International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614
Available Online at www.journalijcar.org
Volume 10; Issue 05 (A); May 2021; Page No.24322-24325
DOI: http://dx.doi.org/10.24327/ijcar.2021.24325.4824

Research Article

SYNTHESIS, PHOTOLUMINESCENCE, OPTICALLY STIMULATED LUMINESCENCE AND THERMO LUMINESCENCE CHARACTERISTICS OFCe^{3+} DOPED $ZnNaPO_4$ PHOSPHOR

Milind Jog [1]*., Patil R. R[2]., Nerkar D. M[3] and Yogesh More[4]

[1]Kirti M. Doongursee College, Dadar, Mumbai – 400028, India
[2]Department of Forensic Sciences, Institute of Science Building, Nagpur- 440008, India
[3]Sathaye College, Vile Parle (E), Mumbai – 400057 India
[4]Bhiwapur Mahavidyalaya, Bhiwapur -441201 India

ARTICLE INFO

Article History:
Received 06th February, 2021
Received in revised form 14th March, 2021
Accepted 23rd April, 2021
Published online 28th May, 2021

Key words:

$ZnNaPO_4$, XRD, Photoluminescence, Thermoluminescence, Optically stimulated luminescence

ABSTRACT

Zinc Sodium phosphate phosphor has been studied in recent times to know its dielectric, optical, Ultrasonic properties. It also shows wide applications in Solid State Lighting (SSL) as in SSL white LEDs are receiving great importance due to their longer life span, higher efficiency, and less power consumption. Recent technological applications have shown more interest in the studies of pure phosphate glass due to their superior chemical and physical properties. This study reports the synthesis of $ZnNaPO_4$: Ce^{3+} via the co-precipitation method. The characterization wasdone by X-ray diffraction (XRD). The photoluminescence (PL), optically stimulated luminescence (OSL) along thermo luminescence (TL) were studied. PL Spectra consisting an excitation peak at 285nm with a shoulder at 275nm and is assigned to an emission peak at 340nm.The emission corresponds to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Ce^{3+} ion. CW-OSL properties were studied for the test dose of 100mGy,^{90}Sr β-source, and LM- OSL properties were studied using 0.6 Gy of ^{90}Sr β-source. Thermoluminescence was studied and a glow curve was recorded for 100mGy, ^{90}Sr β-source. The conclusion is Ce^{3+} doped $ZnNaPO_4$ phosphor may use as a good thermoluminescent material.

INTRODUCTION

Phosphates are compounds that contain P-O linkages. Such compounds may contain three, four, five, or six oxygen atoms linked to a central phosphorous atom. Over the past six decades, several phosphate compounds have been studied for interesting properties. They exhibit properties like luminescence, lasing, superionic conductivity, etc. and their applications have been found accordingly in various fields of modern technology. As phosphates show good thermal and chemical stability they have been the great attraction of researchers sincelong back. The alkaline earth halophosphates were found to be efficient UVstimulable phosphors as early as 1942 [1]. Since then, in these halophosphates intensive theoretical and experimental investigations are carried out. An extensive literature has been surveyed by Johnson [2]. Nazarova [3] reported on the blue-violet cathodoluminescence of strontium meta, pyro and orthophosphates activated with Eu^{2+}, Levshin, *et al.* [4] described in detail the cathode-ray response of $Sr_3(PO_4)_2$:Eu^{2+} as a function of excitation conditions.

Corresponding author:* **Milind Jog
Kirti M. Doongursee College, Dadar, Mumbai – 400028, India

Activator doped Phosphors have their applications mainly in solid State light, White light-emitting diodes, and dosimetric applications. Rare earth-activated phosphors play a vital role in radiotherapy, environmental release, and nuclear plants. The crystalline phase and optical properties of $NaZnPO_4$:Er^{3+}/Yb^{3+}/M(Li^+/Ba^{2+}) phosphors synthesized by conventional solid-state reaction method have been characterized and observed to be showing promising properties required for optical Thermometry[5].A study on Manganese-doped sodium zinc phosphate $ZnPO_4$:Mn phosphor was reported and observed to be very much helpful for the possibility of producing inexpensive white-light-emitting devices for the future[6].With Differential scanning calorimetry, high-temperature oxide melt solution calorimetry, the enthalpy of the α–β phase transformation of $NaZnPO_4$ and enthalpies of formation of α-$NaZnPO_4$, $NaH(ZnPO_4)_2$, $NaZnPO_4 \cdot H_2O$, and $NaCo_xZn_{1-x}PO_4 \cdot 43H_2O$ (x=0, 0.1, 0.2, 0.3) was studied[7]. Electrical properties and conduction mechanism study by OLPT (overlapping large polaron tunneling) model of $NaZnPO_4$ compound was studied and reported. Ac conductivity of NaZn PO4 compound obeys Joncher's law [8]. Ce3+,Tb 3+ doped NaZn PO_4 Phosphor for UV-based LEDs was extensively studied and several studies on crystal structure and energy transfer are reported. In the photoluminescence spectra of NZPO:Ce^{3+} phosphors broad emission in the 300–380 nm region with a peak maximum at 341 nm is observed. The photoluminescence emission spectrum of Tb^{3+} singly doped NZPO shows several sharp peaks at 488, 543, 585, and 622 nm related to 4f–4f transitions. Doubly doped NZPO:Ce^{3+}/Tb^{3+} phosphors are very promising as green-emitting phosphors for lighting applications [9]. Luminescence and advanced mass spectroscopic characterization of Mn-doped sodium zinc orthophosphate phosphor for low-cost light-emitting diodes was studied and reported by Savvi Mishra and others [10]. The results obtained suggested that this new phosphor powder has interesting applications in semiconductor physics, as low cost-effective light-emitting diodes (LEDs), and as solar cells, and in photo-physics. Cu-doped sodium zincophosphate [NaZn1−*x*(Cu)*x*PO4; *x*=0.05, 0.10, 0.15, and 0.20] powders were prepared for the possible application as a dark heat-reflective material. The visible and NIR near-infrared reflective properties of NaZn1−*x*(Cu)*x*PO4 doped with different amounts of Cu at varied calcination temperatures were investigated [11-12].NaZnPO4:Er3+/Tm3+/Yb3+/Li+ phosphors were successfully synthesized by conventional solid-state reaction method and characterized through XRD, FESEM, EDAX, diffuse reflectance spectra, and FTIR analysis [13]. The use of NaZnPO4 in the Dehydrogenation of Alcohols was studied and reported by Aramendia M. Angeles and others [14]. A sodium zinc phosphate pigment synthesized using a co-precipitation method and characterized by X-ray diffraction was investigated for its corrosion inhibition activity in comparison with the commercial zinc phosphate by Eiman Alibakshi [15].

Experimental

For preparing $ZnNaPO_4$ was prepared by co-precipitation method. $ZnCl_2$ was first dissolved in double-distilled water. The solution was then transferred to the beaker containing NaH_2PO_4 dissolved in double-distilled water. The aqueous solution of desired impurity $Ce^{3+}$was added to the solution. The mixture was then allowed to dry overnight on a hot plate at 80^0 C. The dried precipitate thus obtained was then washed several times with the help of double-distilled water and dried under lamps for several hours. The powder was then heated in the furnace at 650 C for an hour and cooled slowly .The impurity concentrations are optimized to 0.1 mol% for $Ce^{3+.}$XRD was recorded.

Chemical reaction:

$$ZnCl_2 + NaH_2PO_4 = ZnNaPO_4 + 2\,HCl$$

All PL measurements were taken on Hitachi spectrofluorometer F-7000 with excitation and emission band pass 2.5 nm. The Thermoluminescence (TL) and optically stimulated luminescence (OSL) measurements were done on Riso TL/OSL-DA-20 (Riso National Laboratory, Denmark) reader system. The reader uses a bia-alkali photomultiplier tube for light detection (ET 923QB15) and a set of optical filters like Hoya 340, Schott BG -39,and BG-3. The continuous wave (CW) OSL readouts were taken using blue (470 nm ± 20 nm) LEDlight stimulation available in the reader system. For recording OSL the LED power was kept at ~ 50 mW/cm^2 and the CW OSL signal was recorded for 60 s with an acquisition time of 0.1 s. The TL measurements were taken at a 4^0C /s heating rate. Before TL or OSL measurements the samples were irradiated and given a test dose of 100 mGy using the built-in ^{90}Sr / ^{90} Y beta source.

RESULTS AND DISCUSSIONS

X- RAY Diffraction (XRD) study

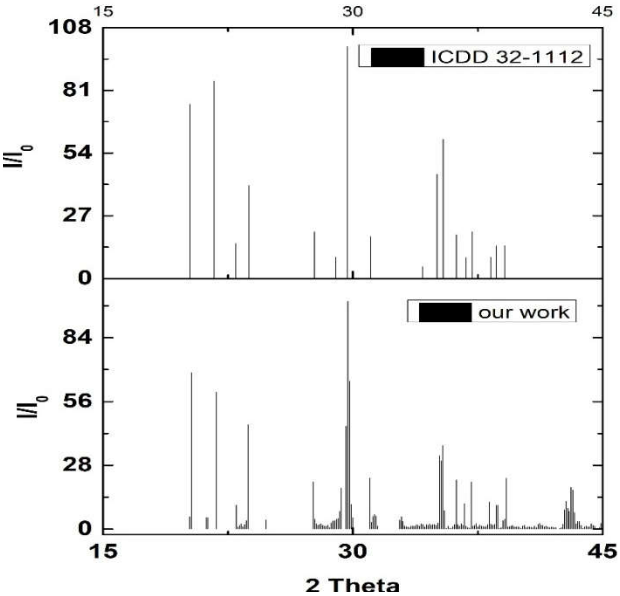

Figure 1 X-Ray Diffraction Patternof $ZnNaPO_4$ Phosphor

The XRD pattern of $ZnNaPO_4$is shown in fig 1. It matches with the reported in the ICDD database (File No. 32- 1112) .which confirms the ZnNaPO4 .phase.

Photoluminescence (PL) Study of ZnNaPO4: Ce^{3+}

In the PL spectra of Ce^{3+} doped $ZnNaPO_4$. Ce^{3+} (For 0.1% molar concentration) emission is observed at 340 nm (figure 2, curve b). The main excitation band for the phosphor was observed at 300 nm with a shoulder at 275 nm (figure 2, curve a).

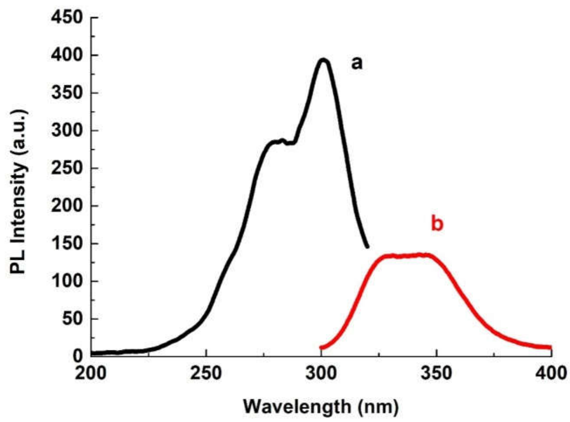

Figure 2 Photoluminescence Curve of $ZnNaPO_4$: Ce $^{3+}$PhosphorCW- OSL Curve

Figure 3 shows the CW-OSL curve for $ZnNaPO_4$:Ce^{3+} for the test dose of 100 mGy of ^{90}Sr beta source using blue LEDs with 22 mW/cm^2 optical power. The CW-OSL sensitivity of the phosphor was compared with that of the commercial phosphor Al_2O_3:C (Landauer). The CW-OSL sensitivity of the phosphor was found to be 9% of the Al_2O_3:C on averaging out the OSL counts for the first 3 seconds. The decay profile of CW-OSL curves for the phosphors is shown in the inset of figure 3. CW-

OSL curve for $ZnNaPO_4:Ce^{3+}$ decays much rapidly as compared to CW-OSL decay of $Al_2O_3:C$. The decay of the CW-OSL curve for $ZnNaPO_4:Ce^{3+}$ was found to be 8 times faster than in the case of $Al_2O_3:C$.

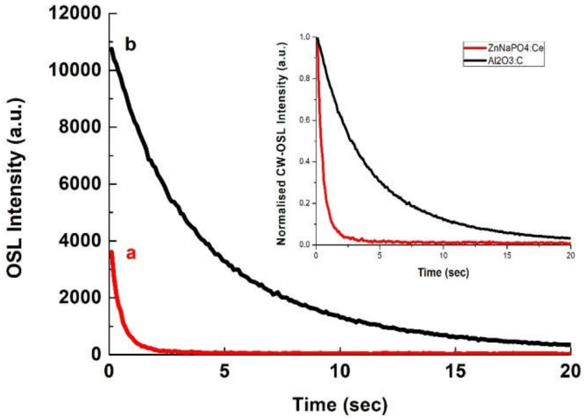

Figure 3 CW OSL Curve of $ZnNaPO_4$ Phosphor

The CW-OSL curve for the phosphor was deconvoluted to its components. Figure 4 shows the CW-OSL curve for the phosphor along with fitted components. The curve was exactly fitted with two components given by the equation

$I_{OSL} = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$

where I_{OSL} is the initial OSL intensity. A_1 and A_2 are the coefficients and τ_1 and τ_2 are the decay constants of the respective OSL traps.

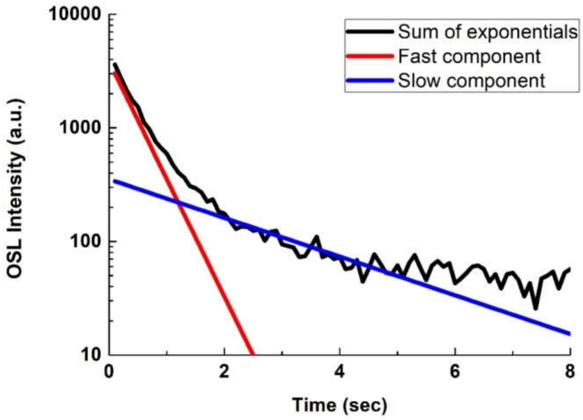

Figure 4 CW OSL Curve with Fitted Components of $ZnNaPO_4$ Phosphor

Table 1 CW-OSL parameters

CW-OSL component	Coefficient A	Decay constant τ (sec)	Photo ionization cross-section σ (cm^2)	R^2
Fast	A_1: 3828	0.42	4.46×10^{-17}	0.99907
Slow	A_2: 353	2.55	7.35×10^{-18}	

The ratio of fast to slow coefficient (A_1/A_2) for the phosphor was found to be nearly 11 which means that the number of charge carriers responsible for the fast component is 11 times more than that contributing to the slow component. The CW-OSL parameters for the phosphor are given in following table 1.

Figure 5 shows the LM-OSL curve for the ZnNaPO4:Ce. The LM-OSL curve was recorded for 0.6 Gy of 90Sr beta source. The stimulation intensity, in this case, was varied from 0 to 22 mW/cm^2 The LM-OSL parameters as described earlier for the phosphor are given in the following table 2.

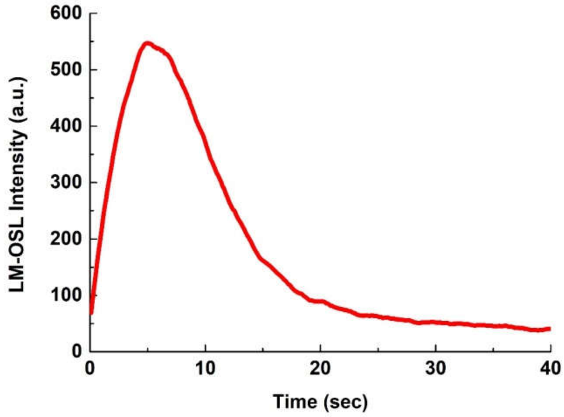

Figure 5 LM OSL Curve of $ZnNaPO_4$ Phosphor

The value of shape parameter μ_g was about 0.65 which means that phosphor may obey second-order kinetics or may have the order of kinetics between one and two.

Table 2 LM-OSL parameters

Sr. No.	Sample Name	δ/t_m	τ/t_m	ω/t_m	$\mu_g = \frac{\delta}{\omega}$
1	$ZnNaPO_4:Ce^{3+}$	1.35	0.74	2.09	0.65

The LM-OSL curve for ZnNaPO4:Ce was exactly fitted with three curves with an R^2 value ~1. The fitted LM-OSL curve for the phosphor along with the component is as shown in figure 6. Hence one can argue that the phosphor may have more than one optically sensitive trap with relatively different energies. This fact is well supported by the TL response of the Phosphor

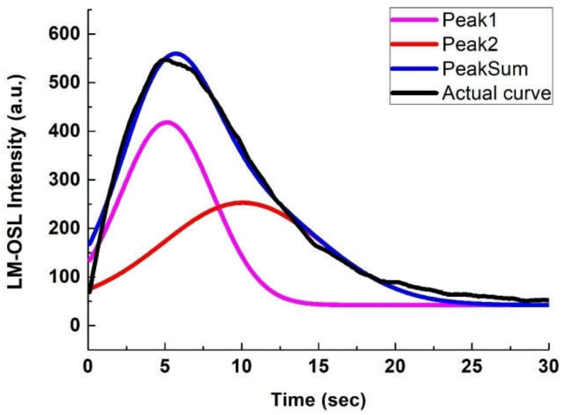

Figure 6 LM OSL Curve with Fitted Components of $ZnNaPO_4$ Phosphor

Figure 7, curve a shows the TL glow curve for $ZnNaPO_4:Ce^{3+}$ recorded for the test dose 100 mGy of ^{90}Sr beta source with a heating rate of 5 C/s. The glow peak for the phosphor was observed at 120 C with a shoulder at 160 C. a small TL peak was also observed at 225 C. Since the glow peak was observed at low temperature, one can conclude that the TL traps are originating from the shallow traps.

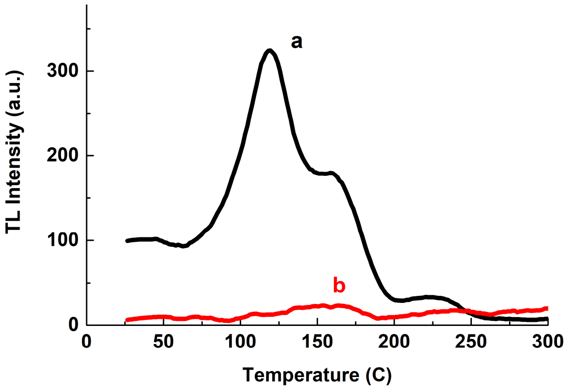

Figure 7 TL Glow Curve of $ZnNaPO_4$ Phosphor

TL traps in the phosphors are found to be light-sensitive and completely correlating with OSL traps which can be observed in figure 10, curve 'b'. Curve 'b' was immediately recorded after OSL being taken. From curve 'b' it is seen that almost all TL traps get depleted confirming the presence of one or more optically sensitive traps.

CONCLUSION

Photoluminescence, Optically Stimulated Luminescence (OSL), and Thermoluminescence (TL) of Ce^{3+} doped $ZnNaSO_4$ phosphor were studied for 0.1% molar concentration.Ce^{3+} emission in the phosphor was observed at 340 nm for 254 nm excitation. The excitation for the phosphor was observed at 300 nm with a shoulder at 275 nm. Stokes shift for the phosphor was found to be 40 nm. LM –OSL curve was observed to be exactly fitted with three curves with R^2 value ~1 hence one can argue that the phosphor may have more than one optically sensitive trap with relatively different energies. This fact is well supported by the TL response of the phosphor. The CW-OSL sensitivity of the phosphor was found to be 9% of the Al_2O_3:C on averaging out the OSL counts for the first 3 seconds. The decay of the CW-OSL curve for ZnNaPO4:Ce was found to be 8 times faster than in the case of Al_2O_3:C.A weak glow peak was observed for the TL glow curve of the Ce^{3+} doped $ZnNaSO_4$ phosphor.

References

1. A. H. McKeag and P. W. Ranby, British Patent No. 578, 192 (1942).
2. P.D. Johnson, "Luminescence of Inorg. Solids," P. Goldberg, Editor, Chap.5, Academic Press, New York (1966).
3. V.P. Nazarova, Bull A Cad USSR Phy. Set 25,322 (1961)
4. V.L.Levshin *et al*, Trans, P.N. Lebedev Institute 23 Soviet Research on Luminescence, D.V. Skobeltysn English Translation Chapter 3, Consultant Bureau, New York (1964)
5. Lakshmi Mukhopadhyay, Vineet Kumar Rai, Renuka Bakodia, K.Shrinivas, 980 nm Excited Er^{3+}, Yb $^{3+}$/ Li^{+}/ Ba^{2+} $NaZnPO_4$ up converting in Optical Thermometry. *Journal of Luminescence,*2017, 187, 368-377
6. D.Harnath, S. Mishra, S.Yadav, R.K.SharmaRare-earth free yellow green-emitting $NaZnPO_4$, Mn phosphor for Lighting applications, *AIP Applied Physics Letters*, 2012101,221905
7. So Nhu Le, Alexandra Navrotsky, Energies of Phosphate frameworks containing Zink and Cobalt $NaZnPO_4$ $NaH(ZnPO_4)_2$, $NaZnPO_4$, H_2O, $NaZnPO_4$, 4/3H_2O, NaCoX Zn (1-x) PO_4 4/3H_2O, *Journal Of Solid State Chemistry*, 2007, 180(9), 2443-2451
8. N.Chakchouk, B. Lauati, K. Guidara, Electrical Properties and Conduction Mechanism Study by OPLT model of $NaZnPO_4$ Compound, *Material Research Bulletin*, 2018, 99,52-60
9. K.Saidi, M.Dammak, Crystal Structure, Optical Spectroscopy, and Energy transfer Properties in $NaZnPO_4$; $Ce^{3+,}$ Tb^{3+} Phosphors for UV based LEDs, *Royal Society of Chemistry*, 2020, 10, 21867- 21175.
10. Savvi Mishra, G.Swati,Kirti Tyagi, Bhaskar Gahtori, B. Si Vaiah, N.Vijayan, M.K.Dalal, A.Dhar, S.Auluck, M.Jayasimhadri, D. Havnath, Luminescence and advance Mass Spectroscopic Characterization of Sodium Zink Orthophosphate Phosphor for low-cost Light Emitting Diodes. *Luminescence – The Journal of Biological and Chemical Luminescence*.2016,31(2), 348- 355
11. Da Wang, Da Gen Su, Ming Feng Zong, Hui Xia, Preparation and near infrared-reflective Characterization of Cu Doped Sodium Zincosulphate. *Physica B: Condensed Matter*, 2012,407 (3), 384-387
12. MF Zhong, WX Fu, W Da, DG Su, Study on Preparation and Near-Infrared Reflective properties of $NaZnPO_4$, *Advanced Material Research*,2011,399, 1289-1293
13. Laxmi Mukhopadhyay, Vineet Kumar, Upconversion based nearWhite Light Emission, intrinsic optical bistability, and Temperature Sensing in Er $^{3+}$/ Yb $^{3+}$/ Li^{+}/Tm^{3+}, $NaZnPO_4$ Phosphor, *New Journal of Chemistry*,2017, 15 (41), 7650-7661
14. Aramendia M. Angeles, Borau Victoriano,Jimenez Cesar, M. Marianas Jose, Romaro Jose, Selectivity of $NaZnPO_4$ in Dehydrogenation of Alcohols, *Chemistry Letters*, 1994, 23(8), 1361- 1364
15. Eiman, Alibakshi, Ebvahim Ghasemi, Mohamad Mahadivian, Sodium Zinc Phosphate as a Corrosion Inhibitive Pigment, *Progress In Organic Coating*, 2014, 77(7), 1155-1162

How to cite this article:

Milind Jog *et al* (2021) 'Synthesis, Photoluminescence, Optically Stimulated Luminescence and Thermo Luminescence Characteristics OFCe^{3+} Doped $ZnNaPO_4$ Phosphor', *International Journal of Current Advanced Research,* 10(05), pp. 24322-24325. DOI: http://dx.doi.org/10.24327/ijcar.2021. 24325.4824

****