VUV investigation of blue emitting $\text{MAl}_{12}\text{O}_{19}$: Eu (M = Ca, Sr, Ba) phosphors synthesized by combustion method

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Abstract. Synthesis of europium doped alkaline earth aluminates $\text{MAl}_{12}\text{O}_{19}$ [M=Ca, Sr, Ba] by low temperatures (500ºC) solution combustion method. It corresponds to maintain the ratio of metal nitrate and urea solution mixtures. The characterization of Eu doped $\text{MAl}_{12}\text{O}_{19}$ [M=Ca, Sr, Ba] materials were done by X-ray diffraction, scanning electron microscope analysis and the optical properties were studied under 147 nm and 172 nm from synchrotron radiation excitation. The Eu-doped $\text{MAl}_{12}\text{O}_{19}$ phosphor shows broad and strong absorption in VUV region and exhibits intensive emission in blue region. The $\text{CaAl}_{12}\text{O}_{19}$: Eu$^{2+}$ shows strong blue emission band at 414 nm while in $\text{SrAl}_{12}\text{O}_{19}$:Eu$^{2+}$ two emission peaks are observed at about 395 nm and another around 418 nm. Both $\text{CaAl}_{12}\text{O}_{19}$: Eu$^{2+}$ and $\text{SrAl}_{12}\text{O}_{19}$:Eu$^{2+}$ display two very weak red emission bands at 592, 613 and 591, 613 nm respectively due to co-existence of Eu$^{3+}$. $\text{BaAl}_{12}\text{O}_{19}$: Eu$^{2+}$ phosphor shows emission around 440 nm in the blue region of the spectrum.

Keywords: $\text{MAl}_{12}\text{O}_{19}$: Eu$^{2+}$ (M=Ca, Sr, Ba); Combustion synthesis; VUV; Photoluminescence.

1. Introduction

The development of VUV radiation excited luminescence materials has attracted much attention with their potential industrial applications such as mercury-free fluorescent lamps, plasma display panels (PDPs) etc [1]. In these applications the luminescence materials are excited by the radiation lines of Xe atoms at 147 nm and a molecular Xe at 172 nm to emit visible luminescence, therefore high luminous efficiency; thermal stability, radiation resistivity and narrow size distribution are required for the luminescence materials [2]. Some oxide compounds with aluminate, borate and silicate groups have a strong absorption in the VUV region. Recently, compounds of the aluminate doped with rare earth ions family seem to be promising for high luminoscent efficiency and good thermal stability [3–7].

Alkaline-earth aluminate materials are one of the important luminescence materials are use in luminescent devices [8-10]. Recently, increasing attention is being paid to binary hexa-aluminate phosphors owing to their application in opto-electronics [11-13]. Hexa-aluminate based materials have also found application in the field of nuclear waste storage [14]. Further, porous hexa-aluminate ceramics...
are expected to be used as light structural components and catalyst carriers at high temperatures [15]. The phosphors with rare-earth doped alkaline-earth aluminates systems fall into three broad classes:

1. Binary alkaline earth aluminates such as SrAl₂O₄.
2. Alkaline earth hexa aluminates related to magnetoplumbite and beta-alumina and their superstructures.
3. Rare earth hexa aluminates with the magnetoplumbite structure.

With a variety of activators were used, the most important among them are Eu²⁺, Ce³⁺/Tb³⁺, and to a lesser extent, Mn²⁺ [9]. Eu²⁺ activated phosphors MAI₂O₄ and MAI₂O₁₉ (M = Sr, Ba, Ca, Mg) are well known since the studies by Blasse [16]. Their researches lead to the conclusion that these compounds were adequate phosphorescent materials because of their high quantum efficiency in the visible region. The binary hexa aluminates are compounds with the formula MAI₁₂O₁₉ where M = Ca and Sr have the magnetoplumbite structure [17,18]. But BaAl₁₂O₁₉ does not exist and instead there are two compounds, one deficient in barium and one with excess barium, that were shown to have the beta-alumina structure [19–21].

Various researchers have reported hexagonal alkaline earth aluminates (MAI₁₂O₁₉) doped by divalent europium as efficient photoluminescent materials with a blue emission which is characterized by high quantum efficiency under UV region [9,16, 22-24]. Literature reveals that very few report exist about photoluminescence studies of europium doped alkaline earth aluminates of MAI₁₂O₁₉ (M:Ca, Sr, Ba) type phosphors under Vacuum Ultra Violet (VUV) mainly at 147 and 172 nm excitation. Therefore, the massive photoluminescence potential in Eu doped MAI₁₂O₁₉ type alkaline earth aluminates is interesting to study the materials for VUV applications.

In this report, we have successfully employed a relatively low temperature, fast, simple and safe solvent combustion process for the preparation of Eu²⁺ doped MAI₂O₁₉ [M=Ca, Sr, Ba] phosphors. Also the main emphasis on VUV studies of the synthesized samples under 147/172 nm synchrotron radiation excitation. The prepared phosphor has been further characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

2. Experimental

2.1. Synthesis

The (Ca, Sr, Ba)₁₋ₓAl₁₂O₁₉:Euₓ (x = 5%) phosphor doped with Eu ions were prepared through a low temperature solution combustion synthesis. It is a simple, time saving and cost effective method [25]. The starting material were taken as aluminium nitrate [Al(NO₃)₃•9H₂O], alkaline earth metal nitrates like M(NO₃)₂ (M=Ca, Sr, Ba). Europium nitrate was prepared by dissolving europium oxide [Eu₂O₃] in nitric acid.

All the reagents were analytical purity and used without further purification. For a quick material screening, material elaboration was done following the flow chart given in Fig. 1. The correct amount of each excess urea [CO(NH₂)₂] were injected into the precursor solution or these compositions. The amount of metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. After stirring for about 15 min, precursor solution was transferred to a furnace preheated to 500°C. Initially, the solution underwent dehydration followed by decomposition with the evolution of large amounts of gases. The mixture then froths and swells forming foam, which ruptures with a flame and glows to incandescence. During incandescence the foam further swells to the capacity of the container. The entire combustion process completes within 5 min leading to the foamy porous products. The foamy and voluminous combustion product was easily crushed into powder using pestle and mortar. The prepared (Ca, Ba, Sr)₁₋ₓAl₁₂O₁₉:Euₓ⁺ samples were post-treated at 1000°C under a reducing atmosphere of activated carbon for 6h. The obtained white colored powdered products were used for further analysis.
2.2 Characterizations

The X-ray diffraction (XRD) pattern of host sample of MAI_{12}O_{19}: Eu (M=Ca, Sr, Ba) was recorded on Rigaku miniflex X-ray diffractometer with scan speed 2,000 deg/min and with Cu Kα radiation. The morphology of the phosphor particles was studied by using Hitachi model S-4800 type-2 field emission scanning electron microscope and elemental analysis by Bruker EDS. The VUV spectra were recorded at Department of Physics S.G.B. Amravati University, Amravati by using remote access mode of Beamline 4B8 in Beijing synchrotron radiation facilities (BSRF) under dedicated synchrotron mode (2.5 GeV, 150-60mA). A 1 m Seya monochromator (1200 g/mm, 120–350nm, 1 nm bandwidth) was used for the synchrotron radiation excitation spectra measurement, and an Acton SP-308 monochromator (600 g/mm, 330–900nm) was used for the emission spectra measurement. The signal was detected with a Hamamatsu H8259-01 photon counting unit. The vacuum in the sample chamber was about 1 × 10^{-5} mbar. The effect of the experimental set-up response on the relative VUV excitation intensities of the samples were corrected by dividing the measured excitation intensities of the samples with the excitation intensities of sodium salicylate (α-C_{6}H_{4}OHCOONa) measured simultaneously in the same excitation conditions. The region of excitation spectra was from 100 nm to 300 nm and the emission spectra recorded at 147 and 172 nm excitation.
3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction pattern (Fig. 2a, b, c) shows the Bragg diffraction peaks of europium-doped CaAl$_{12}$O$_{19}$, SrAl$_{12}$O$_{19}$ and BaAl$_{12}$O$_{19}$ phosphors synthesized by solution combustion synthesis. The XRD results indicated that the as synthesized products are highly pure, single-phase. The XRD peaks of doped and undoped CaAl$_{12}$O$_{19}$, SrAl$_{12}$O$_{19}$ and BaAl$_{12}$O$_{19}$ are similar since the level of impurity doping is low (5 mol%) in the CaAl$_{12}$O$_{19}$, SrAl$_{12}$O$_{19}$ and BaAl$_{12}$O$_{19}$ host lattice. The binary hexa aluminates (SrAl$_{12}$O$_{19}$ and CaAl$_{12}$O$_{19}$) have the magnetoplumbite structure [17, 18]. In comparison, the compound BaAl$_{12}$O$_{19}$ does not exist and instead there are two compounds, one with excess barium an done deficient in barium, and that were shown to have the beta alumina structure [19]. Both the samples of CaAl$_{12}$O$_{19}$, SrAl$_{12}$O$_{19}$ synthesized and post treated in reduced atmosphere exhibit almost identical XRD patterns corresponding to the pure hexagonal magnetoplumbite phase of CaAl$_{12}$O$_{19}$ and SrAl$_{12}$O$_{19}$ matching perfectly with the JCPDS Card No.26-976.

The XRD pattern for BaAl$_{12}$O$_{19}$ deviates from ideal magnetoplumbite pattern due to the presence of secondary phase as BaAl$_2$O$_4$ in BaAl$_{12}$O$_{19}$ system. The fact is reported in the literature [26, 27] that phase-pure BaAl$_{12}$O$_{19}$ does not exits always, except as a mixture of two distinct non stoichiometric phases, referred to as phase I and phase II by Kimura et al. [19]. More recently, Wang and et al. [28] reported presence of secondary phase as BaAl$_2$O$_4$ in BaAl$_{12}$O$_{19}$ system. It is observed that even after calcination at 1000°C under reduced atmosphere along with the dominate diffraction peaks due to the hexagonal BaAl$_{12}$O$_{19}$ (JCPDS, File-26-0135) phases, in addition the sample demonstrate weak reflex ion lines belonging to BaAl$_2$O$_4$ phase. XRD pattern for our sample of BaAl$_{12}$O$_{19}$ is similar to obtained by other authors matching perfectly with the JCPDS, File-26-0135.

![Fig.2. Powder XRD pattern of MAl$_{12}$O$_{19}$:Eu](image-url)
3.2. Scanning electron microscopy

**Fig. 3**, displays an SEM micrograph of a europium doped MAI$_{12}$O$_{19}$ powder prepared by combustion method and post treated at 1000°C under reduced atmosphere. Fig 3a, b and c represent SEM micrograph of CaAl$_{12}$O$_{19}$:Eu, SrAl$_{12}$O$_{19}$:Eu and BaAl$_{12}$O$_{19}$:Eu respectively. Almost all the three materials display highly agglomerated foamy and porous surface morphology with average particle size in between 5–10 μm. These types of features are inherent in combustion derived powder and are formed due to large number of escaping gases during combustion. The morphology of the prepared (Fig. 3a–c) powder also displays faceted plates of varying sizes and shapes. This irregularity in sizes and shapes is caused by the non-uniform distribution of temperature and mass flow during combustion [23].

![SEM Images of a. CaAl$_{12}$O$_{19}$:Eu, b. SrAl$_{12}$O$_{19}$:Eu and c. BaAl$_{12}$O$_{19}$:Eu Phosphors](image)

3.3. Photoluminescence studies

Europium ions can be stabilized in host lattice in either divalent or trivalent oxidation state. The incorporation and stabilization of Eu ions in the sample were confirmed by the luminescence investigations. The photoluminescence excitation, emission spectra for the M$_{1-x}$Al$_{12}$O$_{19}$: Eu$_x$ (M = Ca, Sr, Ba) (x = 5 mol %) phosphors post treated under reduced atmosphere are studied at 147 and 172 nm excitation shown in **Fig. 4 a-c**. The VUV spectrum of the CaAl$_{12}$O$_{19}$: Eu (5 mol %) sample for excitation at 147 and 172 nm is shown in **Fig. 4a**. The emission spectrum reveals one strong band at 414 nm and two very weak bands at 592 and 613 nm. Similarly for SrAl$_{12}$O$_{19}$: Eu (5 mol %). In **Fig.4b**, two emission peaks were recognized one with low intensity at 395 nm and other with slightly higher intensity at 418 nm and two very weak bands at 591 and 613 nm.
Fig. 4. Excitation and emission spectra of MAl$_{12}$O$_{19}$:Eu (M=Ca, Sr, Ba) phosphor at 172 and 147 nm.

The intense excitation observed in the VUV region is associated with 4f→5d electronic transitions. The excitation bands at 172 nm are due to the 4f$^7$ ($^8$S$_{7/2}$)→4f$^6$ 5d transitions. The emission bands almost of same intensity which is characteristic of Eu$^{3+}$ ions are also present in CaAl$_{12}$O$_{19}$: Eu and SrAl$_{12}$O$_{19}$: Eu samples. The excitation and emission spectra of BaAl$_{12}$O$_{19}$: Eu as-prepared phosphor are shown in Fig. 4c. The broad excitation spectral band is observed at 172 nm. On excitation at 147 and 172 nm the emission spectrum exhibits a well defined asymmetric band with maximum at 440 nm emitting a blue light. Further, it is interesting to note that when all the prepared samples were exited at 172 and 147 nm the emission spectrums are recorded at same wavelengths as discussed earlier but there is difference in intensity of emitted spectrum. The intensity of the emission band is excited by 172 nm is 60% more than those excited by 147 nm and this trend is repeated in all the MAl$_{12}$O$_{19}$: Eu (M = Ca, Sr, Ba) samples synthesized. Fig. 4 a - c shows the relative emission intensity of CaAl$_{12}$O$_{19}$: Eu, SrAl$_{12}$O$_{19}$: Eu and BaAl$_{12}$O$_{19}$: Eu phosphors as a function of Eu doping concentration respectively. All the MAl$_{12}$O$_{19}$: Eu (M = Ca, Sr, Ba) phosphors were annealed at 1000°C reduced atmosphere and the emission spectra were obtained at room temperature under 147 and 172 nm excitation. Vijay Singh et al. have earlier reported the similar Eu$^{2+}$ emission band at about 413 nm and very low intensity Eu$^{3+}$ emission band about at 591 and 614 nm in CaAl$_{12}$O$_{19}$ phosphor [29].
4. Conclusions

Based on the results presented above, the following conclusions may be highlighted:

1. The present VUV investigation on europium-doped MAI$_{12}$O$_{19}$(M=Ca, Sr, Ba) phosphor prepared via a combustion method indicates that europium ions are present both in divalent as well as trivalent oxidation state in the CaAl$_{12}$O$_{19}$:Eu and SrAl$_{12}$O$_{19}$:Eu samples.

2. The Eu-doped MAI$_{12}$O$_{19}$ phosphor shows broad and strong absorption in VUV region and exhibits intensive emission in blue region. The CaAl$_{12}$O$_{19}$: Eu$^{2+}$ shows strong blue emission band at 413 nm while in SrAl$_{12}$O$_{19}$: Eu$^{2+}$ two emission peaks are observed at about 389 nm and another around 420 nm. Both CaAl$_{12}$O$_{19}$: Eu$^{2+}$ and SrAl$_{12}$O$_{19}$: Eu$^{2+}$ display two very weak red emission bands at 592, 613 and 591, 613 nm respectively due to co-existence of Eu$^{3+}$ and BaAl$_{12}$O$_{19}$: Eu$^{2+}$ phosphor shows emission around 460 nm in the blue region of the spectrum.

3. Our work shows that the solution combustion synthesis technique is reliable and can be successfully used to produce pure, crystalline calcium aluminates, with good compositional control of the powders produced. The major advantages of the combustion process are it is easy to synthesise, fast and low cost method.

4. The emission spectra for 172 nm excitation are 3 times superior to 147 nm excitation. These results shows that the MAI$_{12}$O$_{19}$: Eu (M = Ca, Ba, Sr) phosphor exhibit potential application in the VUV region.

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