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Generation of White Light from $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) Phosphors

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Abstract— *Dysprosium doped alkaline earth silicates namely $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x = 0, 1, 2) phosphors was prepared by the traditional high temperature solid state reaction method. The crystal structure of sintered $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x = 0, 1, 2) phosphors were an akermanite type structure which belongs to the tetragonal crystallography with space group P4□2₁m, this structure is a member of the melilite group and forms a layered compound. The optical properties of $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x = 0, 1, 2) phosphors were investigated using photoluminescence (PL) properties. Under the ultraviolet excitation, the emission spectra of $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x = 0, 1, 2) phosphors, the characteristic emission of Dy^{3+} peaking at blue, yellow and red color, originating from the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions. The combination of these three emissions constituted as white light emission confirmed by the Commission Internationale de L'Eclairage (CIE) chromatic coordinate diagram. The possible mechanism of white light emitting $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x = 0, 1, 2) phosphors were also investigated.*

Keywords— *Alkaline earth silicates; XRD; Photoluminescence; CIE color co-ordinates.*

1. INTRODUCTION

Scientists and researchers are conducting research in search for suitable host lattices that can be used to prepare phosphors for white light emitting phosphors. Current research topics on phosphors are focused on the generation of white light that can be used in light emitting diodes (LEDs). White LEDs have several advantages over conventional fluorescent lamps such as reduced power consumption, compactness, efficient light output, and longer lifetimes. The strategies used to produce white light in LEDs include combining blue LED with a yellow phosphor or UV-LED with blue, green and red phosphors or blue, green and red LEDs. Luminescence materials doped with Dy^{3+} have recently drawn considerable interest because it emits white light. Given that Dy^{3+} with $4f^9$ configuration has complicated f-block energy levels, various possible transitions between these levels are highly selective and show sharp line spectra. [1, 2]

In general, Dy^{3+} exhibits three visible emission bands including the blue emission at 480 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition, the yellow emission at 577 nm corresponding to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (ΔJ= 2) and the feeble red emission at 670 nm corresponding to the transition $^4F_{9/2} \rightarrow {}^6H_{11/2}$. [6-9] Consequently, white light can be obtained by creating the appropriate mixture of blue and yellow emissions. Moreover, phosphors doped with Dy^{3+} ions based on their line type f–f transitions, can emit narrow emissions in the visible range, resulting in high efficiency and high lumen equivalence. As a result, there has been growing interest in developing Dy^{3+} doped phosphors with high absorption in the n-UV to blue range. [3, 4] As is known to all, alkaline earth silicates have attracted interest in the field of white light emitting phosphors since they are suitable hosts due to their suitable energy, band structure, high physical and chemical stability, easy preparation and low cost. [5,6]

Mellite are a large group of compounds characterized by the general formula $M_2T^1T^2{}_2O_7$, (M = Sr, Ca, Ba;, T^1 = Mn, Co, Cu, Mg, Zn; T_2 = Si, Ge), have been investigated widely as optical materials. Due to their tetragonal and non-centrosymmetric crystal structure, lanthanides or transition metals can be accepted easily as constituents or dopants by the melilites, allowing the synthesis of high-quality doped single crystals. Recently $SrCaMgSi_2O_7$ phosphor has attracted great interest due to its special structure features, excellent physical and chemical stability. They have been studied widely with Eu^{2+} doping, which shows that a bluish-green emission and long persistent luminescence by co-doping with some other rare earth ions. Solid state reaction technique is a traditional phosphors synthesis techniques is widely used to prepare silicate phosphors because samples prepared using this method have good luminescence and very good morphology, which has advantage over the other techniques. [7,9]

2. EXPERIMENTAL

2.1 Material Preparation

The $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphors was prepared by the high temperature solid state reaction method. The starting materials are $SrCO_3$ (99.9%), $CaCO_3$ (99.9%), MgO (99.9%), SiO_2 (99.99%), and Dy_2O_3 (99.99%), all of analytical purity, were employed in this

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experiment. Boric acid (H_3BO_3) was added as the flux. Initially, the raw materials were weighed according to the nominal compositions of $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (where x = 0, 1, 2). Then the powders were mixed and milled thoroughly for 2 hour using the mortar and pestle. The grinded sample was placed in an alumina crucible and subsequently fired at 1050°C for 3 hours in a weak reducing atmosphere. The weak reducing atmospheres are generated with the help of activated charcoal. Solid state reaction method is widely used to prepare silicate based phosphors because samples prepared using this method has good luminescence and very good morphology also.

2.2 Characterization Techniques

The crystal structures of the prepared $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphors was characterized by powder XRD analysis. Powder XRD pattern has been obtained from Bruker D8 advanced X-ray powder diffractometer using CuKα (1.54060 Å) radiation and the data were collected over the 2θ range 10-80°. The structure of the sample was verified with the help of Joint Committee of Powder Diffraction Standard Data (JCPDS) file (JCPDS: 17-1630). The excitation and emission spectra of sintered phosphors were recorded by Spectroflurophotometer (SHIMADZU, RF 5301 PC) using the Xenon lamp as excitation source. All measurements were carried out at the room temperature.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

In order to determine the crystal structure, the powder XRD analysis was carried out. XRD patterns of the $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) are shown in Fig. 1(a), 1(b) and 1(c). Fig 1(a) can be indexed to $Sr_2MgSi_2O_7$ according to JCPDS card no. 75-1736 [16] and fig. 1(c) can be indexed to $Ca_2MgSi_2O_7$ according to JCPDS card no. 77-1149 [17]. The position and intensity of diffraction peaks of $Sr_2MgSi_2O_7:Dy^{3+}$ and $Ca_2MgSi_2O_7:Dy^{3+}$ were found to be consistent with that of the JCPDS file. The standard XRD patterns of $SrCaMgSi_2O_7:Dy^{3+}$ were not found in the International Center for Diffraction Data (ICDD) database, but compared with the standard patterns of $Sr_2MgSi_2O_7$ (JCPDS 75-1736) and $Ca_2MgSi_2O_7$ (JCPDS 77-1149), it could be seen that the major diffraction peaks of $SrCaMgSi_2O_7:Dy^{3+}$ phosphor is between that of the corresponding peaks of $Sr_2MgSi_2O_7:Dy^{3+}$ and $Ca_2MgSi_2O_7:Dy^{3+}$, which indicates that the change of alkaline earth ions induces a small effect on the structure of the sample. The result reveals that the crystal structure of the $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphors has an akermanite type structure which belongs to the tetragonal crystallography with space group $P42_1m$, this structure was a member of the melilite group and forms a layered compound. The location of diffraction peaks of SCMSED is between the corresponding peaks of $Sr_2MgSi_2O_7:Dy^{3+}$ and $Ca_2MgSi_2O_7:Dy^{3+}$. In addition, the location of $SrCaMgSi_2O_7:Dy^{3+}$ and $Ca_2MgSi_2O_7:Dy^{3+}$. phosphors diffraction peaks shifted towards high angle compared with that of the corresponding peaks for $Sr_2MgSi_2O_7:Dy^{3+}$, indicating that the change of alkaline earth ions induces a little effect on the structure of the phosphors [10].

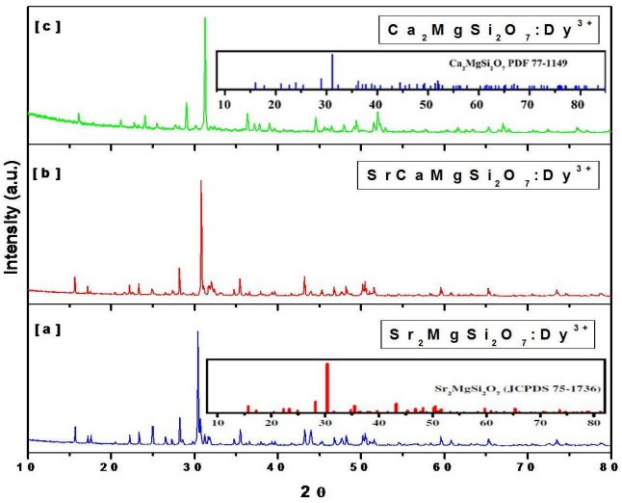


Fig. 1: (a), (b), (c) XRD patterns $Sr_2MgSi_2O_7:Dy^{3+}$; $SrCaMgSi_2O_7:Dy^{3+}$ and $Ca_2MgSi_2O_7:Dy^{3+}$ phosphors

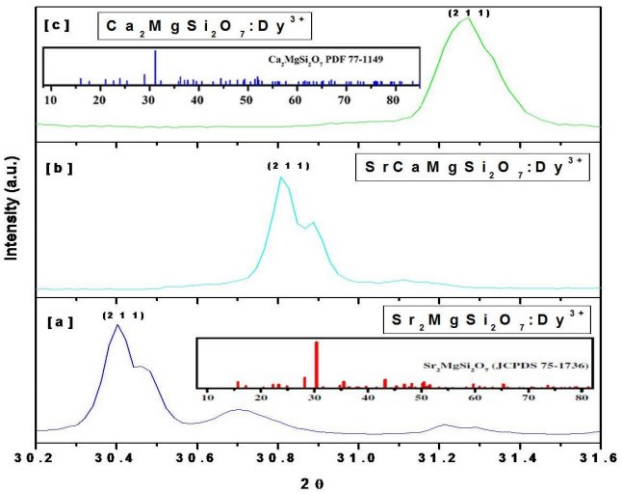
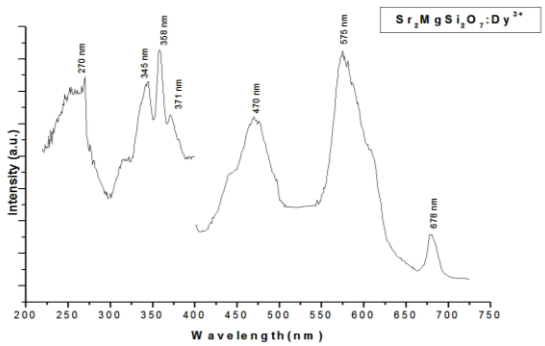


Fig. 2: (a), (b), (c) XRD patterns of $Sr_2MgSi_2O_7:Dy^{3+}$; $SrCaMgSi_2O_7:Dy^{3+}$ and $Ca_2MgSi_2O_7:Dy^{3+}$ phosphors on the (2 1 1) crystal planes

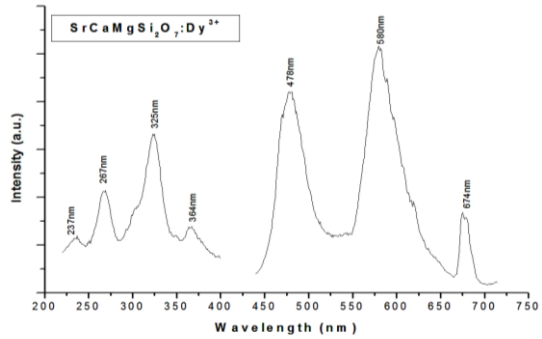
3.2 Photoluminescence (PL)

In order to study the luminescent properties of phosphor, the excitation and emission spectra of prepared $Sr_2MgSi_2O_7:Dy^{3+}$; $SrCaMgSi_2O_7:Dy^{3+}$; $Ca_2MgSi_2O_7:Dy^{3+}$ phosphor was recorded. The excitation spectra were observed in the range of 200 to 400 nm, consists of the f→f transition of Dy^{3+} are observed, and emission spectra were recorded in the range of 400 to 750 nm. When the $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphors were excited at in the UV region, simultaneous emissions of

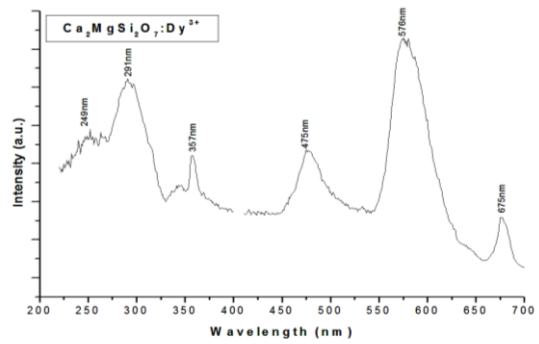
blue, yellow and red nm position were observed. Notice that the red emission is less intense than the blue and yellow emissions. These three different emission bands originated from the one origin owing to their having the same excitation wavelength. The transitions involved in blue, yellow and red bands of Dy^{3+} ion are well known and have been identified as $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions respectively [11].



(a)



(b)



(c)

Fig. 3: (a) Excitation and emission spectra of $Sr_2MgSi_2O_7:Dy^{3+}$ phosphor; (b) Excitation and emission spectra of $SrCaMgSi_2O_7:Dy^{3+}$ phosphor; (c) Excitation and emission spectra of $Ca_2MgSi_2O_7:Dy^{3+}$ phosphor

One can also find that the emission lines of Dy^{3+} are broadened somewhat because there are several Stark levels for the $^4F_{9/2} \rightarrow {}^6H_J$ levels. The emission spectra mainly consist of three groups of sharp lines peaked at about blue, yellow and red, which are associated with the transitions of Dy^{3+} from the excited state $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ respectively. It is well known that the former weak blue emission at 470 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) is corresponded to the magnetic dipole transition, which hardly varies with the crystal field strength around Dy^{3+}. While the later stronger yellow emission $^4F_{9/2} \rightarrow {}^6H_{13/2}$ belongs to the hypersensitive forced electric dipole transition, which is strongly influenced by the outside surrounding environment [12].

According to the Judd–Ofelt theory, when Dy^{3+} locates at a low symmetry local site without inversion symmetry, a yellow emission according to the electric dipole transition ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) will be dominant. Conversely, a magnetic dipole transition ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) will predominate in the emission spectra, resulting in a strong blue emission. In our case, the yellow emission ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) will dominate. The strong yellow emission is also beneficial to decrease the color temperature of the phosphor and generate warm white light emission. The optical properties of the material are often influenced by the structure of the matrix and synthesis technique [13].

4. CONCLUSION

In summary, the $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphors were successfully synthesized by the solid state reaction method. The result reveals that the the $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphors has tetragonal crystallography. Under the ultra-violet (UV) excitation, the prepared $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphor would emit blue, yellow and red light corresponds to the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ respectively. The three emission bands of the $Sr_{2-x}Ca_xMgSi_2O_7:Dy^{3+}$ (x= 0, 1, 2) phosphor combines to give out white light, which were found to be very close to standard white light for human eyes.

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