Photoluminescence Properties of Eu\(^{3+}\) doped KAl(SO\(_4\))\(_2\) Phosphor

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Abstract. A series of KAl(SO\(_4\))\(_2\) phosphors with different Eu\(^{3+}\) doping concentrations have been synthesized by solid-state reaction method. In the present work, the properties of synthesized Eu\(^{3+}\) doped KAl(SO\(_4\))\(_2\) phosphors have been examined by XRD, Photoluminescence (PL), and photometric characterization techniques. Under Near Ultraviolet (NUV) and blue excitation at 395nm and 466nm, PL emission spectra observed at 593nm and 614nm, which are ascribed due to "\(^{5}D_0\rightarrow^{7}F_1\)" and "\(^{5}D_0\rightarrow^{7}F_2\)" transition of Eu\(^{3+}\) ions. The emission band of 614 nm indicates the highest emission intensity compared to the 593 nm emission band. The PL emission spectra depict maximum intensity at 0.7mol% doping of Eu\(^{3+}\) ions. In addition, the synthesized Eu\(^{3+}\) activated KAl(SO\(_4\))\(_2\) phosphors show good color chromaticity coordinates, which is lies in the orange-red region. All these results indicated that the synthesized Eu\(^{3+}\) activated KAl(SO\(_4\))\(_2\) phosphors have potential results for future work in the field of solid state lighting.

Keywords: Solid-state reaction method; Photoluminescence; Photometric characterization; Solid-state Lighting

1. Introduction

In the current scenario, energy plays an important role in the development of any country. Since the beginning of the digitization age, the capacity to harness and utilize various types of energy has changed everyday environments for billions of people, empowering them to appreciate a degree of solace and portability that is remarkable in mankind's history, and liberated them to perform progressively gainful assignments. The consistent development in energy utilization has been intently attached to rising degrees of thriving and economic opportunity in a great part of the world. However, humankind presently winds up going up against a huge energy challenge. This opportunity has at least two basic measurements. It has become evident that present examples of energy utilize are naturally impractical. In the current scenario, White LEDs are novel lighting technology in the field of luminescence devices, it has played an important role in applications of indicator, backlight, automobile headlight and general illumination [1, 2]. In the recent few years, White LEDs revealed marvelous advantages such as low cost, high electro-optical conversion efficiency, stability and reliability, high luminous efficiency, long lifetime, and eco-friendly properties [2–6]. According to the literature, light-emitting diodes (LEDs) have gained much popularity. The effective properties of LEDs will have an important role in lighting in the near future. These will prove to be more
effective than other lighting devices [7, 8]. According to the literature, it is well known that WLEDS can be fabricated by two methods. The first method is based on LED chips and the second method is based on the combination of chips and phosphors [5]. At present, phosphor several approaches are available for generation of White light, (i) By excited yellow-emitting phosphors with blue-emitting diodes (ii) By mixing Red, Green, and Blue LEDs, and (iii) Red, Green, and Blue (RGB) phosphors can be excited by using near ultraviolet (NUV) LED chip [9–11]. Currently used commercial W-LEDs is the combination of Ce3+ activated yttrium aluminum garnet (YAG:Ce3+) with 460 nm blue InGaN LED chip [9, 12]. As per previous studies, this method has some critical problems, which reduce the quality of light such as reduction in red color, high correlated color temperature (CCT), low color rendering index, etc [9, 12]. So, this needs to be advocated that we can search some new materials for LED lighting, in the current scenario, we can use herbal material for LEDs lighting because it has some advantages such as low cost, chemical free, easily available, low cost etc. In the present time, phosphor-converted LEDs widely used it has various advantages. Phosphors with optimized luminescence properties are coveted by industry and the subject of very active development. Indeed, available blue-to-red phosphors exhibit a too wide emission line width or some other drawbacks, such as strong thermal quenching behavior.

Till date, various host materials have been studied such as phosphate, sulfate, molybdate, vanadate, borate, titanate, etc. According to the literature, sulfates are known to be good host materials, exhibiting amazing physical and chemical properties, thermally stable and good electrical performance, low cost, environmentally friendly properties. In recent years, many sulfate-based phosphor materials are investigated and reported such as Ca2.85Li0.15(PO4)1.85(SO4)0.15: Dy3+,Sm3+ [13], K3Ca2(SO4)2F [14], CaNa2(SO4)2 [15], K2Ca2(SO4)3 [16], Na2Pb2(SO4)3Cl [17]. Lanthanide-doped materials are good candidates in the study of photoluminescence, they have proved their ability in the previous years. As per previous studies, SSR approach is generally used for sulphate based phosphor. In this method, the starting materials are used in solid form. SSR approach has various advantages such as inexpensive, easy controlling, simple, and it leads to acceptable results. However, they also have major drawbacks such as high temperature, long time route, multiphase character, non-uniformity of particle size and shape, formation of toxic waste products. In the current study, europium ions have been used as activators. In recent years, the europium ions have developed its image as a promising rare-earth ions in white light production in the research society. As it is known that the europium ions exist two sites Eu2+ and Eu3+. When it exists Eu3+ site, then it emits Orange-red light and when it exists Eu2+ site, then it emits blue green light. In this work, Eu ions exist Eu3+ state with doping of KAl(SO4)2 host material. As per our best knowledge, photoluminescence properties of Eu3+ activated KAl(SO4)2 phosphor never reported by solid-state reaction method.

In the current work, undoped and Eu3+ activated KAl(SO4)2 phosphors have been successfully synthesized by the solid-state reaction (SSR) method and characterized by XRD, PL technique. Photoluminescence properties demonstrated that emission of light in the orange-red region.

2. Experimental
Preparation of material

Undoped KAl(SO4)2 and Eu3+ activated KAl(SO4)2 samples were synthesized by solid-state reaction method. All the required samples have been taken in AR / ACS grade with 99.9% purity. Potassium Carbonate (K2CO3), Aluminum Oxide (Al2O3), Ammonium Sulphate (NH4)2SO4 and Europium (Eu) precursors are used as starting materials during the synthesis. All the starting materials were taken in fixed proportions and crushed properly by a mortar pestle and converted into powder. The obtained powder was transferred to the crucible and placed in a furnace for heating at a temperature of 700 °C. After 24 hours, turn off the furnace and leave it to cool. The obtained samples were again crushed after cooling to room temperature. These prepared samples yield into white crystalline powder is then used for the further characterizations. Chemical reaction takes place during synthesis of proposed phosphor is as given below;
Here, table 1 shows list of starting materials with suppliers’ name and purity %, and table 2 shows stoichiometric ratio of starting materials.

\[
\frac{1}{2} \text{K}_2\text{CO}_3 + \frac{1}{2} \text{Al}_2\text{O}_3 + 2(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{KAl(SO}_4)_2 + \frac{1}{2} \text{CO}_2 \uparrow + 4 \text{NH}_3 \uparrow + (\text{H}_2\text{O})_2 \uparrow
\]

Table 1. List of starting materials with suppliers’ name and purity %.

| Sr. No. | Chemical name with Formula | Molecular Weight | Supplier | Purity % |
|---------|----------------------------|------------------|----------|----------|
| 1.      | Potassium Carbonate (K$_2$CO$_3$) | 138.21           | Lobachemie, CAS No: 584-08-7 | 99%      |
| 2.      | Aluminium oxide (Al$_2$O$_3$)    | 101.94           | Lobachemie, CAS No: 1344-28-1 | 99%      |
| 3.      | Ammonium sulphate (NH$_4$)$_2$SO$_4$ | 132.14         | Lobachemie, CAS No: 7783-20-2 | 98.5%    |
| 4.      | Europium oxide (Eu$_2$O$_3$)     | 352              | Lobachemie, CAS No: 1308-96-9 | 99.9%    |

Table 2. The amount of reagents added in the synthesis methods.

| Concentration of Eu$^{3+}$ | K$_2$CO$_3$ (gm) | Al$_2$O$_3$ (gm) | (NH$_4$)$_2$SO$_4$ | Eu$_2$O$_3$ (gm) |
|---------------------------|------------------|------------------|-------------------|------------------|
| 0 mol%                    | 3gm              | 1.1065gm         | 1.43gm            | 0gm              |
| 0.1 mol%                  | 3gm              | 1.105gm          | 1.43gm            | 0.0038gm         |
| 0.2 mol%                  | 3gm              | 1.104gm          | 1.43gm            | 0.0764gm         |
| 0.5 mol%                  | 3gm              | 1.101gm          | 1.43gm            | 0.0191gm         |
| 0.7 mol%                  | 3gm              | 1.098gm          | 1.43gm            | 0.02674gm        |
| 1.0 mol%                  | 3gm              | 1.095gm          | 1.43gm            | 0.0382gm         |

3. Results and Discussion

3.1 XRD Measurement

Figure 1 shows the XRD pattern of synthesized Eu$^{3+}$ activated KAl(SO$_4$)$_2$ phosphor. As clearly seen from the figure, the XRD pattern of synthesized material is well-matched with the standard XRD pattern of the host. Some impurity peaks can also be observed which may be possible due to the presence of Eu$^{3+}$ ions and other impurities. In addition, figure 1 depicts sharp XRD peaks which are indicated that the homogeneous and crystalline nature of the synthesized phosphor.
3.2 Photoluminescence Properties

Figure 2 demonstrates PL excitation spectra of KAl(SO₄)₂:0.7mol%Eu³⁺ phosphor monitored at 614nm emission. As can be seen in this figure, the PL excitation spectra present three sharp excitation bands at about 395 nm, 409nm, and 466nm, which are ascribed due to ⁷F₀→⁵L₆, ⁷F₀→⁵D₁ and ⁷F₀→⁵D₂, transition of Eu³⁺ ions [18]. But here the 395nm and 466nm excitation band are dominant peaks which are indicated that these bands are matched with near-UV chip and blue LED chip. These results indicated that synthesized phosphors are a potential candidate for WLED in the near future.

**Figure 1.** XRD pattern of synthesized Eu³⁺ activated KAl(SO₄)₂ phosphor

**Figure 2.** PL Excitation spectra of Eu³⁺ activated KAl(SO₄)₂ phosphor under 614nm emission wavelength

Further, PL emission spectrum of KAl(SO₄)₂ phosphor was observed with the variation of Eu³⁺ ions under 395nm and 466 nm excitation wavelength. Both emission band examined in the range of 550nm to 650nm as shown in figure 3 (a) and (b). The PL emission spectra of all samples exhibited two emission
peaks around 593nm and 614nm, which can be attributed to the transitions of $^3\text{D}_0 \rightarrow ^7\text{F}_0$ and $^3\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu$^{3+}$ ions [19, 20]. As can clearly be seen from the figure, the nature of the spectrum is the same for both excitation wavelengths. It has also been demonstrated that the PL emission peaks have the same nature for each concentration of Eu$^{3+}$ ions. The variation in PL intensity of the synthesized samples was observed due to the variation of concentrations in Eu$^{3+}$ ions. It is very clear that PL intensity increases with increasing the concentration of Eu$^{3+}$ ions up to 0.7mol%, beyond 0.7mol% concentration of Eu$^{3+}$ ion, PL emission intensity reduced because of concentration quenching mechanism[18]. Apart from this, the dominant peak of the spectrum has been observed at around 614nm. To obtain white light, the synthesized KAl(SO$_4$)$_2$ orange-red emitting phosphor can be combined with blue, green phosphors, and excited by a near-UV LED chip.

![Figure 3. PL Emission spectra of Eu$^{3+}$ activated KAl(SO$_4$)$_2$ phosphor monitored at (a) 395nm and (b) 466 nm excitation wavelength](image)

### 3.3 Photometric Characterization

As per previous studies, the color characteristics of light can be described by basic parameters which are known as Commission International de l’Eclairage (CIE) chromaticity coordinates[21]. The color coordinate is the key factor for practical lighting applications [22]. Figure 4 shows the CIE Chromaticity coordinate of synthesized KAl(SO$_4$)$_2$:0.7mol% Eu$^{3+}$ phosphor monitored under 395nm and 466nm excitation. The calculated coordinate of CIE is found to be (0.5675, 0.4316) and (0.6354, 0.3642) which are analyzed at 395nm and 466 nm excitation, respectively. These coordinates are located very close to the bottom of the red region. It is clear from the result that the synthesized red emitting KAl(SO$_4$)$_2$: Eu$^{3+}$ phosphors combine with green and blue phosphor can aid the development of WLEDs.
4. Conclusion

Novel KAl(SO₄)₂:Eu³⁺ phosphors were successfully synthesized by the solid-state reaction method. In this work, the synthesized samples were characterized by XRD and PL techniques. The XRD result shows that the prepared samples are crystalline and homogeneous. The PL excitation spectrum shows two excitation bands around 395nm and 466nm, which are ascribed due to ⁷F₀→⁵L₆, and ⁷F₀→⁵D₂ transition of Eu³⁺ ions. Under 395nm and 466nm excitation, PL emission spectra exhibit two emission bands at around 593nm and 614nm. Further, CIE chromaticity coordinates confirmed that KAl(SO₄)₂:Eu³⁺ phosphors exhibits orange red emission. All these results indicated that KAl(SO₄)₂:Eu³⁺ phosphors may be excellent host material for future study in the field of solid-state lighting.

5. Reference

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