Role of defect centres in thermoluminescence mechanism of Tb$^{3+}$ doped MgAl$_2$O$_4$

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Magnesium aluminate (MgAl$_2$O$_4$) doped with terbium was prepared by combustion synthesis. Defect centres of MgAl$_2$O$_4$:Tb$^{3+}$ are studied by correlating various techniques such as Electron Spin Resonance (ESR), Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL). TL studies on MgAl$_2$O$_4$:Tb$^{3+}$ show two TL peaks at 120 and 340°C. MgAl$_2$O$_4$:Tb$^{3+}$ exhibits OSL when stimulated with 470 nm blue light. ESR study shows two defect centres with $g = 2.011$ and $g = 2.0052$ which are assigned to V-centre and F$^-$ centre, respectively. Step annealing ESR technique study suggests that V-centre is correlated to 120°C TL peak whereas F$^-$ centre is correlated with both the 120 and 340°C TL peaks. A TL mechanism is proposed. ESR–OSL correlation studies are carried out. The results of ESR–OSL correlation study along with TL bleaching study support the proposed TL mechanism of 120°C TL peak.

**Keywords:** Thermoluminescence, MgAl$_2$O$_4$, Defect centres, Electron spin resonance

1 Introduction

Magnesium aluminium oxide spinel (MgAl$_2$O$_4$) is an important material in technological applications as host materials for various phosphors and light emitting devices including laser, and for various optical and electrical applications and some being in radiation environment. Many of its properties are intermediate between those of its constituent oxides (MgO and Al$_2$O$_3$). Consequently, although much is now known about anion vacancy centers and cation vacancy (V-type) centers in both MgO and α-Al$_2$O$_3$, relatively little is known about these centers in MgAl$_2$O$_4$.

The spinel crystalline structure is a face centered cubic lattice of oxygen ions, with a lattice parameter of 8.08 Å for MgAl$_2$O$_4$. It has the cubic space group Fd3m. Eight molecules form its unit cell, in which there are 64 tetrahedral symmetry sites and 32 octahedral ones. Only 8 magnesium ions occupy tetrahedral sites and 16 aluminum ions occupy octahedral sites in MgAl$_2$O$_4$ of natural origin. However, upto 30% of cation antisite disorder occurs in synthetic MgAl$_2$O$_4$ crystal. Antisite formation due to interchange of the ions on tetrahedral and octahedral lattice positions by divalent and trivalent ions causes numerous trapping sites for the electron and hole on irradiation in the synthetic as prepared samples of MgAl$_2$O$_4$. Further, irradiation causes damage to the defects centre and impurities by changing their charge states. This plays a vital role in many of the luminescent and optical properties of the crystal, especially thermoluminescence (TL) and optically stimulated luminescence (OSL). OSL was reported in pure MgAl$_2$O$_4$ crystal. Rare earth doped MgAl$_2$O$_4$ are reported to be a long persistent afterglow emission phosphors used in light emitting device and colour display. A detailed study on V-type centres (hole trapped in a cationic vacancy) and F-centres in MgAl$_2$O$_4$ were carried out extensively by optical absorption and Electron spin resonance (ESR) on irradiation with neutron, UV and γ-rays in correlation with MgO and Al$_2$O$_3$. Various TL studies have also been carried out to find the defects responsible for the TL peaks. The defects responsible for the observed first TL glow peak (80°C) were ascribed to electron traps (Al$^{13+}$ ion at Mg$^{2+}$ site). Combustion synthesis or self-propagating high temperature synthesis (SHS) provides an attractive practical alternative to the conventional synthesis of producing advanced materials, such as ceramics, ceramics-composites etc. The underlying basis of SHS is highly efficient energetic exothermic reaction with the evolution of various gases along with the high intense flame. It volatilizes low boiling point impurities and results in purer products than those produced by the other conventional synthesis. Preparation of MgAl$_2$O$_4$ sample by combustion synthesis has been reported.
Photoluminescence (PL), TL and OSL properties of MgAl$_2$O$_4$ doped with terbium prepared by combustion synthesis. TL-ESR correlation studies are carried out and a model for TL mechanism in this phosphor is proposed.

2 Experimental Details
Magnesium nitrate, aluminum nitrate, urea and terbium nitrate (dopant) are used as starting materials. Stoichiometric (Mg$^{2+}$ and Al$^{3+}$ ions in 1:2 ratio) samples of MgAl$_2$O$_4$ are prepared with equivalent ratios (ratio of oxidation and reducing valency, O/F = 1). Metal nitrates, urea and desired amount of dopant are dissolved in de-ionised water in a glass beaker. The beaker was kept inside a furnace at ~550ºC. Once the water has boiled off, the metal nitrate and urea react and ignite. The entire combustion process was over in about 5 minutes.

The structural phases of as prepared samples of MgAl$_2$O$_4$ has been studied by X-ray diffraction using Rigaku D/max-II X-ray diffractometer using CuK$\alpha$ ($\lambda$=1.5405 Å) radiation. Gamma cell with Co-60 source having dose rate of 4.7 Gy/min is used for irradiation of the phosphor. PL spectra are recorded using Hitachi F-4500 fluorescence spectrophotometer. TL glow curves are recorded using an indigenously developed TL reader at a constant heating rate (5°C/s). TL emission spectra are recorded on an indigenously developed TL emission spectrometer with EMI 9924 PM tube having S11 response and a prism monochromator. In this system, TL emission can be recorded in the spectral range 320-650 nm. Optically stimulated luminescence studies are carried out using an indigenously developed OSL reader with GG-435 filters. Stimulation is carried out with 470 nm light. ESR measurements are carried out on a Varian E-112 E-line Century series X-band ESR spectrometer. TCNE ($g$=2.00277) is used as a standard for $g$-factor measurements. Step heat treatments are performed to follow the decay and evolution of the defect centres. These are carried out in-situ in the ESR cavity using the Varian variable temperature accessory.

3 Results
Figure 1 shows the XRD pattern for MgAl$_2$O$_4$ and standard XRD pattern (JCPDS file 75-0905). Figure 2(a) shows the PL excitation and emission spectra of Tb$^{3+}$ doped MgAl$_2$O$_4$. The emission spectrum consists of several lines at 380, 415, 440, 490, 545, 580 and 620 nm corresponding to transitions $^5D_3$-$^7F_6$, $^5D_3$-$^7F_5$, $^5D_3$-$^7F_4$, $^5D_4$-$^7F_6$, $^5D_4$-$^7F_5$, $^5D_3$-$^7F_6$, injecting energy from the $^5D_3$ level to the lower level $^7F_n$. The variation of PL emission intensity of MgAl$_2$O$_4$:Tb$^{3+}$ with Tb$^{3+}$ concentration is shown in Figure 2(b).

Fig. 1—XRD of powder sample of undoped NS, undoped S, standard XRD pattern (JCPDS file 75-0905)

Fig. 2(a)—PL excitation (a) & emission spectrum (b) for the Tb$^{3+}$ doped MgAl$_2$O$_4$ ($\lambda_{exc}=245$ nm, $\lambda_{em}=545$ nm)

Fig. 2(b)—Variation of PL emission intensity of MgAl$_2$O$_4$:Tb$^{3+}$ with Tb$^{3+}$ concentration
$^5D_4-^7F_4$ and $^5D_4-^7F_3$, respectively. The excitation spectrum (emission wavelength=545 nm) shows an intense peak at 245 nm corresponding to 4f-5d transition and less intense peaks at 320, 355 and 370 nm corresponding to f-f transitions in Tb$^{3+}$. Figure 2(b) shows that 0.5 mol % concentration of Tb$^{3+}$ gives the maximum PL intensity.

Figure 3 shows the TL glow curves recorded for the doped and undoped MgAl$_2$O$_4$. Two TL peaks at 120 and 340$^\circ$C are observed for all the samples. Tb$^{3+}$ doped sample is about 6 times sensitive than the corresponding undoped sample. Figure 4[(a) and (b)] shows the TL emission spectra of undoped and Tb$^{3+}$ doped samples. The undoped sample of MgAl$_2$O$_4$ shows an emission around 520 nm. Tb$^{3+}$ doped sample shows the emission at 380, 415, 440 and 545 nm for both TL peaks, which corresponds to the characteristic f-f transitions of Tb$^{3+}$ on ($^5D_4-^7F_J$).

Continuous wave OSL (CW-OSL) spectra of Tb$^{3+}$ doped are shown in Fig. 5. Figure 6(a) shows the ESR spectrum at room temperature after gamma irradiation (3 kGy) of MgAl$_2$O$_4$. The observed spectrum appears to be superposition of at least two distinct centres. This inference is based on thermal annealing experiments as shown in Fig. 7. It is possible to identify two centers and these are labeled in Fig. 6(a). The ESR line labeled as I is due to a centre characterized by a single broad ESR line with an isotropic $g$-value 2.011 and 42 gauss line-width. The thermal annealing behaviour of centre I is shown in Fig. 8(a). The ESR line labeled as II in Fig. 6(a) is due to a centre characterized by a single ESR line with an isotropic $g$-value 2.0052 and 10 gauss line-width.
4 Discussion

The 520 nm TL emission for undoped MgAl$_2$O$_4$ can be assigned to Mn$^{2+}$ impurity ion, which acts as luminescent centre$^{11}$. TL emission of Tb$^{3+}$ doped MgAl$_2$O$_4$ indicates that Tb$^{3+}$ acts as luminescent centre, which gets excited when the energy is transferred from an unknown recombination site.

ESR spectra of the undoped and Tb$^{3+}$ doped S exhibits a large line-width of centre I indicating a unresolved hyperfine structure. The unresolved structure results from the interaction of the unpaired electron with nearby nuclear spins. Aluminium ($^{27}$Al) as well as magnesium ($^{25}$Mg) in MgAl$_2$O$_4$ has isotopes with nuclear spin 5/2. $^{27}$Al is much more abundant (100 %) than $^{25}$Mg (10.1%) and its nuclear magnetic moment is higher (3.6385) than that of $^{25}$Mg (0.8545)$^{13,20}$. It is likely, therefore, that the electronic spin will be interacting with aluminum ions. It is known that the cation disorder and non-stoichiometry of MgAl$_2$O$_4$ provide a large number of lattice defects, which may serve as
trapping centres. In such a case, oxygen vacancies should lead to F\(^{+}\) centres by trapping electrons after irradiation. The observed broad ESR line of centre I and the associated unresolved hyperfine structure indicates that the unpaired electron is delocalized and interacts with nearby aluminum nuclei. It has been speculated that in oxides, the charges must be trapped near double (or more) charged defects in order for the charge to be delocalized, thus allowing it to interact with surrounding nuclei\(^{21}\). Hence centre I is assigned to a V-centre i.e., a hole trapped on an oxygen ion, forming an O\(^{−}\) ion, adjacent to an Al\(^{3+}/Mg^{2+}\) ion vacancy. The observed positive g-shift of centre I is also in accordance with the expectations for a V-centre. It may be mentioned that a similar centre in neutron irradiated MgAl\(_2\)O\(_4\) has also been ascribed to a V-centres\(^{13,22}\).

The thermal annealing behaviour of V-centre is shown in Fig. 8(a). It is observed that the centre shows a single decay stage. The stage is in the temperature range 80-170°C and this stage relates to the TL peak at 120°C. Hutchison\(^{21}\) first observed F\(^{+}\) centre in neutron irradiated LiF. In LiF, a single broad line (linewidth ~ 100 gauss) with a g-factor 2.008 was observed. Such centres are characterized by (1) a small g-shift, which may be positive or negative, (2) a large line width (caused due to unresolved hyperfine structure) and (3) saturation properties characteristic of an inhomogeneously broadened ESR line. Irradiation leads to the trapping of an electron at an anionic vacancy and such trapping is the basis for the formation of F\(^{−}\) centres. Hyperfine interaction with the nearest-neighbor cations is the major contribution to the line-width. Defect centre II formed in the present system is characterized by a small g-shift and the linewidth is reasonably large. The centre also does not exhibit any resolved hyperfine structure. Recently such a centre was observed in LiAlO\(_2\) phosphor\(^{24}\). 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 MgAl\(_2\)O\(_4\);Tb\(^{3+}\), centre II is assigned to F\(^{−}\) centre. The thermal annealing behaviour of centre II is shown in Fig. 8(b). It is observed that this centre also shows two decreasing stages. The temperature range 70-160°C appears to be associated with the low temperature TL peak at 120°C. The actual decay of the centre occurs at high temperature and this may be associated with the high temperature TL peak at 340°C.

From the TL, ESR and PL studies we propose the following mechanism for the low temperature TL peak at 120°C: (1) electron-hole pair is created during irradiation (2) the hole is trapped at the V centre, cation vacancy stabilized by the surrounding oxygen ions and the electrons are trapped to form F\(^{−}\) centre (3) during heating, the hole from the V centre is released and recombines with the electron trapped in F\(^{−}\) centre (4) the recombination energy is transferred to nearby Tb\(^{3+}\) ions (since MgAl\(_2\)O\(_4\) is ionic crystal, the F\(^{−}\) centres are the nearest neighbours to Tb\(^{3+}\) ion and not V centres) and (5) Tb\(^{3+}\) ion gets excited and on de-excitation emits its characteristic emission. TL process for the second peak is not clear although the electron centres may be assigned to F\(^{−}\) centre on the basis of ESR data.

5 Conclusions

OSL emission is observed in the Tb\(^{3+}\) doped MgAl\(_2\)O\(_4\). Two defect centres are identified in irradiated MgAl\(_2\)O\(_4\);Tb\(^{3+}\) phosphor and these centres are assigned to V-centre and F\(^{−}\) centre. V-centre appears to correlate with the 120°C TL peak while F\(^{−}\) centre is correlated with both TL peaks at 120°C and 340°C. TL emission results indicate Tb\(^{3+}\) acts as the luminescent centre. A model for TL mechanism is proposed for the first TL peak at 120°C.

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