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Luminescence and EPR investigations of Mn activated calcium aluminate prepared via combustion method

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Abstract

Luminescence investigations of Mn-activated calcium aluminate phosphors prepared using the combustion method are described. An efficient phosphor can be prepared by this method at reaction temperatures as low as 500 °C in a few minutes without the need for any further calcination. The phosphor has been characterized by powder X-ray diffraction, scanning electron microscope. Optical properties were studied by photoluminescence spectra. Photoluminescence studies of the prepared phosphors showed prominent red emission from Mn^{4+} ions, while EPR investigations indicated the presence of Mn^{2+} as well as Mn^{4+} ions in the prepared phosphors. EPR spectra of the phosphor samples suggest that Mn ions occupy distorted lattice sites in the phosphors.
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Keywords: Doping; Photoluminescence; EPR; Phosphors; Combustion

1. Introduction

The demand for economically viable phosphors for newly emerging display devices is increasing with on-going technological advancements. Major applications of the phosphors are in fluorescent lamps and emission display devices such as electroluminescence panels (EL), plasma display panels (PDP), field emission displays (FED) and so on [1,2]. This has revived interest in the research on new methods of phosphor synthesis in recent years. Mn^{2+} luminescence can be useful in obtaining a low cost green or red emitting phosphor. In recent years, a number of publications related to the synthesis and properties of Mn^{2+} doped aluminates as well as other host materials have appeared. For example, Mn^{2+} emission has been studied in $BaAl_{12}O_{19}$ [3,4], $SrAl_{12}O_{19}$ [5], $(Ce,Tb)MgAl_{11}O_{19}$ [6], $CaAl_2O_4$ [7], $Ca_2Al_2SiO_7$ [7], $MgSiO_3$ [7], $LaMgB_5O_{10}$ [8], Zn_2SiO_4 [9], ZnS [10,11], ZnSe [12], CdS [13], $ZnGa_2O_4$ [14] etc. A relatively new phosphor, $Sr_3Gd_2Si_6O_{18}$:Pb, Mn [15], relies on strong Pb^{2+} absorption which leads to efficient energy transfer to Mn^{2+} ions and strong green emission of the latter, for use as a green component of a tricolour lamp phosphor.

Alkaline earth aluminates used as luminescent materials or in cements have been studied already for decades [16–18]. They have been prepared traditionally by solid state reactions [18–21]. However these routes demand usually high annealing temperatures for long duration, ca. 1300 °C and 5–10 h, respectively. Also, the products can be strongly sintered and the doping luminescent ions may not be homogeneously dispersed. Alternatively low temperature combustion method can be used instead of the direct solid state reaction, due to economical interest and to enhance the properties of materials. Currently, rare earth doped aluminate phosphors are of special interest, since they show long phosphorescence and a short-time decay depending on the differing conditions of preparation used [21,22].

However, there are very few reports on (a) the luminescence and EPR of phosphors doped with non-rare earth

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elements such as Mn doped calcium aluminate phosphors and also (b) calcium aluminates prepared by low temperature combustion methods. In view of these, Mn doped aluminate phosphors were prepared in our study via combustion process, and investigated using XRD, SEM, PL and EPR in order to identify the compounds formed and understand the role of Mn ions in their fluorescence properties.

2. Experimental

The stoichiometry of the redox mixtures used for combustion was calculated using the total oxidizing (O) and reduction (F) valencies of the components. These serve as the numerical coefficients for the stoichiometric balance so as to make the equivalence ratio ϕe (i.e. O/F = 1) unity and thereby maximize the released energy during combustion [23].

In the present investigation, materials were prepared according to the chemical formula $Ca_{0.98}Al_{12}O_{19}:Mn_{0.02}$. All the reagents were of analytical purity, and were used without further purification. The details of synthesis are reported elsewhere [24–27]. Briefly, 5 g $Al(NO_3)_3 \cdot 9H_2O$, 0.2570 g $Ca(NO_3)_2 \cdot 4H_2O$, 2.1127 g CH_4N_2O and 0.0043 g $MnCl_2$ were mixed in an agate mortar and the resulting paste was transferred into a china crucible. The crucible containing the paste was introduced into a muffle furnace maintained at 500 °C. Initially, the paste melts and undergoes dehydration followed by decomposition with the evolution of large amounts of gases (oxides of nitrogen and ammonia). The mixture then froths and swells forming foam, which then ruptures with a flame and glows to incandescence. This process lasted for about 5 min and resulted in voluminous and foamy powder. The voluminous powder was crushed into powder using pestle and mortar and was used for characterization.

Philips X' pert (Eindhoven, The Netherlands) X-ray diffractometer employing a Cu Kα radiation ($\lambda = 0.15418$ nm) was used in the 2Θ range of 10°–80° and scan rate of 4°/min, to identify the phases of the products. Powder morphology was evaluated using a Scanning Electron Microscope (SEM) (JSM-5610LV, Jeol, Japan). PL measurements were carried out using an AMINCO-Bowman Series 2 luminescence spectrometer at room temperature and also performed with a confocal laser micro-Raman spectrometer (Raman, LABRAM-HR) with 488 nm laser excitation. EPR measurements were carried out using a Bruker EMX 10/12 X-band EPR spectrometer.

3. Results and discussions

X-ray diffraction pattern of the as-prepared $CaAl_{12}O_{19}:Mn$ is shown in Fig. 1. The diffraction peaks correspond to all the planes which can be indexed to the pure hexagonal phase for $CaAl_{12}O_{19}$. The XRD pattern matched perfectly with the JCPDS (07-0085) of $CaAl_{12}O_{19}$. No peak of any other phase was detected.

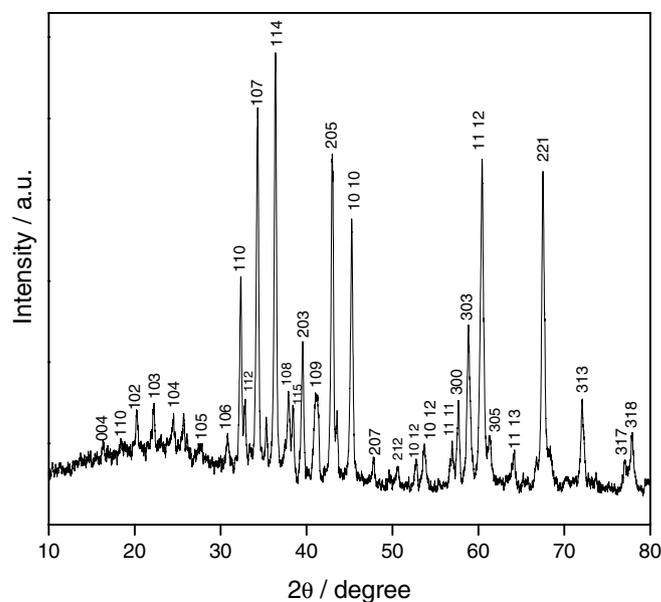Fig. 1. X-ray powder diffraction patterns of $CaAl_{12}O_{19}:Mn$.

The micrograph of as prepared $CaAl_{12}O_{19}:Mn$ and its surface is shown in Fig. 2. It is clear from this SEM picture that the calcium hexa-aluminate phosphor formed by the combustion process has platelet particles. All samples contained foamy agglomerated particles with a wide distribution (low-magnification) and most of the hexa-aluminates took the form of hexagonal platelets with rough surface in their structure (high-magnification). The morphology of the powders reflects the inherent nature of the combustion process.

Manganese ions can be stabilized in host lattice in divalent, trivalent or tetravalent oxidation state. The incorporation and stabilization of Mn ions in the sample were confirmed by the luminescence investigations. The photoluminescence spectrum of the sample excited at 467 nm is shown in Fig. 3. The emission spectrum reveals peaks at 643, 656 and 667 nm which are due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+} ions. These emission peaks positions are similar as reported [28] wherein the phosphors were synthesized using a conventional solid state reaction at 1923 K, 3 h in air. However, our combustion process involves temperatures as low as 500 °C and completes within few minutes and therefore, is economical. The excitation spectra corresponding to these peaks are also shown in Fig. 3. In this sample, broad excitation peaks were observed at 348, 398 and 467 nm. The details of these spectral profiles are similar to the previous reports [28–34].

The emission from Mn^{2+} ions expected in the region, 500–570 nm, is either absent or very weak in the prepared phosphor. Therefore in order to confirm the possibility of Mn^{2+} emission in the present system, PL of the sample was recorded with 488 nm laser excitation wavelength, wherein very weak emission around 517 nm, attributable to Mn^{2+} ions could be observed. The emission band peak at 517 nm is typical emission of Mn^{2+}, which is due to

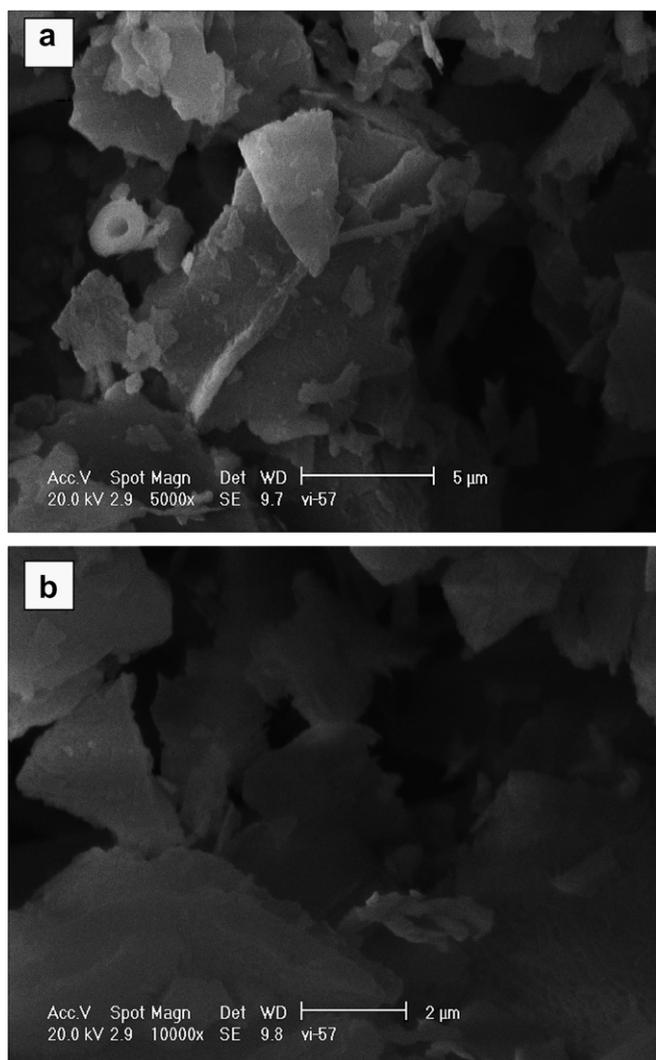Fig. 2. SEM micrographs of the $CaAl_{12}O_{19}$:Mn (a) low-magnification (5000×) and (b) high-magnification (1000×).

Fig. 3. Typical photoluminescence spectra of Mn doped $CaAl_{12}O_{19}$: (a) excitation spectra of $Ca_{0.98}Mn_{0.02}Al_{12}O_{19}$, ($\lambda_{em}$ = 656 nm), (b) emission spectra of $Ca_{0.98}Mn_{0.02}Al_{12}O_{19}$, ($\lambda_{ex}$ = 467 nm) and the inset is emission spectra with 488 nm laser excitation wavelength.

Fig. 4. EPR spectra of $CaAl_{12}O_{19}$:Mn.

the $^4T_1$ (^4G) → $^6A_1$ (^6S) transition of Mn^{2+}. Bo et al. [29] also have observed Mn^{2+} emission at 517 nm, in $SrAl_{12}O_{19}$ doped with Mn^{2+} ions, for excitation at 386 nm. The inset in Fig. 3 shows the spectrum recorded on $CaAl_{12}O_{19}$:Mn, indicating the presence of weak green emission, which corresponds to the Mn^{2+} ions. This may be due to high intensity of laser beam excitation, since using Xenon lamp, this emission could not be observed. In view of the different excitation characteristics of Mn^{2+} and Mn^{4+} ions, it is not possible to get exact idea about the ratio of these ions in the samples. However the intensity of the emission peaks definitely suggests that Mn^{4+} ions are dominant in the prepared samples.

Electron Paramagnetic Resonance spectra of Mn^{2+} doped calcium aluminates were recorded at room temperature. Fig. 4 shows the EPR spectrum of Mn^{2+} doped $CaAl_{12}O_{19}$. Mn^{2+} ion has d^5 electronic configuration. Generally the EPR of this ion is expected to show a signal around $g = 2.0$ in case of cubic symmetry, which is further split into six hyperfine lines due to interaction of the
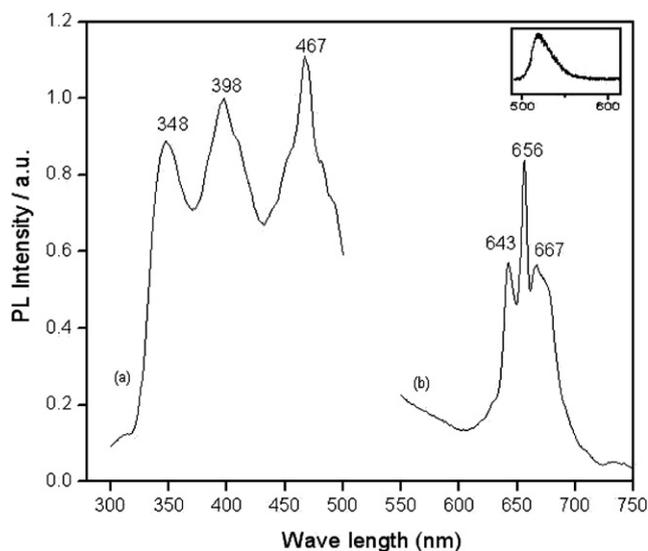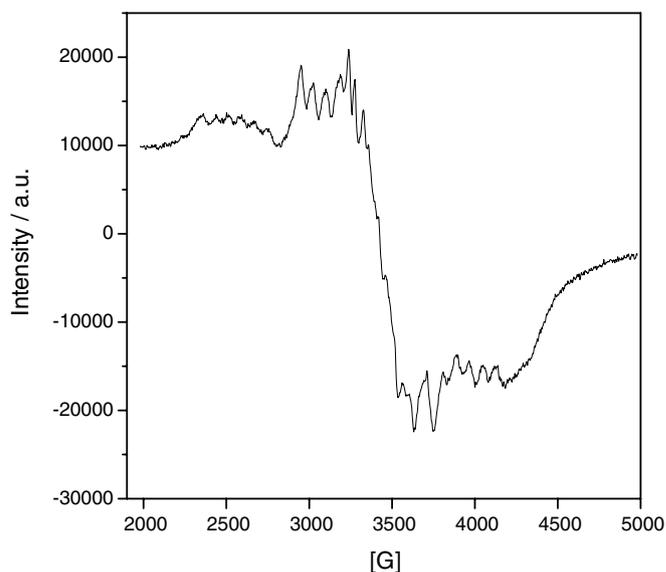
unpaired electron with ^{55}Mn nucleus having spin value, 5/2. For lower symmetries of Mn^{2+} ion, fine structure transitions between the crystal field split levels, corresponding to 5/2 ↔ 3/2, 3/2 ↔ 1/2, 1/2 ↔ −1/2, −1/2 ↔ −3/2 and −3/2 ↔ −5/2, can be observed. However due to large anisotropy, only a broad central signal (with its six hyperfine components), corresponding to 1/2 ↔ −1/2 is only observed generally [35] and the other transitions are usually not resolved due to a large anisotropy. In the case of $CaAl_{12}O_{19}$, the spectrum recorded between 2900–4200 G shows one broad central line with sextet hyperfine splitting, around 3420 G. As seen from Fig. 4, there are two sets of sextet lines in the field region, 2500–3400 G. Similarly
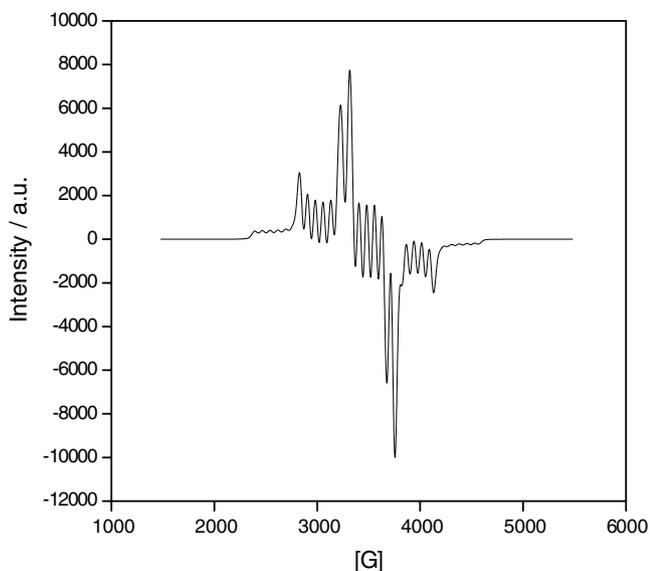
Fig. 5. Simulated EPR spectrum for Mn^{4+} ions in $CaAl_{12}O_{19}$:Mn.

another set of sextet can be observed around 3900 G. These lines are assigned to Mn^{4+} ions occupying axially symmetric lattice sites. Mn^{4+} ion has 3 d^3 electronic configuration with $S = 3/2$. The EPR fine structure of this ion should contain lines from $3/2 \leftrightarrow 1/2$, $1/2 \leftrightarrow -1/2$ and $-1/2 \leftrightarrow -3/2$. The relatively weaker sextet around 2650 G corresponds to the parallel components of $3/2 \leftrightarrow 1/2$ transition of Mn^{4+} ion, while the sextet lines around $G = 3200$ G, are the corresponding perpendicular components. The sextet lines centered around 3900 G are attributed to perpendicular components of $-1/2 \leftrightarrow -3/2$ transition, while the corresponding parallel features are very weak and buried in the broad line around 4200 G. As far as the lines corresponding to $1/2 \leftrightarrow -1/2$ transition of Mn^{4+} ion are concerned, they are buried in the relatively more intense and broad central line around 3420 G, attributed to Mn^{2+} ions. The hyperfine coupling corresponding to Mn^{2+} is about 90 G, while that corresponding to Mn^{4+} ions is about 80 G. A simulated EPR spectrum of Mn^{4+} ions using $g = 2.002$, $A = 80$ G, $D = 450$ G and $E = 0$, is given in Fig. 5. It can be seen that the features are in reasonable agreement with the experimental spectrum. All these observations indicate Mn^{2+} and Mn^{4+} ions are axially distorted in $CaAl_{12}O_{19}$. It is not possible to get an idea about the ratio of Mn^{2+} to Mn^{4+} ions in the prepared samples. Being S state ions, Mn^{2+} ions are more sensitive and easily amenable to detection by EPR technique, even in trace quantities. In view of the clear signature of Mn^{4+} ions in the observed EPR spectra, it is presumed that most of the Mn ions exist as Mn^{4+} ions.

4. Conclusions

Our experiments reveal that Mn ions are stabilized both as Mn^{2+} and Mn^{4+} ions in $CaAl_{12}O_4$ crystal lattice. Further the present results, though preliminary in nature, sug-

gest that Mn^{4+} doped $CaAl_{12}O_{19}$ phosphors have the potential to be used as red emitting phosphors for ultra violet/blue light emitting diodes. EPR investigations reveal that the doped Mn ions occupy distorted lattice sites in these aluminates. Using combustion synthesis method, these phosphors could be prepared within several minutes. This might be useful in lowering the cost of the phosphor.

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