A rapid combustion process for the preparation of MgSrAl$_{10}$O$_{17}$:Eu^{2+} phosphor and related luminescence and defect investigations

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Abstract

Blue-emitting europium-ion-doped MgSrAl$_{10}$O$_{17}$ phosphor, prepared using the combustion method, is described. An efficient phosphor can be prepared by this method in a muffle furnace maintained at 500 °C in a very short time of few minutes. The phosphor is characterized by powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy and BET surface area measurements. Photoluminescence (PL) spectra revealed that europium ions were present in divalent oxidation state. The thermoluminescence (TL) glow curve shows two peaks at around 178 and at 354 °C. The defect centres formed in the phosphor are studied using electron spin resonance (ESR). The ESR spectrum indicates the presence of Fe^{3+} ions in the non-irradiated system. Irradiated MgSrAl$_{10}$O$_{17}$:Eu exhibits lines due to radiation-sensitive Fe^{3+} ion and a defect centre. The centre is characterized by an isotropic g-value of 2.0012 and is assigned to a F^{+} centre. The radiation-sensitive Fe^{3+} ion appears to correlate with the main TL peak at 178 °C. During irradiation an electron is released from Fe^{2+} and is trapped at an anion vacancy to form F^{+} centre. During heating, an electron is liberated from the defect centre and recombines with Fe^{3+} emitting light.
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1. Introduction

There is a growing demand for economically viable phosphors for newly emerging display devices with on-going technological advancements. Various aluminates are used as hosts for doping rare earth ions in luminescent applications, e.g. BaMgAl$_{10}$O$_{17}$:Eu^{2+} and CeMgAl$_{11}$O$_{19}$:Tb^{3+} as lamp phosphors [1] and RAlO$_3$:Ce^{3+} (R = Y and Gd) as scintillator materials [2]. The Eu^{2+}-doped barium and strontium magnesium aluminates, MMgAl$_{10}$O$_{17}$:Eu^{2+} (M = Ba, Sr), are among the recent commercially exploited luminescent materials [3–5]. For full-colour plasma display panels (PDPs), the blue phosphor BaMgAl$_{10}$O$_{17}$: Eu^{2+} (BAM) has more demerits to be resolved [6]. However, the stabilized BAM has never been obtained so far. To replace BAM, Takashi Kunimoto and his co-workers have prepared CaMgSi$_2$O$_6$: Eu^{2+} and pointed out that it was a promising blue phosphor for PDP applications [7,8]. Most recently, Xing et al. [3] have proposed that SrMgAl$_{10}$O$_{17}$:Eu^{2+} prepared by high-temperature solid-state reaction would be a promising blue phosphor material for PDP application.

Alkaline earth aluminates have been studied already for decades [9–11] for use in cements or as luminescent materials. Among these, MgSrAl$_{10}$O$_{17}$ has drawn more attention. Several recent papers report on the synthesis, characterization and applications of europium-ion-doped MgSrAl$_{10}$O$_{17}$ phosphor [3,4,12–14]. These aluminates have been prepared traditionally by solid-state reactions [11,15–17], which demand high annealing temperatures and long durations, ca. 1300 °C and 5–10 h, respectively.

We describe an alternative low-temperature combustion process, which rapidly yields MgSrAl$_{10}$O$_{17}$: Eu^{2+} phosphor, and report on the thermally stimulated luminescence (TSL) and electron spin resonance (ESR) of this system, as

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the information available about these properties is scanty. The prepared product was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and BET surface area measurements. The PL spectra confirm the co-existence of Eu^{2+} in the samples. In addition, the gamma-radiation-induced defect centres were identified and their role in the TSL glow peaks was examined.

2. Experiment

2.1. Sample preparation

The stoichiometric compositions of the metal nitrates (oxidizers) and urea (fuel) were calculated according to the total oxidizing (O) and reducing (F) valencies of the components such that the equivalence ratio (O:F ratio) is unity and the energy released is maximum [18].

Analytical grade aluminium nitrate $[Al(NO_3)_3 \cdot 9H_2O]$, strontium nitrate $[Sr(NO_3)_2 \cdot 4H_2O]$, magnesium nitrate $[Mg(NO_3)_2 \cdot 6H_2O]$, europium oxide (Eu_2O_3) and urea (CH_4N_2O) were used as the starting materials. The details of synthesis are reported elsewhere [19,20]. These five materials were mixed to get a product of chemical formula $Mg_{1-x}Eu_xSrAl_{10}O_{17}$, where $x = 0.01–0.10$. These five materials were mixed in an agate mortar, and due to the presence of large crystallization water in aluminium nitrate a thick paste was formed upon mixing. The resulting paste was transferred into a china dish and the dish 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. 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 is over in < 5 min. The synthesis procedure in the combustion process is summarized in the flowchart illustrated in Fig. 1.

2.2. Instruments

Powder XRD was obtained using a Philips X' pert X-ray diffractometer with graphite monochromatized CuK_α radiation ($\lambda = 0.15418$ nm) and nickel filter at a scanning step of $0.03°$ in the 2θ range from $10°$ to $80°$. Scanning electron micrographs were taken using a JEOL JSM-5610LV scanning electron microcopy. BET surface area measurements were made by nitrogen adsorption employing a Micromeritics Accusorb ASAP 2020 instrument. The PL spectra were acquired with an AMINCO-Bowman Series 2 luminescence spectrometer at room temperature. TSL glow curves were recorded with the usual setup consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (931B), dc amplifier and a mV recorder. ESR measurements were carried out using a Varian E-112 E-line Century series
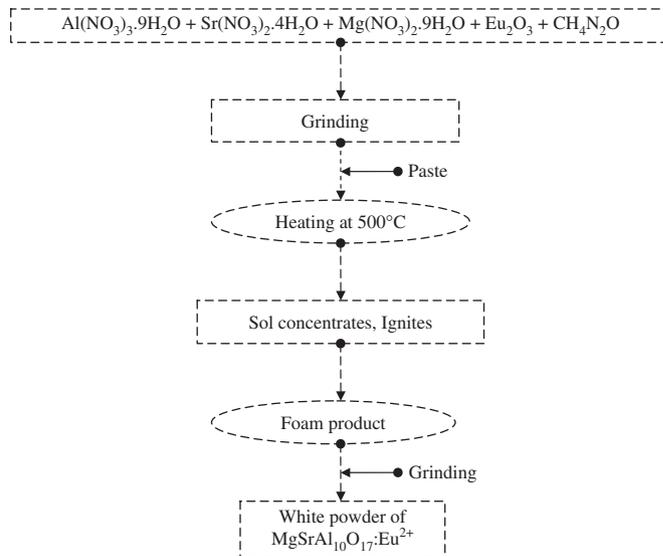

Fig. 1. Flowchart for the synthesis of combustion derived $MgSrAl_{10}O_{17}:Eu^{2+}$.

X-band ESR spectrometer. TCNE ($g = 2.00277$) was used as a standard for g-factor measurements. Step heat treatments were performed to follow the decay and evolution of the defect centres. These were carried out *in situ* in the ESR cavity using the Varian variable temperature accessory.

3. Results and discussion

3.1. XRD, SEM and BET studies

Fig. 2 shows the XRD pattern for $MgSrAl_{10}O_{17}:Eu$ phosphor powder. The obtained product has a hexagonal lattice with the lattice parameters $a = 5.61$, $c = 22.45$. These lattice parameters are consistent with the JCPDS no. 26-0879 for the same phosphor powder.

Fig. 3 shows the SEM micrograph of the $MgSrAl_{10}O_{17}:Eu$ foam. The foamy structure of $SrMgAl_{10}O_{17}:Eu$ reflects the nature of the reaction. Urea enhances combustion and this process results in crystal facets growing in different directions. Most of the hexa-aluminates took the form of hexagonal platelets. It can be observed that the crystallites have no uniform shape. This is believed to be related to the non-uniform distribution of temperature and mass flow in the combustion flame. High-resolution SEM micrographs show the presence of several micro- and nanoparticles within the grains. The micrographs also show a number of voids and pores, which may be formed by the evolving gases during combustion.

The BET surface area of as-prepared $MgSrAl_{10}O_{17}:Eu$ phosphor by the urea process is $6.3728 \, m^2/g$. Patil and Ekambaram [19] reported the specific surface areas of $BaMgAl_{10}O_{17}:Eu$ phosphor prepared by the urea process to be $10 \, m^2/g$. $MgSrAl_{10}O_{17}:Eu$ phosphor has lower BET surface area. If some other fuel is used, it is possible that this value will be different.
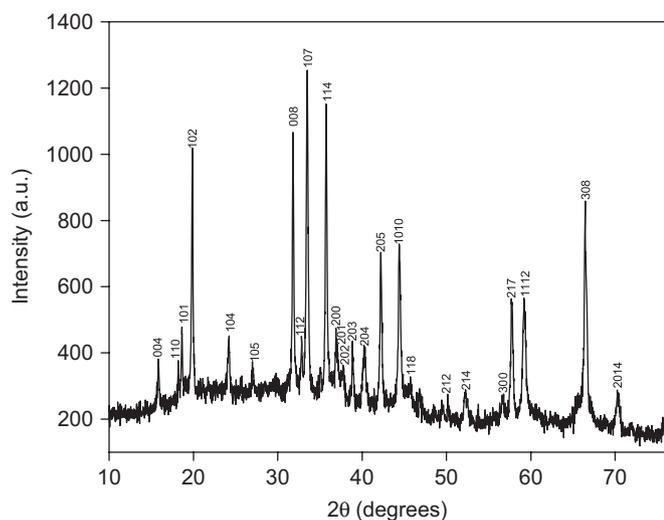
Fig. 2. Powder XRD patterns of MgSrAl$_{10}$O$_{17}$:Eu phosphor.

3.2. Photoluminescence studies

The excitation and emission spectra of Eu^{2+}-doped MgSrAl$_{10}$O$_{17}$ phosphors are given in Fig. 4(a) and (b), respectively. Room temperature emission spectra of MgSrAl$_{10}$O$_{17}$:Eu showed a band at 461 nm. This band is due to the transition of Eu^{2+} from the excited state of 4f^{6}5d^1 configuration to the ground state ^{8}S$_{7/2}$. These results are in good agreement with the reported observations [4]. Previous studies [21] showed that different doping of activation ion could influence photoluminescence (PL) characteristics of a phosphor. Usually, low doping gives weak luminescence but excess doping perhaps causes quenching of luminescence. Hence, it is worth to know the optimum activator concentration of Eu^{2+} ion required in SrMgAl$_{10}$O$_{17}$ without luminescence quenching. In order to optimize the Eu^{2+} doping in MgSrAl$_{10}$O$_{17}$, a series of Mg$_{1-x}$Eu$_x$SrA1$_{10}$O$_{17}$ with different Eu^{2+} content ($X = 0.01$–0.10) were prepared. The PL spectra of all the

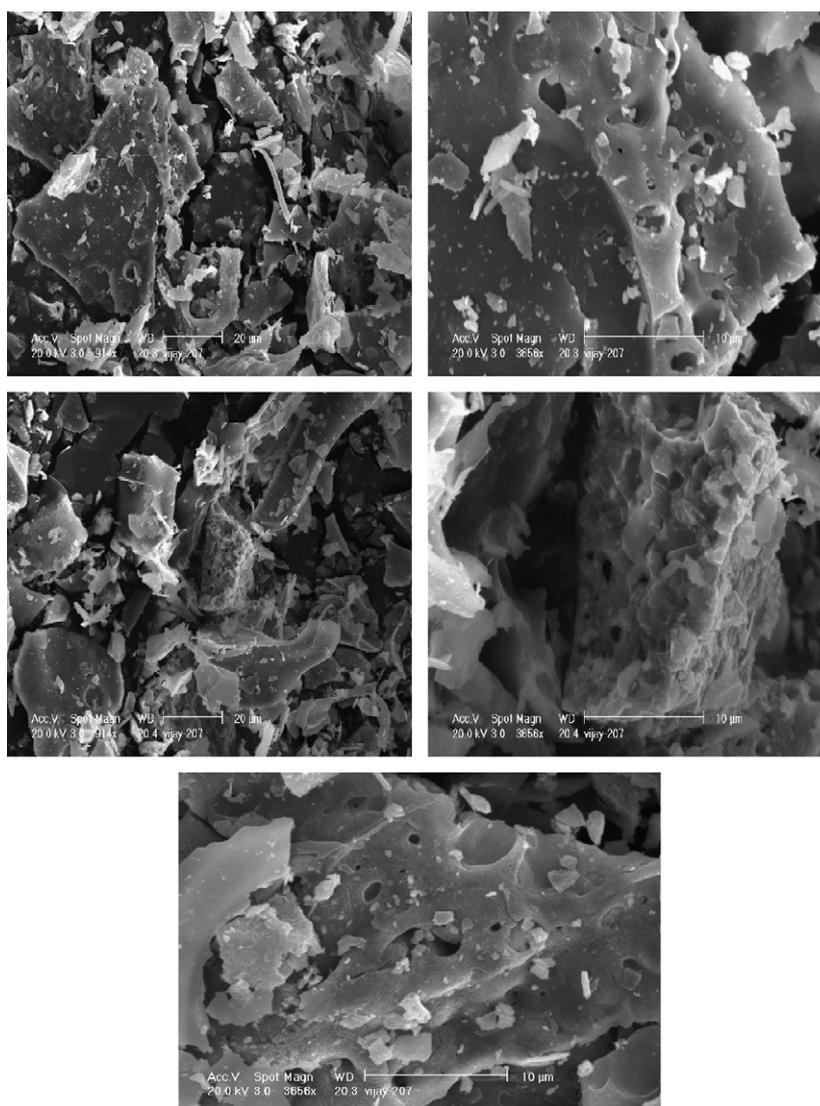
Fig. 3. SEM images of MgSrAl$_{10}$O$_{17}$:Eu phosphor.

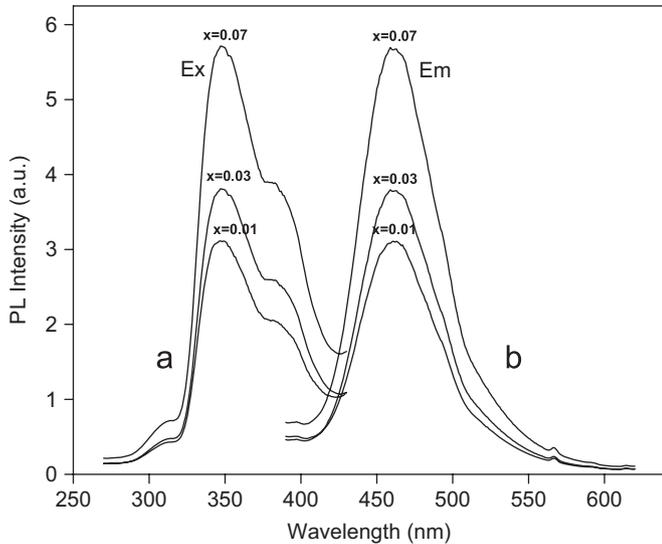Fig. 4. Photoluminescence (a) excitation spectra ($\lambda_{em} = 461$ nm) and (b) emission spectra ($\lambda_{ex} = 347$ nm), for Eu^{2+}-doped $MgSrAl_{10}O_{17}$ phosphor.

Fig. 5. Thermoluminescence glow curve of $MgSrAl_{10}O_{17}$:Eu phosphor.

Fig. 6. (a) Room temperature ESR spectrum of unexposed $MgSrAl_{10}O_{17}$:Eu phosphor. (b) ESR spectrum of irradiated phosphor (gamma dose: 3000 Gy). Centre I line is due to F^+ centre and lines labelled as centre II are due to radiation-induced Fe^{3+} ion.

powder was recorded under the same conditions by exciting at 347 nm and the relative intensity of the emission peak was monitored. It revealed that the relative intensity increased with the activator concentration. Above the 7% Eu concentrations, sudden drop in relative intensity and 10% Eu^{2+} overlaps with that for 1% (not shown in Fig. 4). The maximum relative intensity was observed for the $x = 0.07$ of activator concentration. The sudden drop in the relative intensity of the phosphors may be due to concentration quenching. Xing et al. [3] reported an emission peak at about 469 nm for Eu-doped $MgSrAl_{10}O_{17}$ phosphors. The small differences in peak position may arise due to the use of different synthesis methods. They also reported that the relative PL intensity increased with activator concentration without any change in the peak position. However, they synthesized this phosphor using firing temperature ranging between 1300 and 1600 °C. This phosphor of the hexa-aluminate family has a fairly narrow emission band. As in Eu^{2+}-activated $MgSrAl_{10}O_{17}$ sample, intense excitation regions are found in the UV spectral region, and are associated with $4f \rightarrow 5d$ electronic transitions. In this sample, we get excitation peaks at 311 and 347 nm. The excitation peaks are due to the $4f^7(^8S_{7/2}) \rightarrow 4f^6 5d$ transitions. It is observed that the more intense excitation peak occurs at 347 nm instead of at 311 nm.

3.3. TSL and ESR studies

TSL studies on the freshly prepared $MgSrAl_{10}O_{17}$:Eu sample did not show any glow peak. Fig. 5 shows a typical TSL glow curve for $MgSrAl_{10}O_{17}$:Eu phosphor at a test gamma exposure of 15 kGy. The main TSL glow peak appeared at around 178 °C and also another peak was observed at 354 °C (heating rate = 5 °C/s); the former one was more intense than the latter one.
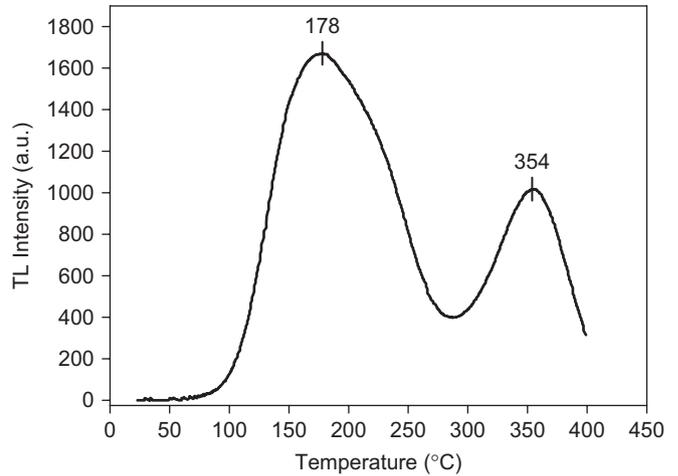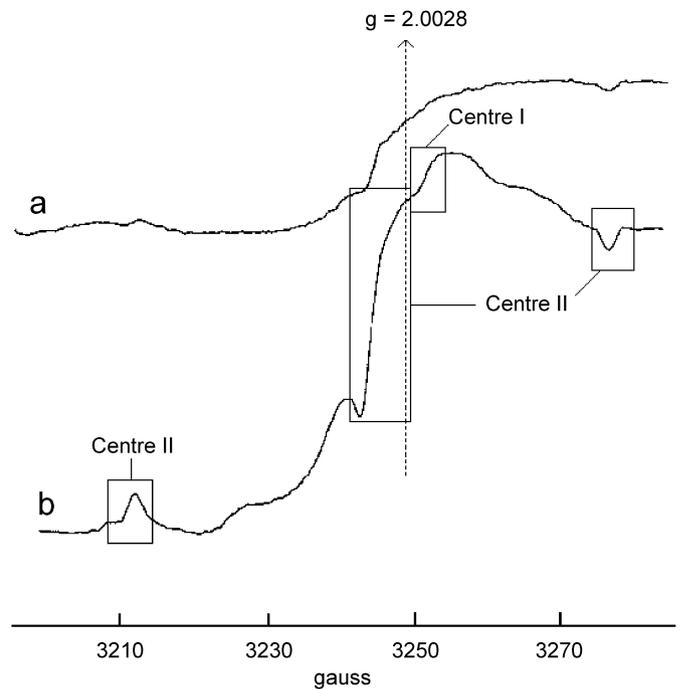
Fig. 6(a) shows the ESR spectrum of unexposed $MgSrAl_{10}O_{17}$:Eu at room temperature. A broad ESR line is seen along with additional weak lines, which are found to increase in intensity with gamma irradiation. The observed ESR spectrum after gamma irradiation (3 kGy) is shown in Fig. 6(b). It was possible to distinguish two centres, which are labelled as centres I and II. Spectrum akin to centre II has been observed in dicalcium silicate (β-Ca_2SiO_4) (unpublished results) and this is shown in Fig. 7(a). Similar spectra were reported by Dvir and Low [22]. These authors attributed these spectra to the presence of Fe^{3+} in substitution of cation in the lattice. In dicalcium silicate,
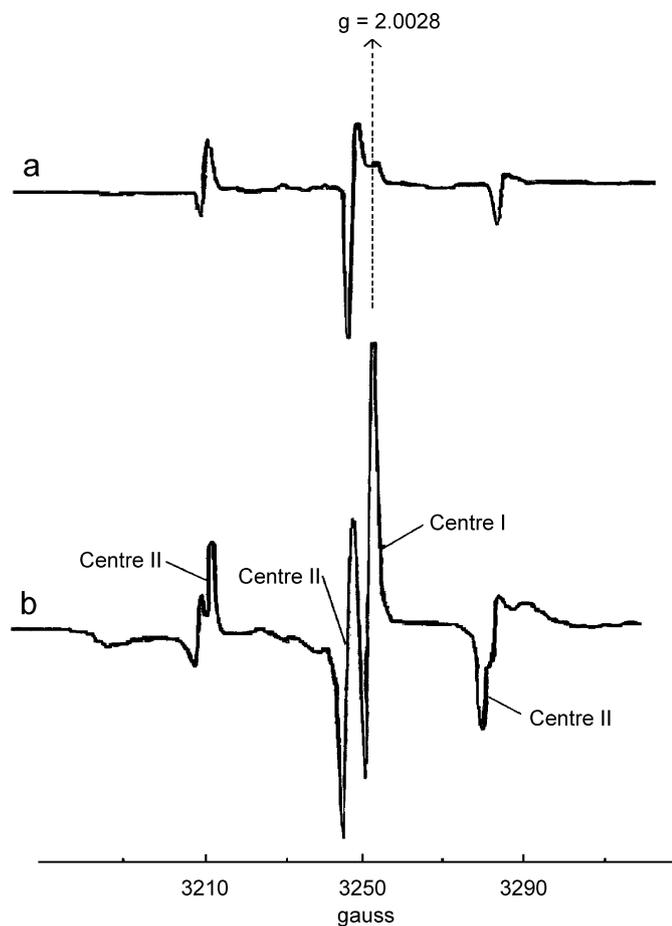
Fig. 7. (a) Observed room temperature ESR spectrum in unirradiated dicalcium silicate due to radiation-insensitive Fe^{3+} ion. (b) Lines labelled II are due to radiation induced Fe^{3+} ion and line I arises from a defect centre. The ESR spectrum is recorded at room temperature after a gamma dose of 1000 Gy.

the intensity of Fe^{3+} ESR signal, observed in unexposed sample, does not show any considerable variation after gamma irradiation. On the other hand, a new Fe^{3+} signal appears after gamma irradiation. The ESR lines due to this ion are shown in Fig. 7(b). It is seen that the new lines arising from gamma irradiation almost overlap the lines due to radiation-insensitive Fe^{3+} ion. Based on these observations, centre II lines in $MgSrAl_{10}O_{17}$:Eu have been attributed to a radiation-sensitive Fe^{3+} ion.

In $MgSrAl_{10}O_{17}$:Eu, the ESR line to the left of the TCNE marker ($g = 2.0028$) [Fig. 6(b)] is due to the Fe^{3+} ion and the line on the right of the marker is due to a defect centre (centre I). The ESR line labelled as centre I in Fig. 6(b) is due to a centre characterized by a single ESR line with an isotropic g-value 2.0012 and 4 G line width. Not many defect centres are expected to be formed in a system like $MgSrAl_{10}O_{17}$:Eu and the most probable centre which can be observed is the F^+ centre (an electron trapped at an anion vacancy). Hutchison [23] first observed such a centre in neutron-irradiated LiF. In LiF, a single broad line (line width ~ 100 G) with a g-factor 2.008 was observed. X-ray or gamma irradiation also produces such a

centre in other systems like alkali halides [24]. Such centres are characterized by (1) a small g-shift, which may be positive or negative, (2) a large line width and (3) saturation properties characteristic of an inhomogenously broadened ESR line. Unresolved hyperfine structure causes large line widths.

Irradiation leads to the trapping of an electron at an anionic vacancy, and such a trapping is the basis for the formation of a F^+ centre. Hyperfine interaction with the nearest-neighbour cations is the major contribution to the line width. Defect centre I formed in the present system is characterized by a small g-shift and the line width, however, is relatively small. The centre also does not exhibit any resolved hyperfine structure. On the basis of these observations and considerations of the characteristic features of the defect centres likely to be formed in a system such as $MgSrAl_{10}O_{17}$:Eu, centre I is tentatively assigned to a F^+ centre.

The stability of centres I and II was measured using the step-annealing technique. It was difficult to individually measure the intensity of the centres as the ESR lines overlap. As the intensity of the Fe^{3+} line is higher, it is assumed that the measured intensity largely represents the intensity of the Fe^{3+} ESR line.

The thermal annealing behaviour of Fe^{3+} ion (Fig. 8) shows temperature regions where there is a reduction in intensity of the corresponding ESR line. The region from 100 to around 250 °C is likely to arise from recombination of charges, released from traps, at Fe^{3+} ion sites. The
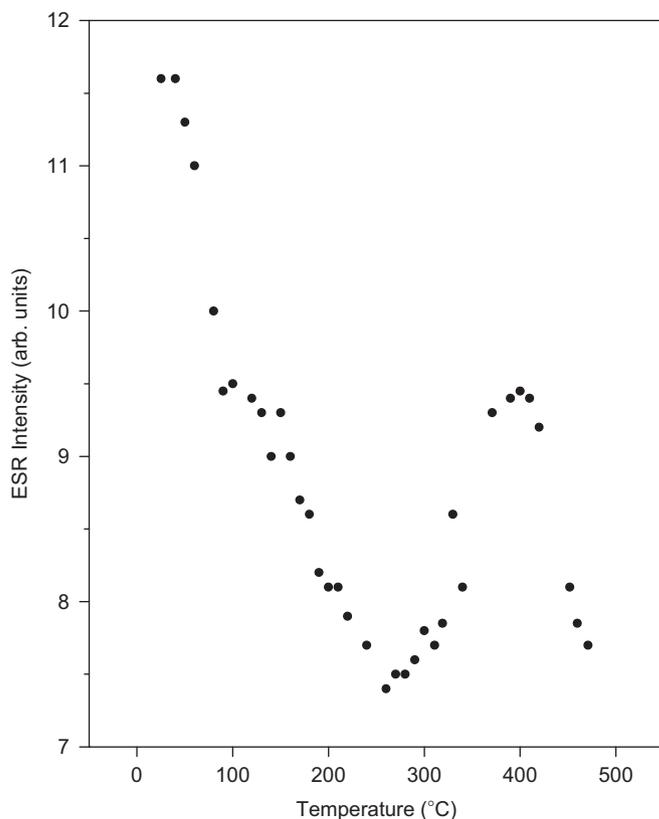

Fig. 8. Thermal annealing behaviour of radiation-induced Fe^{3+} ion.

subsequent decay region above 400 °C is related to the decay of the radiation-induced Fe^{3+} ions. As some reduction in intensity of F^+ centre is observed approximately in the above temperature range, it is speculated that the electrons released from F^+ centres are involved in the above-mentioned recombination process. It is to be noted that during irradiation Fe^{2+} ions lose electrons, while being converted into Fe^{3+}, whereas the subsequent thermal annealing during TSL experiment causes the opposite conversion from Fe^{3+} to Fe^{2+}. The results presented in this work suggest that irradiation possibly releases electrons from Fe^{2+} ions, and these electrons are subsequently trapped at anion vacancies to form F^+ centres.

4. Conclusion

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

(1) A blue emitting Eu^{2+}-doped magnesium strontium aluminate-based phosphor $MgSrAl_{10}O_{17}:Eu^{2+}$ was synthesized by the low-temperature combustion method. The major advantages of the combustion process are: energy saving, improvement in processing time and commonly available materials like urea, and nitrate as fuel and oxidizer. It could be suggested that the synthesized product would be a promising material for obtaining blue fluorescence colour, in the form of phosphor-coated screens for certain electronic devices.
(2) A radiation-induced Fe^{3+} ion relates to the TSL peak at 178 °C.
(3) The 178 °C TSL peak may also possibly correlate with a defect centre which is tentatively assigned to a F^+ centre.
(4) A defect centre, which shows specific correlation with the 354 °C TSL peaks, could not be observed in the present study.

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