

Influence of alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphors.

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Abstract. Eu^{2+} doped and Nd^{3+} co-doped $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{and Ba}$) phosphors were prepared by a solution-combustion method. The obtained powders were investigated in terms of their phase composition, particle morphology and photoluminescence (PL) by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM) and Ultraviolet-Visible Spectroscopy (UV-VIS) techniques respectively. XRD analysis depicts a monoclinic phase for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ and a hexagonal structure for $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor. SEM results showed generally agglomerated particles with non-uniform shapes and sizes with irregular network structures having lots of voids and pores. PL excitation revealed broadband spectra with peaks corresponding to the crystal field splitting of the Eu^{2+} d-orbital. The emission spectra were also broadband with peaks at 447 nm for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$, at 507 nm for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ and at 497 nm for $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ due to the $4f^65d^1-4f^7$ emission of Eu^{2+} . Sharp emission lines were observed arising from the f-f transitions of the Eu^{3+} ions. The differences in emissions from the three phosphors arise from the crystal field splitting of the 5d electron shell due to the changes in the crystalline environment of the Eu^{2+} ions caused by the substitution of the divalent alkaline earth metal cations with different ionic sizes in the MAl_2O_4 host lattice. UV-VIS spectra showed absorption edges at 330, 342 and 340 nm in agreement with the observed PL excitation peaks. The luminescence decay characteristics showed that these materials possess persistent luminescence whereby $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ gave a longer afterglow as compared to the other two phosphors.

Keywords: $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$, Substitution, Crystal field, Luminescence, Transition, Long afterglow.

1. Introduction

Phosphors from alkaline earth aluminates exhibit stronger brightness and a persistent afterglow time. The luminescent properties of divalent europium ion (Eu^{2+}) doped alkaline earth aluminates $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) have been widely studied owing to their high quantum efficiency in the visible region [1]. As compared with traditional sulphide based phosphors Eu^{2+} doped aluminate (Al_2O_4) phosphors have shown excellent photo-resistant, high chemical stability, endurance in storage, radiation resistance and can withstand different environmental conditions [2]. In these phosphors, the emission emanates from the $4f^65d^1 - 4f^7$ transition of Eu^{2+} . Depending on the host structure this emission can be colour-tuned from ultraviolet to the red since the excited $4f^65d^1$ configurations of Eu^{2+} ion is highly sensitive to the change in the lattice environment [1,3]. Several methods have been used to synthesis Al_2O_4 phosphors such as solid state reaction [1] and sol-gel [4] among others. The synthesis of phosphors in this study has been achieved via a solution combustion route where the starting materials were mixed in solution phase. This process is very facile, safe, energy and time saving [5]. The method makes use of the heat energy liberated by the redox exothermic reaction between metal nitrates and urea as fuel [6]. In this study the effect of different alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors were investigated.

2. Experimental

The polycrystalline Eu^{2+} doped and Nd^{3+} co-doped $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors were prepared by a low temperature urea-nitrate solution combustion reaction between stoichiometric mixtures of $\text{Ba}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_2$, $\text{Nd}(\text{NO}_3)_3$, urea $\text{CO}(\text{NH}_2)_2$ as a fuel and boric acid (H_3BO_3) as a flux. The masses were weighed and mixed in 10ml of deionised water and stirred for 15 minutes at room temperature on a magnetic stirrer. The solutions were then poured into China crucibles and placed one at a time in a muffle furnace pre-heated at 500 °C. Exothermic reaction occurred producing white, voluminous foam-like ash which was then milled to obtain the phosphor powders. The structure and phase purity of the phosphor samples was checked with a Bruker-AXS D8 Advance X-ray diffractometer operating at 40 kV and 4 mA using $\text{Cu K}\alpha = 0.15406$ nm. The morphologies of the phosphor powders were obtained by using a Shimadzu Super scan SSX-550 scanning electron microscope (SEM). Absorption spectra were recorded using a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer. The PL excitation, emission and decay spectra were measured using a Cary Eclipse luminescence spectrometer (model LS-55) with a built-in 150 W xenon flash lamp as the excitation source and a grating to select a suitable excitation wavelength.

3. Results and discussions

3.1. Structure (XRD)

XRD patterns of the $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphor powders are shown in fig. 1(a)-(d). The peaks indexed well with the JCPDS card numbers 71-1323, 70-0134 and 74-0794 for the BaAl_2O_4 , CaAl_2O_4 and SrAl_2O_4 respectively [3,7,8]. These compounds have a stuffed tridymite structure with a 3D frame work of corner sharing AlO_4 tetrahedra in which charge balance is achieved by the divalent cations that occupy interstitial sites. At room temperature, BaAl_2O_4 is hexagonal with space group P_{63} having unit cell parameters $2a, c$ [9]. There are two different barium (Ba^{2+}) sites, one occurring 3 times more frequently than the other. Both Ba^{2+} sites are coordinated by 9 oxygen (O_2) ions (O^{2-}). The channels are along the c -axis and the two different Ba^{2+} sites occur in separate chains [10]. SrAl_2O_4 belongs to the monoclinic P_{21} space group at room temperature [11]. The strontium (Sr) chains are along the a axis [1]. There are two sites available for Sr^{2+} ions. Both sites occur in equal amounts in the lattice and are coordinated by 9 O^{2-} ions. The coordination of Sr by O_2 is less regular than the coordination of Ba by O_2 in BaAl_2O_4 [10]. CaAl_2O_4 has a monoclinic structure with space group $\text{P}_{21/n}$ and three different sites for the Ca^{2+} ion one having 9-fold coordination and others are 6-fold coordinated with O_2 atoms [12].

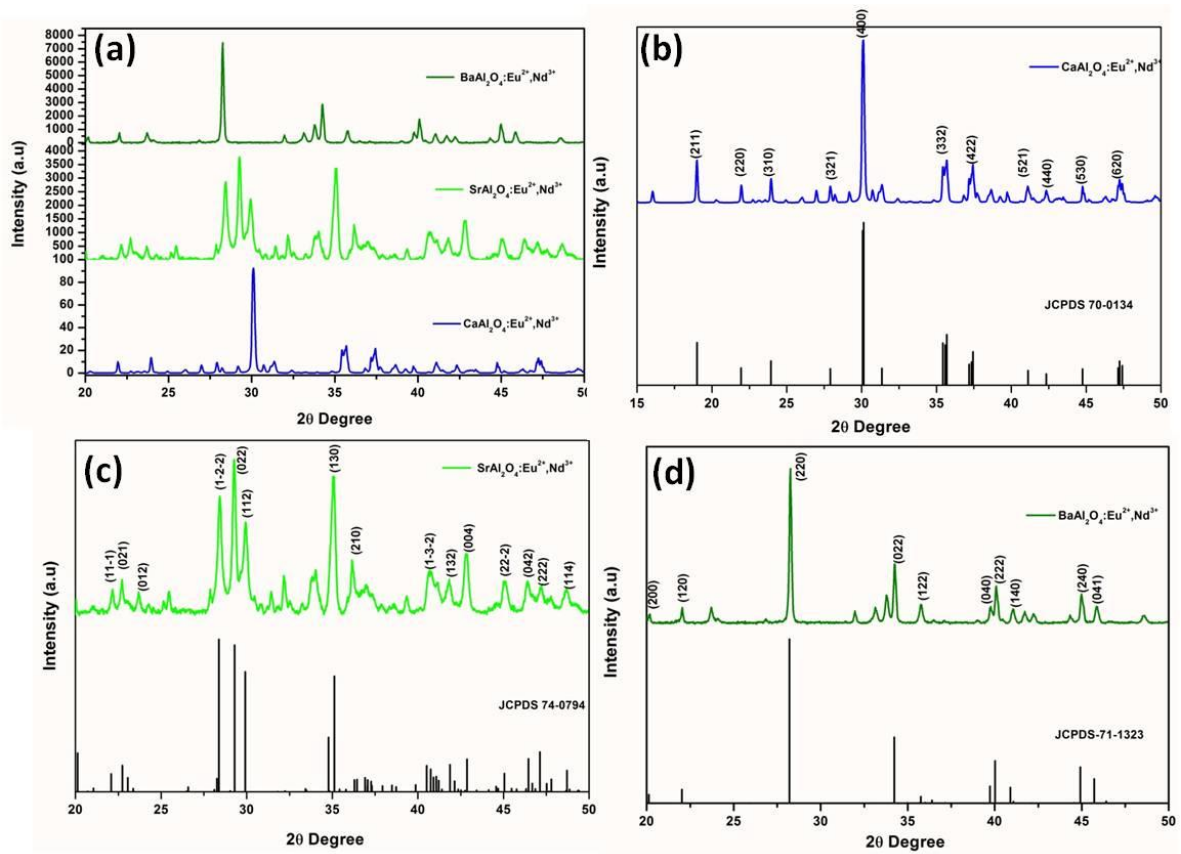


Fig. 1. (a)-(d): XRD patterns of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$, $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ phosphor powders.

3.2. Morphology (SEM)

Fig. 2(a), (b) and (c) show SEM micrographs for as – prepared $MA_2O_4:Eu^{2+}$ ($M = Ca, Ba, Sr$) phosphors. From fig. 2(a) and (b) it can be observed that powders are in the form of agglomerates with non-uniform shapes and sizes caused by non-uniform distribution of temperature and irregular mass flow during combustion [13]. In fig. 2(c) the nanostructures of $BaAl_2O_4:Eu^{2+},Nd^{3+}$ crystallized to form fine, regular hexagonal platelets exhibiting smooth surface and well developed faces [3]. In all these the surfaces of the particles contained fine pores and voids or cracks, which may be attributed to the evolved gases during combustion [14].

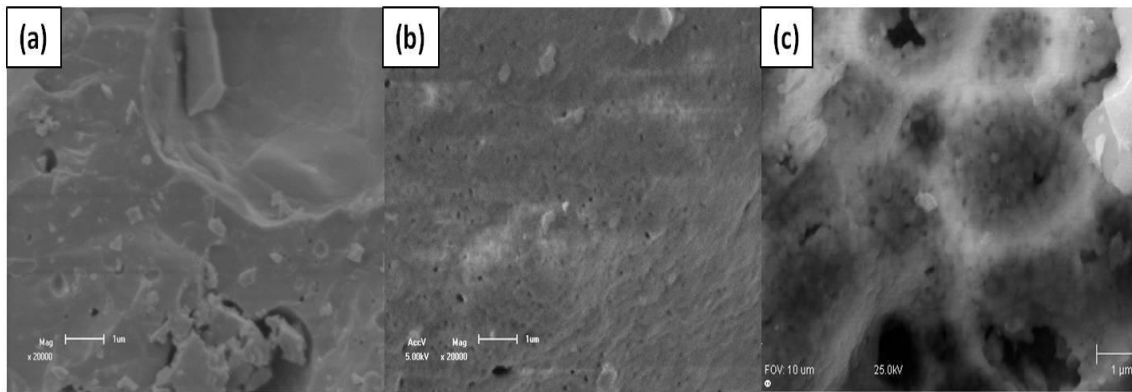


Fig. 2: (a), (b) and (c); SEM micrographs as – prepared $CaAl_2O_4:Eu^{2+}; Nd^{3+}$, $SrAl_2O_4:Eu^{2+}; Nd^{3+}$ and $BaAl_2O_4:Eu^{2+}; Nd^{3+}$ phosphors respectively.

3.3. Photoluminescence (PL)

Fig. 3(a) and (b) show the PL excitation and emission measurements from $MA_2O_4:Eu^{2+}$ ($M = Ca, Ba, Sr$) phosphors. Excitation spectra were broadband revealed peaks corresponding to the crystal field splitting of the Eu^{2+} d-orbital [15,16]. These phosphors are wide band gap materials; $SrAl_2O_4$ (6.52 eV) [7], $BaAl_2O_4$ (6.5 eV) [17] and $CaAl_2O_4$ (5.78 eV) [18] so that no transition between the valence band (VB) and conduction band (CB) can occur under UV irradiation or the light with wavelengths ranging from 280 to 480 nm cannot excite the electrons from the VB to the CB it is the electrons of emission centre (Eu^{2+}) that is excited but not that of the host crystal [19,20]. The emission spectra were also broadband with peaks at 447 nm for $CaAl_2O_4:Eu^{2+}, Nd^{3+}$, at 507 nm for $SrAl_2O_4:Eu^{2+}, Nd^{3+}$ and at 497 nm for $BaAl_2O_4:Eu^{2+}, Nd^{3+}$ due to the $4f^65d^1-4f^7$ emission of Eu^{2+} . Sharp emission lines were observed at 612 and 652 nm for $CaAl_2O_4:Eu^{2+}, Nd^{3+}$, at 615 nm for $SrAl_2O_4:Eu^{2+}, Nd^{3+}$ and at 610 nm for $BaAl_2O_4:Eu^{2+}, Nd^{3+}$ arising from the f-f transitions of the Eu^{3+} ions. This could be attributed to the presence of residual unreduced Eu^{3+} ions resulting in simultaneous emissions from Eu^{2+} and Eu^{3+} [21].

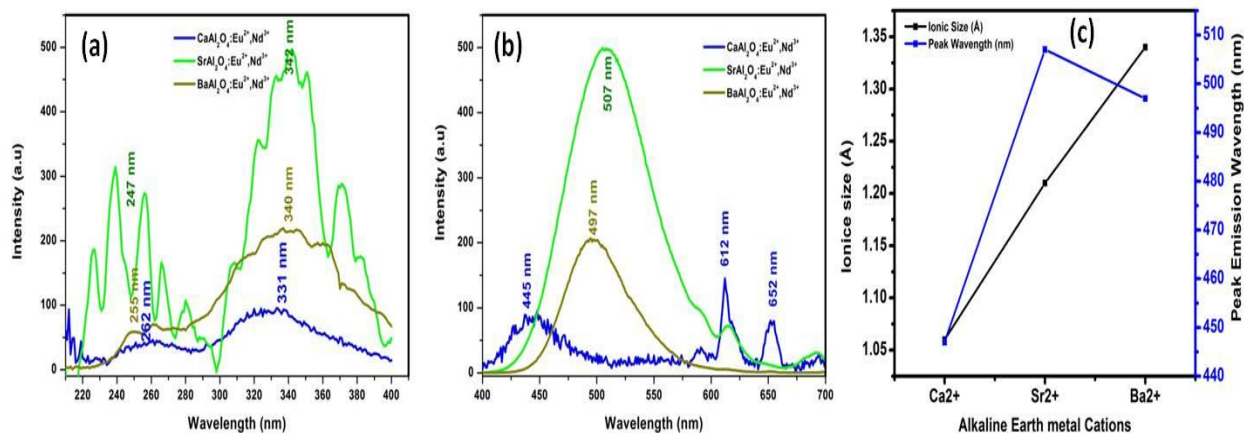


Fig. 3 (a) Excitation, (b) emission spectra of $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$ ($M = \text{Ca}, \text{Ba}, \text{Sr}$) phosphor powders respectively and (c) emission peak as a function of different ionic sizes.

Differences in emissions peak maxima from the phosphors was observed as presented in fig. 3(c) which arise from the crystal field splitting of the 5d electron shell due to the changes in the crystalline environment of the Eu^{2+} ions caused by the substitution of the divalent alkaline earth metal cations with different ionic sizes Ca^{2+} (1.06Å), Sr^{2+} (1.21Å) and Ba^{2+} (1.34Å), in the MA_2O_4 host lattice resulting a small shift of the emission maxima from 445 nm to 507 nm. It was reported that substitution of the substitution of Sr^{2+} ions by smaller Ca^{2+} ions in the SrAl_2O_4 lattice increases the covalency of Eu-O bond. This led to decrease in the energy splitting between the 5d levels of Eu^{2+} ions. On the other hand substitution of Sr^{2+} by Ba^{2+} ions reduces the covalency and the $4f^65d^1$ band is shifted to the lower energy side that led to the red shift in the emission maximum [22]. It was also observed that $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ had highest intensity followed by $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ phosphors and $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ in that order.

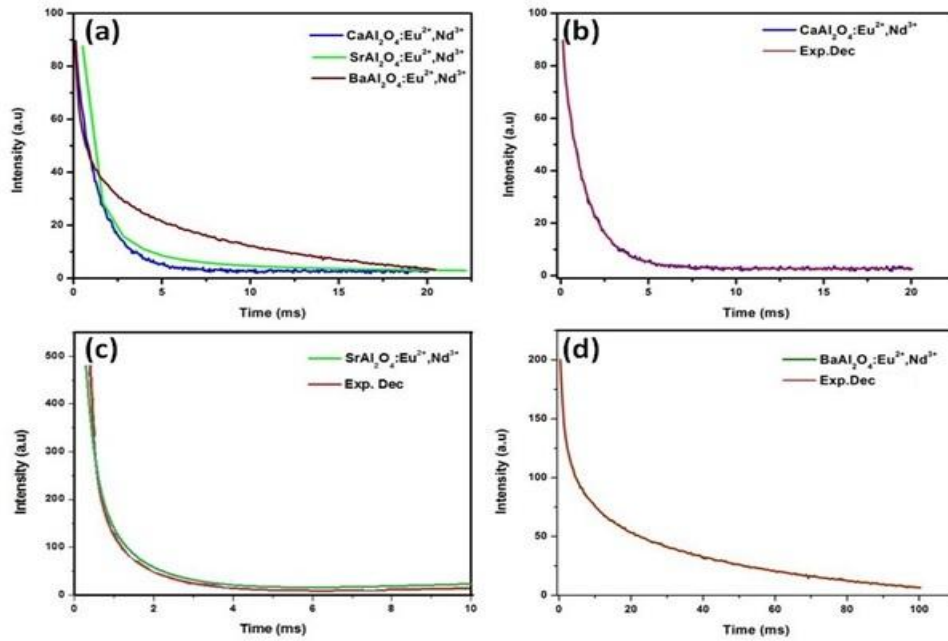


Fig. 4 (a) - (d). Experimental afterglow decay curves of $MA\text{Al}_2\text{O}_4:\text{Eu}^{2+}$ ($M = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors respectively.

The normalized PL decay lifetimes for the $MA\text{Al}_2\text{O}_4:\text{Eu}^{2+}$ ($M = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors are presented in fig. 4(a)-(d). The luminescence decay characteristics show that these materials show persistent luminescence. In this study $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ gave a longer afterglow as compared to the other two phosphors due to the presence of persistent luminescence [23].

The luminescent decay time for the transitions between the $4f-5d$ transition of Eu^{2+} ions levels is typically in the range of μs to ms which could be attributed to energy transfer process between traps and emission states resulting from Eu^{2+} and Nd^{3+} doping [16]. Although the decay process of luminescence is very complicated, it is certain that long decay times can be attributed to traps with different depths [16].

The Commission International de l'Eclairage (CIE) chromaticity co-ordinates of PL spectra and the U-VIS reflectance profiles of all the samples are shown in fig. 4(a) and (b) respectively. From fig. 4(a) it was observed that the CIE coordinates effectively represent the emission wavelength of each phosphor as confirmed by the PL emission spectra. Fig. 4(b) shows how absorption/reflectance is influenced by substitution of Ca^{2+} , Sr^{2+} and Ba^{2+} with different ionic sizes in the $MA\text{Al}_2\text{O}_4$ host structure. The absorption bands of the colour centers were found to be broad and peaked approximately at 330, 342 and 340 nm in the range between 200 nm and 800 nm corresponding with the PL excitation wavelengths of each sample as shown in fig. 3(a). The peaks in the red region; 565 - 760 represent f-f transition due to the possible presence of the unreduced Eu^{3+} ions [21].

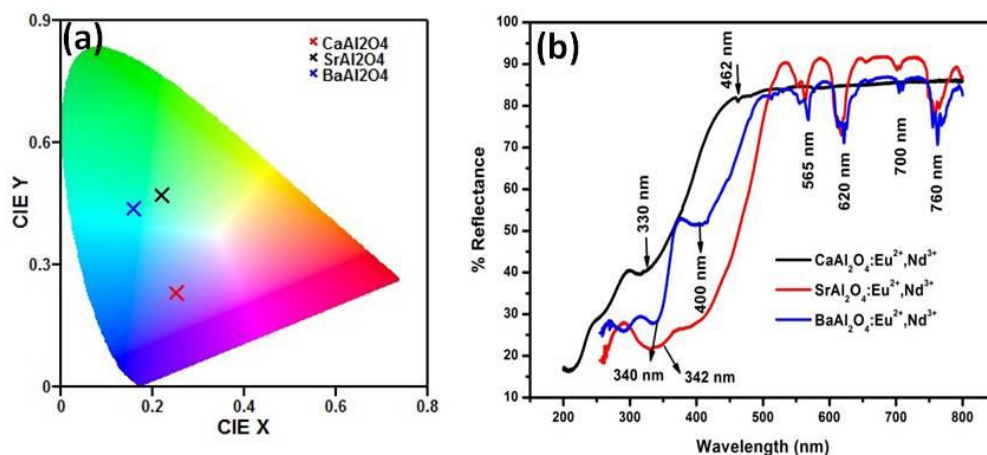


Fig. 4: (a) (CIE) chromaticity co-ordinates and (b) U-VIS reflectance spectra for $MAI_2O_4:Eu^{2+}$ (M = Ca, Ba, Sr) phosphors.

4. Conclusion

In this study $CaAl_2O_4:Eu^{2+};Nd^{3+}$, $BaAl_2O_4:Eu^{2+};Nd^{3+}$ and $SrAl_2O_4:Eu^{2+};Nd^{3+}$ phosphors were prepared using the solution-combustion technique. The effect of varied the effect of different alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of $MAI_2O_4:Eu^{2+}$ (M = Ca, Ba, Sr) phosphors were investigated. It was found that the PL excitation and emission were greatly influenced by the substitution of the metal cations in the host structure resulting in shifts if the peak PL maxima. This was attributed to the different ionic sizes of these metal cations causing lattice distortions of the host matrix and hence affecting the crystal field around the luminescent centre.

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