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Remote control effects of some alkali metal ions on emission intensity of $CaSrO_2:Sm^{3+}$ nano phosphor

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ABSTRACT

A series of $CaSrO_2:Sm^{3+}$ nano-materials co-doped with some alkali metal ions were prepared by combustion synthesis method heated to ~1000 °C for 3 h to improve the crystallinity of the materials whose structure were checked by X-ray diffraction (XRD) and the surface morphology by scanning electron microscopy (SEM) indicating the presences of coagulated particles of irregular shapes with different sizes were observed. Under the excitation of near ultra violet light (405nm) , the nano-phophors show the PL emission spectra obtained due to 4f transition of Sm^{3+} from $^4G_{5/2} \rightarrow {}^6H_J(_{J=5/2,\ 7/2\ ,9/2\ ,11/2})$ consists of four peaks located at 563nm, 611nm, 655 nm and 710 nm *respectively. Among these Peaks, the peak located at 563 nm ($^4G_{5/2}\rightarrow{}^6H_{5/2}$) was purely due to magnetic-dipole transition (MD), and at 655 nm ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) was purely due to electric dipole transition (ED). But the main peak located at 611 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) was due to a partly magnetic and partly a force dielectric-dipole transition. A remarkable increase of photoluminescence intensity was observed by the co-doping of K^+ ions in $CaSrO_2:Sm^{3+}$ nano-phosphor.*

Keywords: $CaSrO_2:Sm^{3+}$; Combustion synthesis; Crystallinity; Magnetic Dipole; Electric dipole.

I INTRODUCTION

More recently, Sm^{3+} activated [1] luminescent materials have received much attention at present. They show bright orange and red emissions due to the transitions mainly from the excited state $^4G_{5/2}$ to the ground state ^6H_J ($_{J\ =\ 5/2\ ,\ 7/2,\ 9/2\ ,11/2}$), which can be used in high density optical storage , various fluorescent devices, color display, and visible solid-state lasers [2]. The synthesis of inorganic phosphor with varied morphology, texture, controlled crystallography, and micro- or nano-scale architectures are main goals because of their novel chemical, physical and optical properties in lighting, display panels, and optoelectronics technology [3]. Very recently, many rare-earth-doped optical materials such as titanates, silicates, oxides and borates with different uniform shapes have been synthesized using different processes like sol gel, co-precipitation and modified solid state methods [4]. When these luminescent materials are synthesized through the traditional high-temperature based method such as solid-state method, the product obtained is mostly found to be either of irregular morphology or agglomerate with serious reunion and high hardness, which directly affects the luminescence efficiency of the phosphors during the later milling. As we know every synthesis methods have some important effects on the material microstructure and physical properties. But the combustion synthesis [5] provides an interesting significance over other techniques because of its simplicity of experimental set-up; surprisingly short time between the preparation of reactants and the availability of the final product; and being cheap due to energy saving. The main advantage of combustion method is the rapid decomposition of the rare earth nitrates in the presence of an organic fuel. During the reaction, various kinds of gases likes CO_2, N_2, NO_2 and H_2O, as well as a large amount of heat are released in a short period of time before the process terminates with white, foamy and crispy products. So this work has been carried out with the aim to prepare and compare the high intensity photoluminescence nano-sized crystalline powders of $CaSrO_2$ doped with Sm^{3+} after sintering at 1000°C. The $CaSrO_2:Sm^{3+}$ and same lattices doped with Eu^{3+} are expected to act as one of the most promising orange-red luminescent materials [6]. A series of $Ca_{1-x}Sm_xSrO_2$ phosphors have been synthesized. It has been pointed out that when a trivalent metallic ion substitutes for divalent metallic ion in a host lattice, there is existence of charge unbalance. Hence to make charge compensation some alkali metals ions were co-doped in the host lattice & the effects of incorporation of alkali metal ions mainly (Li^+, Na^+, K^+) to enhance the photoluminescence intensity of $CaSrO_2:Sm^{3+}$ phosphor have been investigated and the possible mechanism have been proposed. The crystalline structure of prepared materials, morphology of particles and their photoluminescence properties are characterized by XRD, SEM and PL emission spectra with 405 nm lasers for excitation respectively.

II MATERIALS AND METHODS

Synthesis of nano-material:

High purity aldrich chemicals like [$Ca(NO_3)_2$], [$Sr(NO_3)_2$], [$Sm(NO_3)_3$], $LiNO_3$, $NaNO_3$, KNO_3 and [HMTA] hexamethylenetetramine, $(CH_2)_6N_4$ as a combustion fuel were used as a starting materials for synthesis of phosphor. Sm^{3+} doped and M^+ (Li^+, Na^+, K^+) ions co-doped nano-crystals with general formula $Ca_{1-x}SrO_2:Sm_x^{3+}$ and $Ca_{1-x+y}SrO_2:Sm_x^{3+},M_y^+$, where x is 1 to 7 mol %, & y is 0.05 to 2 mole% were prepared by heating a stoichiometric amount of metal nitrates and fuel on a preheated hot plate maintained at 150 °C for 1h, where the mixture undergoes slow dehydration to produce a paste which was again comusted at 1000 °C for 3 h in muffle furnace to enhance the crystallinity of the phosphor. Hexamethylenetetramine amount was calculated using total oxidizing and reducing valencies[7]. The fragile white solid product thus obtained by combustion was easily ground to a fine-sized powder by the pestle mortar and characterized by XRD, SEM, PL measurements.

The combustion reaction can be written as:

$$Ca(NO_3)_2 + Sr(NO_3)_2 + Sm(NO_3)_3 + (CH_2)_6N_4 \xrightarrow{\mathbf{1000\ ^0C}} CaSrO_2{:}Sm^{3+} + CO_2 + NO_2 + H_2O + Heat$$

Characterization of nano-material:

The Crystal structure, Morphology and Photoluminescence intensity was characterized by X-ray diffraction (XRD) using Rigaku Ultima IV diffractometer, Scanning electron microscopy (SEM) using JEOL JSM6300 , UV lamp at 405 nm for excitation respectively. Color purity was determined by color chromaticity triangle. All measurements were carried out at room temperature.

III RESULTS AND DISCUSSION

Crystal structure analysis:

The XRD patterns of Li^+, Na^+, K^+ ions co-doped $CaSrO_2:Sm^{3+}$ nano-crystals as shown in Fig.1, depicts the presence of three phases of CaO_4 (no. JCPDS 21-0155) [8], SrO_2 (no. JCPDS 001-1113, Tetragonal) and Sm_2O_3 (JCPDS Card No. 15-0813, Monoclinic). XRD analysis evident that $CaSrO_2:Sm^{3+}$ co-doped with Li^+ , Na^+ , K^+ ions have the monoclinic structure, where the Sm^{3+} occupied the high symmetric position (O_h) of Ca^{2+} in

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$CaSrO_2$ lattice. But the position of Sm^{3+} ions in the two phases .i.e. SrO_2 and Sm_2O_3 may not be at sites of high symmetry (O_h), as SrO_2 and Sm_2O_3 belongs to tetragonal and monoclinic lattices respectively. The most of the diffraction peaks are assigned to monoclinic crystalline phase of $CaSrO_2$. The presence of separate phase Sm_2O_3 in the $CaSrO_2$:Sm^{3+} show partial incorporation of Sm^{3+} ions in the host lattices. That is why ,the effects of the incorporation of Li^+, Na^+ and K^+ ions on enhanced photoluminescent behavior of the host lattice i.e. $CaSrO_2$:Sm^{3+} had been studied and possible mechanism investigated. Alkali metal ions occupied the position of Ca^{2+} site. As the ionic radius of Li^+ ion is less, there is a possibility of some of the Li^+ ions to remain in interstitial sites between or among the host ions. For Na^+ ions, they could be located at Ca^{2+} sites more easily than for K^+ ions because of their bigger ionic radii. Fig. 1 show that the diffraction peaks of $CaSrO_2$:Sm^{3+} co-doped with Li^+, Na^+ , K^+ ions were obviously almost identical but the relative intensities of crystal faces (111), (200) and (221) were different from each other. The corresponding unit-cell constants and unit cell volumes of $CaSrO_2$:Sm^{3+} phosphors as well as same co-doped with Li^+, Na^+ , K^+ ions were calculated from the distance between the adjacent (200) planes corresponding to direction peaks near 2θ=33.25 and are listed in Table 1. It was observed that the cell volume of the lattice is increased if the ions with larger radius substitute the smaller cations in the crystalline lattice [9,10]. Therefore, as shown in Table 1, the cell volumes of $CaSrO_2$:Sm^{3+},Na^+ and $CaSrO_2$:Sm^{3+} ,K^+ is increased, because the ionic radii of Na^+ ions (102 pm) and K^+ ions (138pm) are larger than that of Ca^{2+} ions (100 pm). If the same rule applied to $CaSrO_2$:Sm^{3+},Li^+ samples. The cell volume should decrease with the co-doping of Li^+ ions. But in actual, the cell volume of $CaSrO_2$:Sm^{3+} co-doped with Li^+ ions is increased, despite the fact that the Li^+ ion have smaller ionic radii than that of Ca^{2+} ion. This increase may be due to the larger size of Li^+ ions than that of interstitial sites in the crystal lattice.

Table 1. The lattice parameters of $CaSrO_2$:Sm^{3+} phosphors with alkali metal ions.

Phosphors	2θ	hkl/200	a (A)	V (A^3)
$CaSrO_2$:Sm^{3+}	33.341	2.4061	4.8120	112.437
$CaSrO_2$:Sm^{3+}, Li^+	33.283	2.4097	4.8194	112.965
$CaSrO_2$:Sm^{3+},Na^+	33.275	2.4104	4.8207	113.017
$CaSrO_2$:Sm^{3+}, K^+	33.258	2.4117	4.8225	113.175

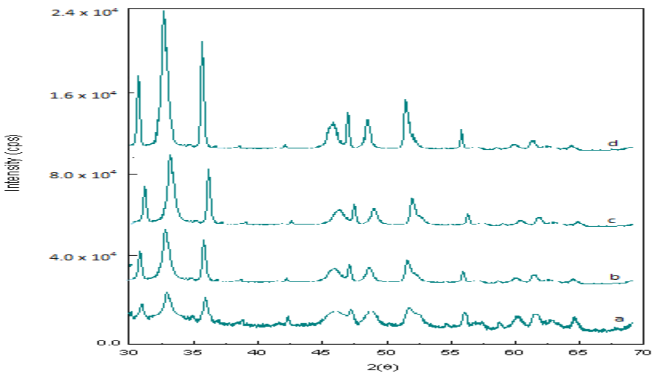
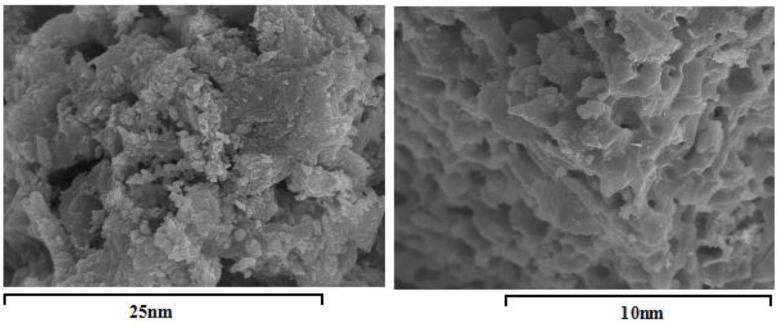


Figure1. XRD spectra of (a) $CaSrO_2$:Sm^{3+} & (b) with Sm^{3+}, Li^+ (c) Sm^{3+},Na^+ & (d) Sm^{3+},K^+ ions respectively.

SEM micrograph & particles size analysis:

The morphology of the crystals was studied by scanning electron microscopy (SEM) using JEOL JSM6300. Figs. 2 (a & b) depict that the SEM micrographs of $CaSrO_2$:Sm^{3+} particles is not so smooth and the coagulated particles of irregular shapes with different sizes were observed. From the SEM results, it was observed that the phosphor have an average particle size about 10±5nm.



(a) **(b)**

Figure 2. SEM micrographs of (a) $CaSrO_2$:Sm^{3+} & (b) with K^+ ions

Optical properties analysis:

The room-temperature emission spectra of $CaSrO_2$: Sm^{3+} crystals co-doped with Li^+, Na^+ and K^+ are shown in Fig. 3(a). Phosphors upon excitation near ultra violet (405nm) light, the phosphors show PL emission spectra obtained due to 4f transition of Sm^{3+} from $^4G_{5/2} \rightarrow {}^6H_J(_{J=5/2,\ 7/2\ ,9/2\ ,11/2})$ consists of four peaks located at 563nm, 611nm, 655 nm and 710 nm respectively. Among these Peaks, the peak located at 563 nm ($^4G_{5/2}\rightarrow{}^6H_{5/2}$) was purely due to magnetic-dipole transition (MD), and at 655 nm ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) was purely due to electric dipole transition (ED). But the main peak located at 611 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) was due to a partly magnetic and partly a force dielectric-dipole transition. [11,12]. These centers emit reddish-orange radiations characteristic of Sm^{3+} ions. The CIE [13], chromaticity coordinates of the synthesized nano-material also fall in the reddish-orange region of the color triangle with x & y value as shown in the Fig. 3(b). It is recognized that interaction of Sm^{3+} ions with the host $CaSrO_2$ lattice is very weak and there is very little energy transfer occurs between Sm^{3+} and host lattice. Low emission intensity of Sm^{3+} ions in $CaSrO_2$ may be due to lack of efficient energy transfer from Ca^{2+} ions to Sm^{3+} ions or due to the of some presence surface impurities or surface defects. But with the introduction of alkali metal ions (Li^+, Na^+, K^+) in the $CaSrO_2$:Sm^{3+} system, we observed a remarkable increase in the energy transfer process between Sm^{3+} and host lattice and the photoluminescence intensity of all emission peaks of Sm^{3+} ion particularly for transition $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ & $^4G_{5/2}\rightarrow{}^6H_{9/2}$ also increased as shown in Fig. 3. It has been pointed out that when a trivalent metallic ion substitutes for divalent metallic ion in a host lattice, there is existence of charge unbalance, which affects the photoluminescence intensity of phosphor. Hence to make charge compensation, some alkali metals ions were co-doped in the host lattice. But it seems that the incorporation of mono-valent ions facilitate the improved energy transfer from Ca^{2+} to Sm^{3+} and creating the oxygen vacancies[9] which may act as sensitizers, facilitate the strong mixing of the Ca-O and Sm-O charge transfer states, and thus promote energy migration from the Ca-O CTS(charge transfer state) to Sm^{3+}, hence increased in the photoluminescence intensity takes place. When Na^+ , Li^+ , and K^+ ions are co-doped, there is an increase in the photoluminescence intensity about 10, 20 and 100 % times respectively and increase order is $K^+ > Li^+ > Na^+$. The emission spectra of $CaSrO_2:Sm^{3+}$ materials are shown in Fig. 3, indicate that the relative intensities of all emission peaks follow the order: $CaSrO_2:Sm^{3+},K^+$ > $CaSrO_2:Sm^{3+},Na^+$ > $CaSrO_2:Sm^{3+},Li^+$ > $CaSrO_2:Sm^{3+}$. The relative positions of all emission peaks in $CaSrO_2:Sm^{3+}$, [Li^+, Na^+, K^+] shown in **table 2**.

Table 2. The positions of emission peaks in $CaSrO_2:Sm^{3+}$, [Li^+, Na^+, K^+]

Phosphors	$^4G_{5/2}\rightarrow{}^6H_{5/2}$	$\mathbf{^4G_{5/2}\rightarrow{}^6H_{7/2}}$	$^4G_{5/2}\rightarrow{}^6H_{9/2}$	$^4G_{5/2}\rightarrow{}^6H_{11/2}$
$CaSrO_2:Sm^{3+}$	563nm	**611nm**	655 nm	711 nm
$CaSrO_2:Sm^{3+}$, Li^+	565 nm	**611nm**	654 nm	711 nm
$CaSrO_2:Sm^{3+}$, Na^+	564 nm	**611nm**	653 nm	712 nm
$CaSrO_2:Sm^{3+}$, K^+	563 nm	**611nm**	653 nm	711 nm

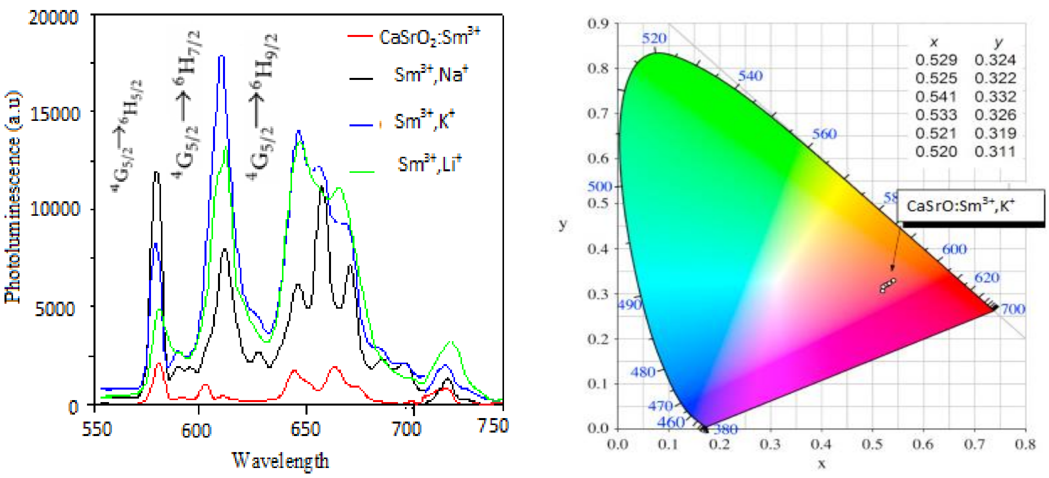


Figure 3. (a) PL spectra of $CaSrO_2:Sm^{3+}$ with Li^+, Na^+, K^+ ions.

(b) Color coordinates diagram with x & y value.

Furthermore, more are the oxygen vacancies generated by co-doping of alkali metal ions, more is the effective energy transfer between Ca^{2+} and Sm^{3+} ions. Finally, it can be concluded that the large increase in the emission intensity of the $^4G_{5/2}\rightarrow{}^6H_{J/2}$ (J = 5, 7, 9) [14-18] transitions is due to improved energy transfer and reduced symmetrical environment around Sm^{3+}. Alkali-metals ions co-doping had different effects on energy transfer ($K^+ > Li^+ > Na^+$), which is in accordance with the sequence of luminescence from $^4G_{5/2}\rightarrow{}^6H_{J/2}$ (J = 5,7,9) transition of the Sm^{3+}.

IV CONCLUSION

$CaSrO_2:Sm^{3+}$ nano-phosphors co-doped with M^+ [Li^+, Na^+, K^+] ions prepared by combustion synthesis method further heated to 1000 °C for 3h to improve the crystallinity of the materials. XRD pattern of phosphors depicts that most of the diffraction peaks are assigned to monoclinic crystalline phase of $CaSrO_2$ along with tetragonal SrO_2 and monoclinic Sm_2O_3 phase which are the main phases in $CaSrO_2:Sm^{3+}$ powders. A remarkable increase in the photoluminescence intensity by co-doping with alkali metal ions (mainly K^+ ion) in $CaSrO_2:Sm^{3+}$ phosphors is observed due to the generation of oxygen vacancies which promote energy transfer from Ca^{2+} to Sm^{3+} and reduce environment symmetry around Sm^{3+} ions.

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REFERENCES

[1] Zhang, Y., Lu, C. H., and Ni,Y.Ni., Materials Research Bulletin, **2009**, 44, 179–183.

[2] Venkatramu, V., Babu, P., Jayasankar, C. K., Optical Materials, **2007**, 29, 1429–1439.

[3] Ding,Y., Fan, F.R. ,Tian, Z.Q., J. Am. Chem. Soc., **2010**, 132, 12480.

[4] Kang, M., Liao, X., Kang, Y., Liu J., and Yin, G., J. Mater. Sci., **2009**, 44, 2388.

[5] K. C Patil, Aruna , S.T., and Sambandan Ekambaram , **1997**, 2, 158-165.

[6] Jeong, J. H., Yang , H. K and Shim, K. S., Appl Surf Sci, **2007**, 253, 8273.

[7] Fu ,J., J Electron Solid-State Lett , **2000**, 3, 350

[8] Joint Commission on Powder Diffraction Spectroscopy (JCPDS)-International Centre for Diffraction Data, Swarthmore, U.S.A., Card No- 43, 1036.

[9] Voort, D.V., A. Imhof, A., and Blasse, G., J. Solid State Chem. ,**1992**, 96, 311.

[10] Li Shi Li, Cheng, Yu Li and Qiang, Su., J.fluorescence, **2011**, 21, 1461.

[11] Liu, G., Hong, G., Wang, J., and Dong, X., J. Alloys Compd, **2007**, 432, 200.

[12] Ningthoujam, R. S., Sudarsan, V., and Kulshreshtha, S.K., J. Lumin, **2007**, 127, 747.

[13] Yang, M. Z.; Sui, Y.; Wang, S. P.; Wang, *Chem. Phys. Lett*. **2010**, 492, 40–43.

[14] He, F., Yang, P., and Wang, D. et al., Dalton Transactions, **2011**, 40, 11023-11030.

[15] Raju, G. S. R., Park, J.Y., and H. C. Jung, H.C. et al., Journal of Materials Chemistry, **2011**, 21, 6136-6139.

[16] Lin, X., Qiao, X. S., and Fan, X. P., "Synthesis and luminescence properties of a novel red $SrMoO_4:Sm^{3+},R^+$ phosphor," Solid State Sciences, **2011**, 13, 579-583.

[17] Yang, Z., Zhao, Z., Que, M., and Wang, Y., Optical Materials, **2013**, 35, 1348-1351.

[18] Puchalska, M., and Zych, E ., Journal of Luminescence, **2012**, 132, 826-831.