Shokouhimehr M and Rafaei S M 2017 Combustion synthesized YVO$_4$:Eu$^{3+}$ phosphors: Effect of fuels on nanostructure and luminescence properties *Ceram. Int.* **43** 11469–73

[28] Mokoena T P, Linganiso E C, Swart H C, Kumar V and Ntwaeaborwa O M 2017 Cooperative luminescence from low temperature synthesized α-Al$_2$O$_3$: Yb$^{3+}$ phosphor by using solution combustion *Ceram. Int.* **43** 174–81

[29] Runowski M, Shyichuk A, Tymiński A, Grzyb T, Lavín V and Lis S 2018 Multifunctional Optical Sensors for Nanomanometry and Nanothermometry: High-Pressure and High-Temperature Upconversion Luminescence of Lanthanide-Doped Phosphates - LaPO$_4$/YPO$_4$:Yb$^{3+}$-Tm$^{3+}$ *ACS Appl. Mater. Interfaces* **10** 17269–79

[30] Kadam A R, Yadav R S, Mishra G C and Dhoble S J 2020 Effect of singly, doubly and triply ionized ions on downconversion photoluminescence in Eu$^{3+}$ doped Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ phosphor: A comparative study. *Ceram. Int.* **46** 3264–74

**Acknowledgements**

One of the authors SJD is thankful to Department of Science and Technology (DST), India (Nano Mission) (Project Ref. No. DST/NM/NS/2018/38(G), dated 16/01/2019) for financial assistance and R. T. M. Nagpur University, Nagpur for constant encouragement.