International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 06 Issue: 10 | October - 2022 Impact Factor: 7.185 ISSN: 2582-3930

A Review on Trivalent Rare Earth Doped Phosphors and their Applications in Displays

Aleem Mian[1], Shahana Khan[1] and Prachi Tadge[1]
Department of Physical Science, Faculty of Science, Rabindranath Tagore University, Bhopal, India

Abstract-

Rare–earth doped phosphors are excellent luminescent materials that are designed to overcome the limitations of conventional sulfide-based phosphors. The increasing research attention on these phosphors over the past decade has led to a drastic improvement in their phosphorescence efficiencies and resulted in a wide variety of phosphorescence colors, which can facilitate applications in various areas. This review article discusses the development of rare–earth doped phosphors with a focus on the various synthesis methods, luminescence mechanisms, activator and co-activator effects, and the effects of compositions. The role of Rare–earth doped phosphors and co-activators in phosphorescence emissions was also emphasized. Finally, we address recent techniques involving nanomaterial engineering that has also produced rare-earth doped phosphors with high luminescence intensity.

Key words- Luminescent materials, Rare–earth, nanomaterial engineering

1. Introduction

The emission of light from a material on proper excitation source is called luminescence and it is treated as a cold body radiation. Luminescence is generally categorized into fluorescence and phosphorescence. The emission which results due to the singlet to singlet state transition is termed as fluorescence whereas the triplet to triplet state transition results phosphorescence. In a broad sense, the emission of light disappears in fluorescence whereas it exists in phosphorescence after removal of the excitation source. These processes can be also verified by lifetime (τ) analysis as in fluorescence the lifetime (τ) is found to be < 10 ms whereas in phosphorescence it is > 0.10 s. The visible part of solar radiation is used to visualize the objects around us. The materials, which emit these emissions, are termed as phosphors [1–3].The phosphors are photoluminescent materials and have large number of applications in different fields, such as display devices, plasma panel devices (PPD), field emission display (FED) devices, light emitting diodes (LEDs), white light emitting diodes (wLEDs), color television, cathode ray oscilloscope (CRO), cathode ray tubes (CRTs), photoluminescent tubes, solid state lighting, lasers, solar cells, photothermal treatment, temperature sensing, optical bi-stable devices, optical devices, memory coding devices, cancer therapy, photo-dynamic therapy, bio-imaging, color topography (CT) scan, magnetic resonance imaging (MRI), etc. [4–21]. Due to these collective applications, the phosphors materials are of the matter of technological importance and they are unique materials to fulfil the requirement the energy related demand. The photoluminescence intensity of the RE ions greatly depends on the morphological properties of the phosphors. The morphological properties of the host matrix play a crucial role in the photoluminescence intensity. The photoluminescence intensity of the phosphor can be enhanced significantly, by incorporating sensitizers and surface modifiers. It has been observed that they not only improve the local crystal structure and morphology but enhance the photoluminescence intensity of the phosphor also.

Among various ions, the rare earth (RE) ions give intense, narrow band width and sharp lines of various emissions extending from UV–vis to NIR regions and their photoluminescence intensity were also influenced considerably on addition of some impurities, such as sensitizers and surface modifiers [22–31].

2. General properties of the rare earth ion

2.1.1. Radiative and non-radiative transitions

The rare earth (RE) ions are rich in producing photoluminescence (PL) of primary colors, such as red, green and blue (RGB) as well as complementary colors, such as cyan, yellow and magenta. They can even produce white light on proper combinations of primary and/or complementary colors. They are also known as lanthanide ions. The RE ions have enormous number of energy levels in which many of them are meta-stable. The meta-stable energy levels have long lifetime compared to the other levels and are responsible for radiative transitions. The RE ions have also tendency to give non-radiative transitions, which occurs due to multi-phonon relaxation of the ions in the excited states. These transitions populate various levels including the metastable from where the emission takes place. The schematic diagram for the radiative and non-radiative transitions is shown in Fig. 1. For radiative transitions, the energy levels of both the ions should match to each other whereas in the case of non-radiative transition the difference in the energy levels is the nth integral order of phonon frequency of the host materials [32–35].

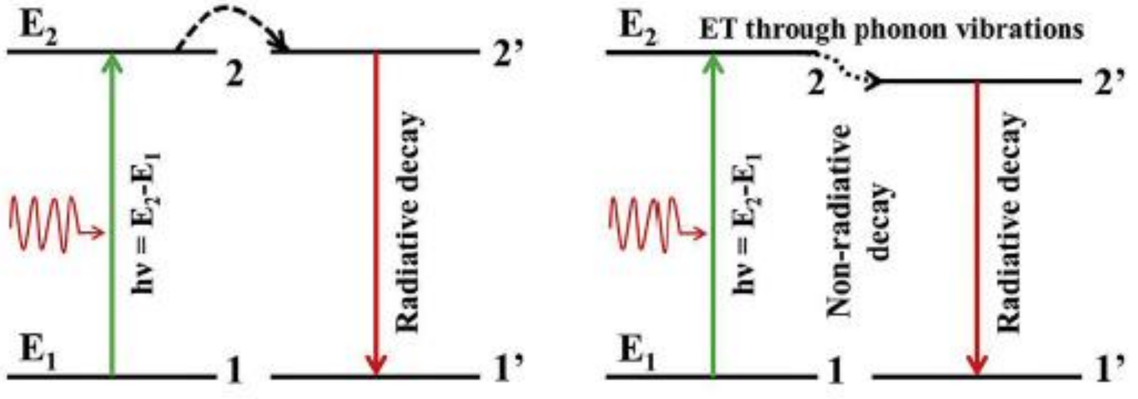

Fig. 1. Schematic diagrams for the radiative and non-radiative transitions.

2.1.2. Down-conversion, Up-conversion and Quantum Cutting Emissions

The down-conversion photoluminescence in RE ions is the emission of light from the RE doped phosphor materials. Basically, the down-conversion is a process in which a high energy ultraviolet (UV) photon is converted into low energy visible or NIR photon. This is a type of linear process and the emission is also termed as Stokes emission. The RE ion also emits upconversion photoluminescence in which two or more low energy NIR photons are absorbed by a material and results into a high energy UV or visible photon. This is a non-linear phenomenon and the emission is a type of anti-Stokes emission. On the other hand, in quantum cutting emission of the RE ion, a high energy UV or visible photon is converted into two or more low energy NIR photons. Thus, the RE ion is a unique activator ion to meet the entire energy requirement at various platforms [36–48]. Fig. 2 shows the down-conversion, upconversion and quantum cutting phenomenon possessed by the RE ion. It is clear from the figure that the light with photon energy (hυ) is incident on the phosphor materials, where h is the Planck's constant and υ is the frequency of the incident photon. The atoms/ions of the phosphor materials are promoted to the excited state due to absorption of the incident photons. On de-excitation, the atoms/ions are relaxed non-radiatively to lower excited state, which is a meta-stable state. As a result, the radiative transition takes place with a photon energy (hυ′) and the emitted photon has larger/lesser energy than the incident photon (i.e. hυ >/<hυ′)

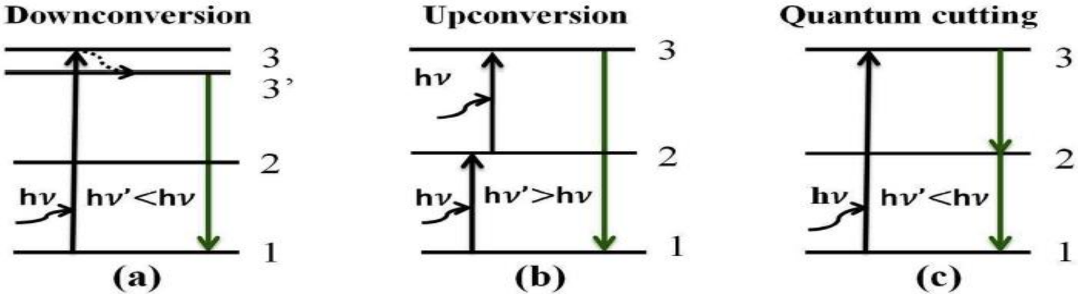

Fig. 2. Schematic diagrams of (a) down-conversion (DC), (b) up-conversion (UC) and (c) quantum cutting (QC) processes in the RE ion

2.1.3. Energy transfer between the RE ions

As mentioned earlier, the RE ion has large number of meta-stable states in which the ions may remain exist until the emission takes place. Alongwith emission, there is a probability of energy transfer among the RE ions. One of the RE ion is known as donor ion while the other is acceptor ion. The energy level of the donor ions should match to that of the activator ion. If there is some mismatch in the energy levels of both the ions the excitation energy is transferred through a non-radiative relaxation of the ions via phonon assisted absorption and multi-phonon relaxation processes. As a result, the emission intensity of the activator ions is enhanced significantly [49–55]. The mechanisms of energy transfer can be understood by Fig. 3. In the above figure, the donor and the acceptor ions are excited with the incident photon energy (hυ), which promotes them to the higher energy states (3). The ions in the upper excited states relax non-radiatively to the lower states (2) and give their own emissions. Since the energy level of the donor ion lies very close to that of the acceptor ion, therefore, there is a chance of energy transfer from the donor to acceptor ions. As a result, the photoluminescence intensity of the acceptor ion is enhanced significantly. The energy of the emitted light (hυ’) is lesser than that of the incident one. In this case, the donor ion acts as sensitizer for the activator ion.

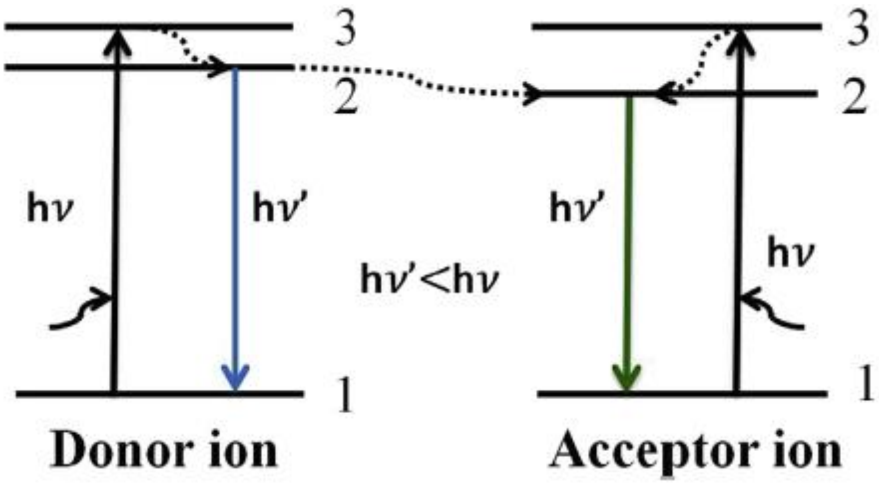

Fig. 3. Schematic energy transfer process between the donor and acceptor ions

3. Selection of the host materials

The phosphor contains two types of materials i.e. an activator ion and a host. The host material is a very important part of the phosphor for achieving large photoluminescence intensity. It provides a platform for the activator ion in which the concentration of the activator, surface modifier and sensitizer can be optimized with the photoluminescence intensity. The selection of the host is generally carried out on the basis of phonon frequency. The host matrix possesses either the higher or lower phonon frequency. If the host has higher phonon frequency the molecules of the host may vibrate rapidly and the activator ions present in the excited states relax non-radiatively due to multi-phonon relaxation. As a result, the photoluminescence intensity of the phosphor is decreased considerably. On the other hand, the host with low phonon frequency strongly reduces the non-radiative relaxation of the ions. If the activator ions present in the excited state may stay for longer time they emit relatively larger photoluminescence intensity. Thus, the host materials should be chosen with low phonon frequency. The morphology of the host matrices can be improved noticeably by incorporating some sensitizers and surface modifiers. These additives not only have improved the morphology of the host matrices but also enhance the photoluminescence intensity of the activator ions to a great extent. Therefore, the host materials should be selected on the ground of low phonon frequency.

The photoluminescence intensity of the RE doped phosphor materials have been studied by various researchers in different host materials. They have reported that the host should contain low phonon frequency. The phonon frequency of the host lattice can be reduced by incorporating some impurity ions, which can occupy the places at the interstitial sites. They can be accommodated in the space present in between the atoms/ions, which can reduce the vibration of the molecules in the host materials. Thus, by reducing the lattice vibrations one can achieve larger photoluminescence intensity arising from the RE ions.

3.1.1. Morphology of the phosphor materials

The morphology of the phosphor materials can be tuned depending on the nature of the host matrix and the RE ions. The synthesis procedure plays a vital role for determining not only the morphology of the phosphor but also the size of the particle.

There are various approaches to synthesize the phosphor materials, such as solid state reaction method, solution combustion method, sol-gel method, co-precipitation method, hydrothermal method, template method, spray pyrolysis, chemical vapor deposition method, etc. In these methods, the particles size varies from sub-micron range to a nano-meter range. In some cases, the ultrafine particles are formed, which are known as quantum dots (QDs). The shapes of the particles are found to vary with the synthesis procedures. It has been well established that the morphology of the phosphor materials can be tuned either by changing the synthesis procedures or by introducing some sensitizers and surface modifiers. The solid state reaction method yields the particles size in sub-micron range whereas the phosphor synthesized by solution reaction method gives the particles size in the range of the sub-micron to nano-meter scale. However, the phosphor materials synthesized by the procedures, such as sol-gel method, co-precipitation method, hydrothermal method, pechini method, spray pyrolysis, chemical vapor deposition method, etc. produce the particles in the nano-meter range.

The nano-meter sized particles are widely used in the biological studies to see the interaction of the tissues with the phosphor materials. They can easily penetrate in the biological cells and tissues. They are used for various applications, such as photo-thermal treatment, cancer therapy, photo-dynamic therapy, bio-imaging, color tomography (CT) scan, magnetic resonance imaging (MRI), etc. The size of the particles is adjusted in such a way that they should have high surface to volume ratio to meet out the specific properties. The optical band gap of the nano-particles can also be tuned to obtain the photoluminescence of the desired colors. The quantum dots (QDs) are suitable materials to accomplish the purpose of photoluminescence via tuning the optical band gap of the particles of the desired materials.

2. A Brief review of the work already done in the field (Literature Survey)

The triply RE doped phosphor materials are of great scientific importance and originate very interesting optical properties. The energy transfer between them yields new era of the applications in different dimensions. They emit color tunable light leading to generation of white light emission. Some efforts have been made to improve the efficiency of these emissions by incorporating some surface modifiers.

The surface modifier can modify the local structure followed by enhancing the photoluminescence intensity of the phosphors. Kumari et *al*. have studied the effect of Li+ ion on the upconverted white light emitted from $Ho^{3+}/Tm^{3+}/Yb^{3+}/Li+:Gd_2(MoO_4)_3$ nanophosphors. When the Li+ ion is co-doped in the $Ho^{3+}/Tm^{3+}/ Yb^{3+}:Gd_2(MoO_4)_3$ nanophosphors the UC emission intensity is enhanced by many times due to local field modifications around the RE ions. The enhancement in the UC emission intensity of white light has also been studied by our group in the $Tm^{3+}/Yb^{3+}/Ho^{3+}$ co-doped $Na_4ZnW_3O_{12}$ nano-crystalline phosphor in presence of Li+ ion. The SEM micrographs show an increase in the particles size of the phosphor in presence of Li+ ion. When the Li+ ion is doped in the phosphor materials the particles size is found to increase. It has been also mentioned earlier that the incorporation of additional surface modifiers improve the morphology of the co-doped materials. As a result, the particles size of the phosphor materials is increased. The larger particle can efficiently absorb large number of the incident photons and can increase the UC photoluminescence intensity of the phosphor.

We give a brief review focusing on the trivalent rare earth based phosphors. Lots of works have already been done in phosphor material and their application in Solar Cell. We have summarized some phosphor material with their excitation, emission and synthesis procedure in Review Table 1

Table 1 A schematic representation of some of work in the literature for trivalent rare earth based phosphors

Host	**Dopant**	**Excitation (nm)**	**Emission (nm)**
YPO_4	Tb^{3+} - Yb^{3+}	489	1000 - 950
$GdAl_3(BO_3)_4$	Yb^{3+} - Pr^{3+} Tb^{3+} - Tm^{3+}	485	542 - 585 622 - 545
SrF_4 $LiYF_4$	Yb^{3+} - Pr^{3+} Yb^{3+} - Ho^{3+}	980 - 480	470 - 800
$Y_3Al_5O_{12}$	Ce^{3+} - Yb^{3+}	450 - 466	550 -1030
Zn_2SiO_4	Tb^{3+} - Yb^{3+}	350 - 485	900 - 1100
Y_2O_3	Bi^{3+}- Yb^{3+}	325, 980	491 - 409 979 -1033
Y_2SiO_5	Ce^{3+} - Yb^{3+}	325 - 380	375 - 500
$KSrPO_4$	Tb^{3+} - Yb^{3+} Ce^{3+} -Tb^{3+}-Yb^{3+} Eu^{2+} - Yb^{3+}	310, 370 - 484	370-484 543-584
$LiYF_4$	Yb^{3+} - Ho^{3+}	1150	1100 - 1200 650 - 1000
$GdPO_4$	Eu^{3+}	395 - 400	260 - 273 360 - 381

Ba_2SiO_4	Eu^{2+}	505	350
Gd_2O_2S	Eu^{3+}	624	200 - 300
$BaGd_2ZnO_5$	Yb^{3+} Ce^{3+} - Yb^{3+}	977 230 - 400	230 - 400 261 - 312

4. Research Gap

More than a century ago, the sulfide phosphors have been used as a phosphor. However, the sulfide-based phosphors have been ignored for a long time as they are not chemically stable. In the recent years there is a great interest for new types of host lattices substitutes. The compounds doped with trivalent rare earth ions are a kind of important luminescent hosts and were paid attention by researchers in the recent years. Over last decades excellent examples have emerged from the focused on synthesis and characterization of alkali earth aluminates and oxide materials for wide range trivalent rare-earth-doped phosphors using X-rays, FESEM and PL (photoluminescence). In order to optimize the effective brightness, the phosphors should satisfy the following requirements: (a) fine particles (5 nm), (b) narrow particle size distribution, (c) large surface area and (d) high purity and homogeneity.

5. Motivation

The trivalent rare earth ions in general give line emissions attributed to $4f$ electrons which are sufficiently protected from perturbations due to the environment of the host matrices. Hence, rare earth activated phosphors lead to high luminescence quantum yield, compared with other phosphors, quenching occurs only at higher, temperatures or higher activator concentrations. Such phosphors find applications ranging from conventional fluorescent lighting (lamp phosphors) to colour TV picture tubes, X-ray photography, luminescence immunoassay, phosphor thermometry.

6. Objective(s) and Scope

In the past decade, various kinds of synthesis methods have been proposed for the synthesis of phosphor, still sufficient scope remains to rationally select the host as well to improve the synthesis methods to achieve precise control over the particle size, morphology and distribution of phosphor particles impacting the luminescence properties for display application. The present work comprised with the exploration of design, solution synthesis and characterization of trivalent rare-earth doped phosphors by various suitable experimental techniques.

7. Expected outcome of the proposed research work:-

Major advances have been made by many research groups around the world recently in demonstrating trivalent rare earth doped phosphors, fabricating new luminescent materials, developing high efficiency phosphors for several applications, such as safety signages, luminescent paints, interior decorations, and as tracer particle for photodynamic therapy and the mechanism involved. There are still many areas that need additional work, including:-

(1) Development of Oxide based trivalent rare earth doped phosphor. This will require a better understanding of Energy Transfer mechanism, and also a better understanding of materials properties and new materials fabrication process.

(2) Development of Silicate based trivalent rare earth doped phosphor.

(3) The structure characterizations of the both oxide and silicate based phosphor doped trivalent rare earth ion was studied in X-Ray Diffraction (XRD), crystal structure and FESEM.

(4) Photoluminescence and phosphorescence properties of the phosphor were investigated respectively. The reason why the photoluminescence and phosphorescence color can be tuned has been discussed.

(5) Decay kinetics will be study in details.

(6) Clearly and direct demonstrations of ET between ions. It is necessary to develop new methods for the measurements of materials properties including QE.

8. Proposed Methodology/ Plan of work during the tenure of the research work

Over the past several years, a number of techniques have been developed for the synthesis of a Phosphor Material. In research methodology, we explain those methods which have been used for the synthesis of phosphor materials which can be applied for synthesis of phosphor materials doped trivalent rare earth ion. We have explain different synthesis routes such as Co-precipitation method, the combustion method, Sol - Gel method, hydrothermal method etc are used for the synthesis of phosphor material.

we have explain synthesis methodologies such as Amorphous Metal Complex Method, Combustion Method, Complex based Precursor Solution Method and Hydrothermal Method, as these synthesis processed have been used for the generation of phosphor materials, which have been investigated in this research work. In the present study, we have adopted a "Complex based Precursor Solution Method" for synthesis of Phosphor.

➢ Complex based Precursor Solution Method

Phosphors can be synthesized by various routes as described in the literature such as Solid-state reaction, Sol-gel, Pechini, Auto combustion, Hydrothermal, Microwave sintering and Floating zone methods. In the present study, we have adopted a "Complex Based Precursor solution Method using TEA as complexing Agent" for synthesis of Phosphor. The preparation procedure involved the evaporation of aqueous precursor solutions, which were composed of stoichiometric amounts of the desired metal ions, complexed with TEA. TEA is an efficient chelating agent that has good coordination properties with the metal ions. One to two moles of TEA per mole of the total metal ions is stoichiometrically required for formation of stable complexes with metal ions. However, TEA in the precursor solution has always been maintained to be in excess of the required stoichiometry. During evaporation of the precursor solution, the TEA present in the system may have probably led to the formation of vinyl functional groups, which causes the polymerization. The reason for using complexing agent i.e. TEA, in our synthesis procedure, is its ability of bond formation with the metal cations by its hydroxyl groups and the nitrogen atom. The amount of TEA should be maintained properly to control the particle size.

References –

[1] J. Zi-Qiang, Y.-H. Wang, G. Yu, Doping effects of Nb^{5+} on red long afterglow phosphor $CaTiO_3:Pr^{3+}$, Chin. Phys. B 19 (2010) 027801.

[2] H. Aizawa, T. Katsumata, J. Takahashi, K. Matsunaga, S. Komuro, T. Morikawa, E. Toba, Long afterglow phosphorescent sensor materials for fiber-optic thermometer, Rev. Sci. Instrum. 74 (2003) 1344.

[3] X. Sun, J. Zhang, X. Zhang, Y. Luo, X.-J. Wang, Long lasting yellow phosphorescence and photostimulated luminescence in $Sr_3SiO_5:Eu^{2+}$ and Sr_3SiO_5: Eu^{2+}, Dy^{3+} phosphors, J. Phys. D. Appl. Phys. 41 (2008) 195414.

[4] D. Haranath, A.F. Khan, H. Chander, Bright red luminescence and energy transfer of Pr^{3+}- doped (Ca,Zn)TiO_3 phosphor for long decay applications, J. Phys. D. Appl. Phys. 39 (2006) 4956. 420 Spectroscopy of Lanthanide-Doped Oxide Materials

[5] T. Jiang, H. Wang, M. Xing, F. Yao, Y. Peng, X. Luo, Luminescence decay evaluation of long-afterglow phosphors, Phys. B Condens. Matter 450 (2014) 94.

[6] J. H€ols€a, Persistent luminescence beats the afterglow: 400 years of persistent luminescence, Electrochem. Soc. Interface 18 (2009) 42.

[7] W.M. Yen, S. Shionoya, H. Yamamoto, Phosphor Handbook, CRC Press, 2007.

[8] M. Lastusaari, T. Laamanen, M. Malkam€aki, K.O. Eskola, A. Kotlov, S. Carlson, E. Welter, H.F. Brito, M. Bettinelli, H. Jungner, J. H€ols€a, The bologna stone: history's first persistent luminescent material, Eur. J. Mineral. 24 (2012) 885.

[9] F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M.H. Whangbo, A. Garcia, T. Le Mercier, On the phosphorescence mechanism in $SrAl_2O_4:Eu^{2+}$ and its co-doped derivatives, Solid State Sci. 9 (2007) 608.

[10] D. Jia, J. Zhu, B. Wu, Influence of co-doping with Cl ———————————— on the luminescence of $CaS:Eu^{2+}$, J. Electrochem. Soc. 147 (2000) 3948.

[11] H.S. Virk, Luminescent Materials and their Applications, Trans Tech Publication, 2015.

[12] C.J. Milner, Sulfide phosphors and the zone theory of solids, Trans. Faraday Soc. 35 (1939) 101.

[13] R.P. Rao, The preparation and thermoluminescence of alkaline earth sulfide phosphors, J. Mater. Sci. 21 (1986) 3357.

[14] D. Jia, J. Zhu, B.Q. Wu, Trapping processes in CaS: Eu^{2+}, Tm^{3+}, J. Electrochem. Soc. 147 (2000) 386.

[15] C.F. Guo, B.L. Chu, J. Xu, Q. Su, Improving the stability of alkaline earth sulfide based phosphors by oxide coating, Chin. J. Lumin. 25 (2004) 449.

[16] Virendra Shankar, Harish Chander, Haranath Divi, Pradeep Ghosh, n.d. Long Decay Luminescent Powder and Process for Preparation Thereof, 2003, U.S. Patent 200,30,18,3807 A1, Published by USPTO.

[17] D.D. Jia, L.H. Jiang, Y.L. Liu, J. Zhu, The luminescent properties of CaxSr1-xS: Bi,Tm,Cu and CaS: Eu, Chin. J. Lumin. 19 (1998) 312.

[18] D. Jia, B.Q. Wu, L.H. Jiang, J. Zhu, The luminescent properties of Ca0.9Sr0.1S: Bi^{3+},Tm^{3+}, Chin. J. Lumin. 21 (2000) 43.

[19] W. Lehmann, Activators and co-activators in calcium sulfide phosphors, J. Lumin. 5 (1972) 87.

[20] L. Gao, E. Wang, S. Lian, Z. Kang, Y. Lan, D. Wu, Microemulsion-directed synthesis of different CuS nanocrystals, Solid State Commun. 130 (2004) 309.

[21] L.M. Gan, B. Liu, C.H. Chew, S.J. Xu, S.J. Chua, G.L. Loy, G.Q. Xu, Enhanced photoluminescence and characterization of Mn-Doped ZnS nanocrystallites synthesized in microemulsion, Langmuir 13 (1997) 6427.

[22] D. Jia, An enhanced long persistent red phosphor: CaS:Eu^{2+},Tm^{3+},Ce^{3+}, ECS Trans. 2 (2007) 1.

[23] Y. Kojima, A. Takahashi, T. Umegaki, Synthesis of orange-red-emitting Eu^{2+}, Pr^{3+}codoped SrS long afterglow phosphor, J. Lumin. 146 (2014) 42.

[24] P.-F. Ai, Y.-L. Liu, L.-Y. Xiao, H.-J. Wang, J.-X. Meng, Synthesis of Y_2O_2S:Eu^{3+},Mg^{2+}, Ti^{4+} hollow microspheres via homogeneous precipitation route, Sci. Technol. Adv. Mater. 11 (2010) 035002.

[25] X. Zhou, M. Xing, T. Jiang, F. Yao, Y. Peng, H. Wang, X. Luo, Afterglow performance enhancement and mechanism studies on Y_2O_2S:Eu,Mg,Ti prepared via cold isostatic pressing, J. Alloys Compd. 585 (2014) 376.

[26] L. Wang, L. Zhang, Y. Huang, D. Jia, J. Lu, Effects of Gd^{3+} and Lu^{3+} co-doping on the long afterglow properties of yellowish-orange phosphor Y_2O_2S:Ti^{4+}, Mg^{2+}, J. Lumin. 129 (2009) 1032.

[27] W. Lehmann, Long-Afterglow Phosphor, U.S. Patent 3,507,805(1970).

[28] J. Wilhelm, J. Freed, D.E. Best, A. Goonewardene, D. Jia, Preparation of green, yellow and red long persistent nanophosphors, ECS Trans. 2 (2007) 7.

[29] L. Hu, B. Yan, J. Zhang, X. Wang, The phosphorescent properties of Er^{3+} in Gd_2O_2S by two-step absorption, J. Phys. D. Appl. Phys. 40 (2007) 7519.

[30] G. Liu, Q. Zhang, H. Wang, Y. Li, A reddish La2O2S-based long-afterglow phosphor with effective absorption in the visible light region, Mater. Sci. Eng. B 177 (2012) 316.

[31] T. Hang, Q. Liu, D. Mao, C. Chang, Long lasting behavior of Gd_2O_2S:Eu^{3+} phosphor synthesized by hydrothermal routine, Mater. Chem. Phys. 107 (2008) 142.

[32] R.P. Johnson, Luminescence of sulfide and silicate phosphors, J. Opt. Soc. Am. 29 (1939) 387.

[33] W. Hoogenstraaten, H.A. Klasens, Some properties of zinc sulfide activated with copper and cobalt, J. Electrochem. Soc. 100 (1953) 366.

[34] F. Clabau, X. Rocquefelte, T. Le Mercier, P. Deniard, S. Jobic, M.-H. Whangbo, Formulation of phosphorescence mechanisms in inorganic solids based on a new model of defect conglomeration, Chem. Mater. 18 (2006) 3212.

[35] T. Maldiney, A. Bessie`re, J. Seguin, The in vivo activation of persistent nanophosphors for optical imaging of vascularization, tumours and grafted cells, Nat. Mater. 13 (2014) 418.

[36] N. Basavaraju, S. Sharma, A. Bessiere, B. Viana, D. Gourier, K.R. Priolkar, Red persistent luminescence in $MgGa_2O_4$: Cr^{3+}; a new phosphor for in vivo imaging, J. Phys. D. Appl. Phys. 46 (2013) 375401.

[37] B.Y. Wu, H.F. Wang, J.T. Chen, X.P. Yan, Fluorescence resonance energy transfer inhibition assay for α-fetoprotein excreted during cancer cell growth using functionalized persistent luminescence nanoparticles, J. Am. Chem. Soc. 133 (2011) 686.

[38] L. Ma, W. Chen, Enhancement of afterglow in ZnS:Cu,Co water-soluble nanoparticles by aging, J. Phys. Chem. C 115 (2011) 8940.

[39] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, New long phosphorescent phosphor with high brightness $SrAl_2O_4:Eu^{2+},Dy^{3+}$, J. Electrochem. Soc. 143 (1996) 2670.

[40] H.N. Luitel, T. Watari, R. Chand, T. Torikai, M. Yada, Giant improvement on the afterglow of $Sr_4Al_{14}O_{25}:Eu^{2+,}Dy^{3+}$ phosphor by systematic investigation on various parameters, J. Mater. 2013 (2013) 613090.

[41] D. Haranath, P. Sharma, H. Chander, Optimization of boric acid content in developing efficient blue emitting, long persistent phosphor, J. Phys. D. Appl. Phys. 38 (2005) 371.

[42] R. Stefani, L.C.V. Rodrigues, C.A.A. Carvalho, M.C.F.C. Felinto, H.F. Brito, M. Lastusaari, J. H€ols€a, Persistent luminescence of Eu^{2+} and Dy^{3+} doped barium aluminate ($BaAl_2O_4:Eu^{2+},Dy^{3+}$) materials, Opt. Mater. 31 (2009) 1815.

[43] D. Jia, X.-j. Wang, W.M. Yen, Electron traps in Tb3+-doped CaAl2O4, Chem. Phys. Lett. 363 (2002) 241.

[44] N. Kodama, T. Takahashi, M. Yamaga, Y. Tanii, J. Qiu, K. Hirao, Long-lasting phosphorescence in Ce^{3+} doped $Ca_2Al_2SiO_7$ and $CaYAl_3O_7$ crystals, Appl. Phys. Lett. 75 (1999) 1715.

[45] J. Zhang, Z. Zhang, T. Wang, W. Hao, Preparation and characterization of a new long afterglow indigo phosphor $Ca_{12}Al_{14}O_{33}$:Nd,Eu, Mater. Lett. 57 (2003) 4315.

[46] T. Wanjun, C. Donghua, M. Wu, Luminescence studies on $SrMgAl_{10}O_{17}$:Eu, Dy phosphor crystals, Opt. Laser Technol. 41 (2009) 81.

[47] A.N. Yerude, S.J. Dhoble, Combustion synthesis of $SrAl_4O_7:Eu^{2+}$, Dy^{3+}, Gd^{3+} long lasting phosphor, IOP Conf. Ser. Mater. Sci. Eng. 73 (2015) 012126.

[48] H. Nakagawa, K. Ebisua, M. Zhanga, M. Kitaura, Luminescence properties and afterglow in spinel crystals doped with trivalent Tb ions, J. Lumin. 102 (2003) 590. 422 Spectroscopy of Lanthanide-Doped Oxide Materials

[49] R.-S. Liu, Phosphors, Up Conversion Nano Particles, Quantum Dots and Their Applications, Springer, 2016.

[50] T. Katsumata, T. Nabae, K. Sasajima, T. Matsuzawa, Growth and characteristics of long persistent $SrAl_2O_4$ and $CaAl_2O_4$ based phosphor crystals by a floating zone technique, J. Cryst. Growth 183 (1998) 361.

[51] H. Yamamoto, T. Matsuzawa, Mechanism of long phosphorescence of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $CaAl_2O_4$:Eu^{2+}, Nd^{3+}, J. Lumin. 72 (1997) 287.

[52] T. Nakamura, K. Kaiya, N. Takahashi, T. Matsuzawa, M. Ohta, C.C. Rowlands, G. M. Smith, P.C. Riedi, High frequency EPR investigations of gadolinium(III)-doped strontium aluminates, Phys. Chem. Chem. Phys. 3 (2001) 1721.

[53] T. Aitasalo, P. Deren, J. Holsa, H. Jungner, J.C. Krupa, M. Lastusaari, J. Legendziewicz, J. Niittykoski, W. Strek, Persistent luminescence phenomena in materials doped with rare earth ions, J. Solid State Chem. 171 (2003) 114.

[54] F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M.-H. Whangbo, A. Garcia, T. Le Mercier, Mechanism of phosphorescence appropriate for the long-lasting phosphors Eu^{2+}-doped $SrAl_2O_4$ with codopants Dy^{3+} and B^{3+}, Chem. Mater. 17 (2005) 3904.

[55] P. Dorenbos, Mechanism of persistent luminescence in Eu^{2+} and Dy^{3+} co-doped aluminate and silicate compounds, J. Electrochem. Soc. 152 (2005) H107.

[56] H. Sun, L. Pan, X. Piao, Z. Sun, Enhanced performance of cadmium selenide quantum dotsensitized solar cells by incorporating long afterglow europium, dysprosium co-doped strontium aluminate phosphors, J. Colloid Interface Sci. 416 (2014) 81–85.

[57] H. Sun, L. Pan, X. Piao, Z. Sun, Long afterglow $SrAl_2O_4$:Eu, Dy phosphors for CdS quantum dot-sensitized solar cells with enhanced photovoltaic performance, J. Mater. Chem. A 1 (2013) 6388.

[58] A. Becue, Emerging fields in fingermark (meta)detection–a critical review, Anal. Methods 8 (2016) 7983.

[59] G. Swati, S. Bishnoi, P. Singh, N. Lohia, V.V. Jaiswal, M.K. Dalai, D. Haranath, Chemistry of extracting high-contrast invisible fingerprints from transparent and colored substrates using a novel phosphorescent label, Anal. Methods 10 (2018) 308.

[60] L. Liu, Z. Zhang, L. Zhang, Y. Zhai, The effectiveness of strong afterglow phosphor powder in the detection of fingermarks, Forensic Sci. Int. 183 (2009) 45.

[61] A.L. Smith, Some new complex silicate phosphors containing calcium, magnesium, and beryllium, J. Electrochem. Soc. 96 (1949) 287.

[62] Y. Lin, Z. Tang, Z. Zhang, X. Wang, J. Zhang, Preparation of a new long afterglow blueemitting $Sr_2MgSi_2O_7$-based photoluminescent phosphor, J. Mater. Sci. Lett. 20 (2001) 1505.

[63] K. Van den Eeckhout, D. Poelman, P.F. Smet, Persistent luminescence in non-Eu^{2+} doped compounds: a review, Materials 6 (2013) 2789.