

# Preparation and luminescence of MgO:Tb phosphors

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In the present investigation, a number of samples of magnesium oxide activated with terbium ( $3+$ ) (MgO:Tb) were prepared from various magnesium salts and their combination with MgO in the presence of a flux and their emission characteristics were studied. XRD analysis of these samples shows the formation of MgO. From the results it was found that the luminescence intensity increases with terbium concentration up to 2 mol% and then decreases with further increase of activator concentration. From the emission spectra, the possible transitions of  $Tb^{3+}$ , such as ( ${}^5D_4 \rightarrow {}^7F_{4,5}$ ) in the MgO matrix have been proposed.

## 1. Introduction

Alkaline earth oxides are known refractory oxides which have the rock salt structure. These oxides have been studied extensively because of their many industrial applications. Magnesium oxide (or magnesia) doped with transition metal ions has been investigated in order to understand the formation and properties of point defects and their role in optical and electrical properties [1–5]. However, not much work has been reported on MgO:RE phosphors. MgO single crystals as well as films are extensively used as substrates for the growth of high  $T_c$  superconductor films because of their lattice matching for  $YBa_2Cu_3O_7$  and their low chemical reactivity [6, 7]. MgO is also important in glass technology in MgO–Al<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>, MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–TiO<sub>2</sub> and CaO–MgO–CoO–SiO<sub>2</sub>–GeO<sub>2</sub> systems [8, 9]. Recently, Huzimura and Ogita [10] have suggested that MgO films can be used to detect soft X-rays from laser-heated cavities and to measure the low-energy radiations in dermatology (skin doses) and in astronomical applications [11]. These oxides are also employed in nuclear reactors, sensitive gas counters, etc. MgO has also been investigated as a possible tunable laser material [12].

Magnesium aluminate is a well known phosphor host with various applications.  $Eu^{3+}$ -activated  $Ba,Mg_2Al_{16}O_{27}$  and  $Tb^{3+}$ - and  $Ce^{3+}$ -activated  $MgAl_{11}O_{19}$  as blue and green components, are extensively used in trichromatic lamp phosphor blends. Fluorescent lamps coated with these phosphors along with  $Eu^{3+}$ -activated  $Y_2O_3$  (red) have better colour rendering index ( $R_a = 80–85$ ) and high luminous efficiency (80–90 lum/W) [13]. Efforts are being made to develop better phosphor systems and improve the overall performance of fluorescent lamps and a large amount of work has been carried out on the above system of phosphors. For green-emitting phosphor, the required activator concentrations of terbium and cerium can be as high as 10%–25% by weight. So that this particular phosphor has become expensive because of its terbium content. In recent years, a con-

siderable amount of effort has been made to obtain an efficient phosphor with smaller amounts of terbium through enhanced energy transfer processes. An example is  $Ce^{3+}/Bi^{3+}$  to  $Tb^{3+}$  and other host matrices such as lanthanum phosphates, silicates and borates. However, no attempt has been made to understand the properties of individual oxide components such as MgO, Al<sub>2</sub>O<sub>3</sub> doped with  $Tb^{3+}$ . In the present investigation the luminescence properties of MgO activated with various rare-earth ions have been studied in order to understand their role in a MgO matrix. In the present paper, we report the preparation of MgO:Tb in the presence of different fluxes and its luminescence characteristics. From the spectra observed, the possible transitions of  $Tb^{3+}$  in a MgO matrix are also proposed.

## 2. Experimental procedure

Polycrystalline MgO powders were prepared from pure hydroxide, acetate, nitrate, chloride or carbonate of magnesium and their combination with MgO. For effective doping of activators, various flux materials such as LiF, LiCl,  $Mg(NO_3)_2$ ,  $Mg(CH_3COO)_2$ ,  $MgCl_2$ , etc., were tried. Stoichiometric amounts of magnesium compounds and impurities were thoroughly mixed and dried. Terbium and cerium impurities were added to the starting chemicals as 0.1N nitrate solutions before firing. Dried mixtures were fired in a loosely sealed high-grade alumina crucible at temperatures in the range 800–1200 °C for different durations (0.5–6 h) in air. A number of samples were prepared to optimize preparative parameters such as firing temperature, duration of firing and rates of heating and cooling. With the help of X-ray diffraction analysis, the phase purity of the final phosphor has been studied. A Siemens XRD unit (D500) with a  $CuK_\alpha$  target, operating at 40 kV and 30 mA was used for powder diffraction analysis.

These phosphor samples were then packed in a specially constructed sample holder and excited with

308 nm from an excimer laser (XeCl). A Displex closed cycled refrigerator was used to vary the sample temperatures from 10–300 K. Emission spectra from these samples were recorded with an EG and G optically multichannel analyser (OMA III) which included a 1024 diode array detector and a grating monochromator.

### 3. Results and discussion

To study the effective doping of RE impurities in the MgO lattice, various magnesium compounds were chosen as starting chemicals. After doping, only MgO prepared from magnesium nitrate exhibited luminescence and also no clusters were observed as with samples prepared from acetate and chlorides. Throughout this investigation  $\text{Mg}(\text{NO}_3)_2$  and MgO (99.99% purity) were used. Initially all samples were fired at 1200 °C for 6 h in air. From the results it was found that the formation of MgO and doping of impurities in the presence of  $\text{Mg}(\text{NO}_3)_2$  begins at 800 °C. For charge compensation, a small quantity (2–5 mol %) of one of alkali halides such as LiF, LiCl or NaCl were added to the mixture before firing [14]. To avoid the inclusion of other impurities, various magnesium compounds of low melting points were tried. The idea of adding flux here was to reduce the doping temperatures. Because of its high melting temperature, MgO needs a very high reaction temperature (> 2000 °C) for effective doping without any flux material. Of them all,  $\text{Mg}(\text{NO}_3)_2$  was found to be the best flux.  $\text{Mg}(\text{NO}_3)_2$  can be introduced into the mixture at levels between 0 and 20 mol %. Samples prepared with 90 mol % MgO and 10 mol %  $\text{Mg}(\text{NO}_3)_2$  showed a high luminescence yield. Heating MgO with  $\text{Mg}(\text{NO}_3)_2$  to about 800 °C led to chemical interaction between MgO and  $\text{Mg}(\text{NO}_3)_2$  flux, with the formation of a liquid phase and the resulting introduc-

tion of impurity ions into the MgO lattice. Ultimately, at higher temperatures,  $\text{Mg}(\text{NO}_3)_2$  can be converted to MgO. If the proportion of  $\text{Mg}(\text{NO}_3)_2$  exceeds 20 mol %, the luminescence intensity is reduced. This may be due to the formation of clusters between nitrate and activator. Fig. 1 shows the X-ray powder diffraction pattern of MgO. The complete formation of MgO with trace impurities such as BaO, CaO (from starting chemicals) has been found from the X-ray analysis.

To understand the variation of luminescence intensity with terbium activator concentration, a number of samples were prepared with terbium concentrations varying from 0.1–10 mol %. The overall luminescent intensity increased with terbium concentration up to 2 mol %, and then decreased drastically with a further

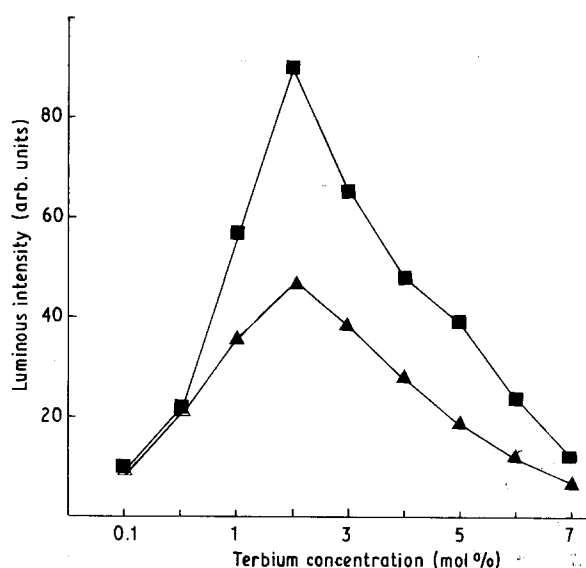


Figure 2 Variation of luminescence intensity with terbium concentration in MgO:Tb phosphors. (■) 549.59 nm, (▲) 553.52 nm.

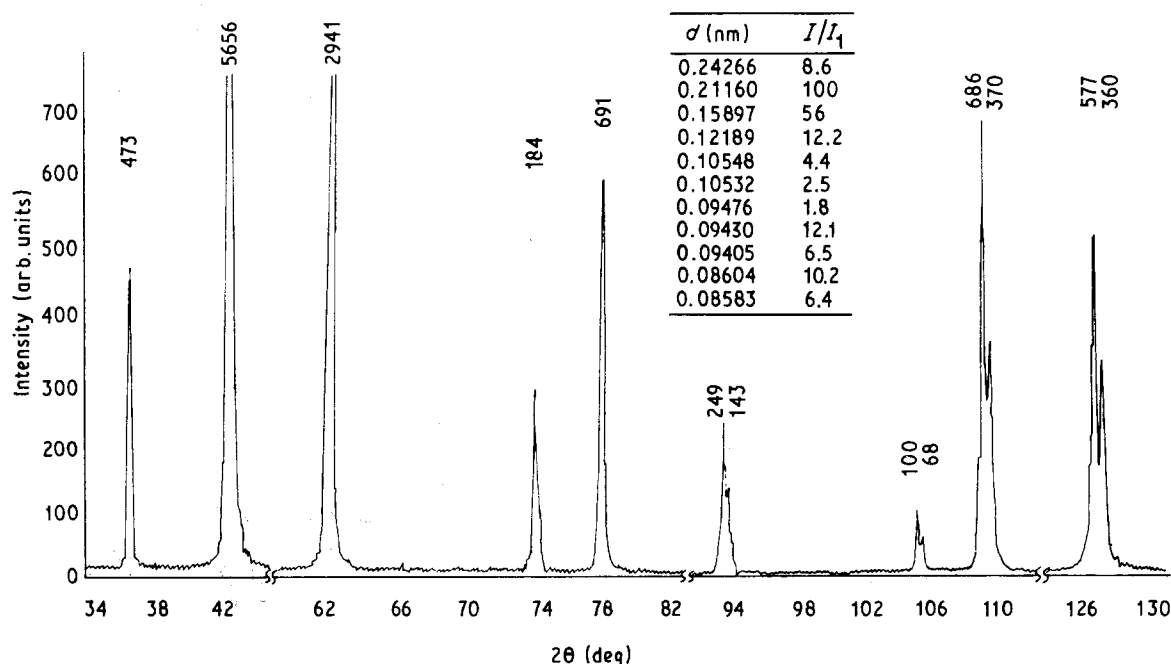


Figure 1 X-ray diffraction of MgO prepared from MgO and  $\text{Mg}(\text{NO}_3)_2$ .

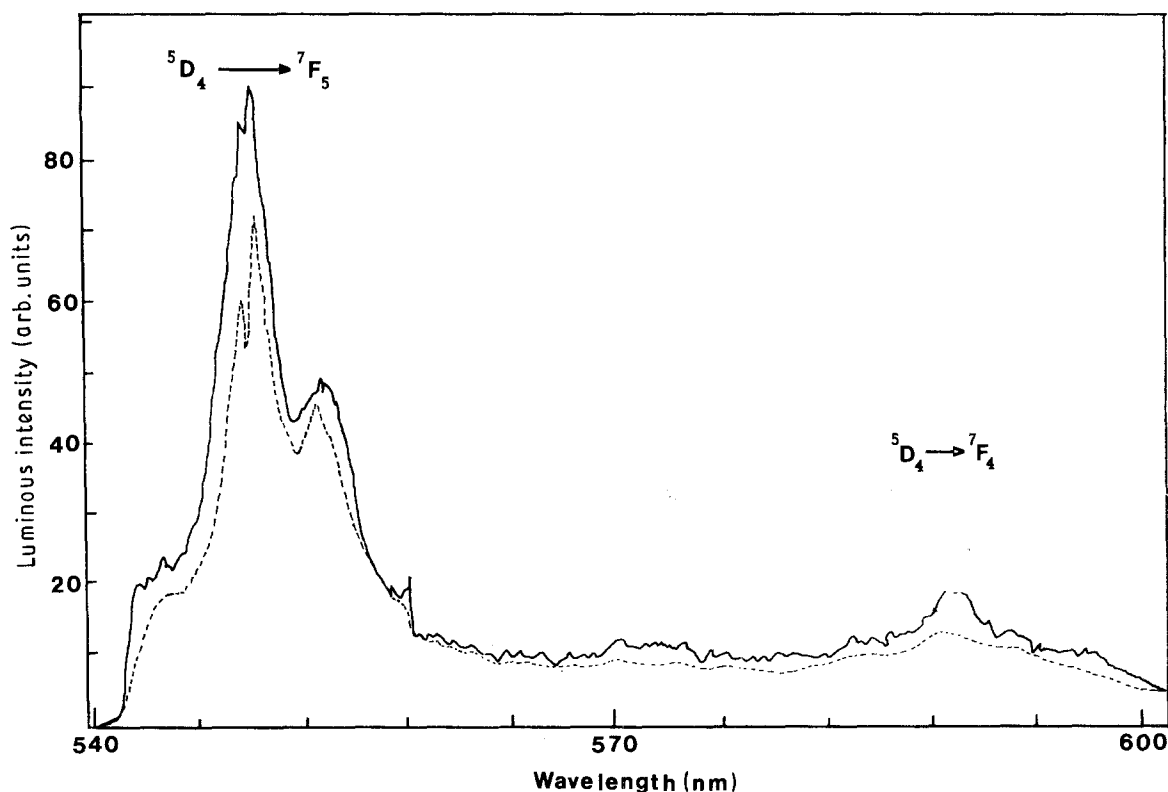


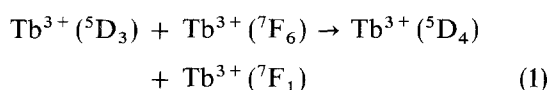
Figure 3 Emission spectra of MgO:Tb (2 mol %) phosphor recorded at (---) 90 and (—) 300 K for an exposure time of 0.166 33 s.

increase in concentration. Samples prepared without alkali halides exhibited weak emission. The presence of alkali ions, such as  $\text{Li}^+$  and  $\text{Na}^+$ , increased the emission intensity. This may be possible when two  $\text{Mg}^{2+}$  ions are replaced by one  $\text{Tb}^{3+}$  and one alkali ion. Fig. 2 shows the luminescence variation of activator concentration. From these results it is found that the optimum terbium concentration is 2 mol %. The body colour also changes from white to pale yellow with a further increase in terbium concentration. The decrease in luminescence with increasing concentration was due to the well-established phenomenon of concentration quenching.

The fluorescence of  $\text{Tb}^{3+}$  mainly occurs in the transitions  $^5\text{D}_3 \rightarrow ^7\text{F}_j$  and  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  (where  $j = 1-6$ ). The spectral energy distribution of terbium emission is strongly dependent on terbium concentration in various matrices [15]. This is also true in the case of MgO:Tb phosphors. At lower concentrations of terbium (0.01–0.05 mol %), a weak emission in the blue region is observed. This may correspond to the emission from  $^5\text{D}_{3,2}$  levels of  $\text{Tb}^{3+}$ . With an increase in terbium concentration, emission in the blue region disappears completely. Fig. 3 shows the emission spectra of MgO:Tb (2 mol %) recorded at 90 and 300 K. In all samples, five peaks at 558.46, 553.52, 549.56, 549.01 and 544.40 nm were observed which were due to  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transitions. The wave numbers corresponding to these peaks are 17901.4, 18061.2, 18191.3, 18209.5 and 18363.7  $\text{cm}^{-1}$ . An additional peak at 589.43 nm (16960.8  $\text{cm}^{-1}$ ) was observed in samples with higher concentrations, which may be from  $^5\text{D}_4 \rightarrow ^7\text{F}_4$  transitions. The relative intensity of the emission peaks in the green spectral region was com-

parable with that of emission from standard green emitting phosphors.

At lower temperatures, some of the peaks were well resolved into lines. At lower terbium concentration, when the cross relaxation probability was small, the transition from the  $^5\text{D}_3$  state dominated as a blue emission. With an increase in terbium concentration, the cross relaxation mechanism produced rapid population of the  $^5\text{D}_4$  state at the expense of  $^5\text{D}_3$ , giving a strong emission in the green region. The  $^5\text{D}_3$  emission may be quenched by [16]



Preliminary results on the cerium- or terbium-activated MgO phosphors show that MgO requires higher concentrations of terbium in the presence of cerium. Emission in the green region was observed only in samples having terbium concentrations greater than 0.5 mol %. As reported by others, for magnesium aluminates activated with terbium and cerium, an increase in  $\text{Tb}^{3+}$  concentration decreased the  $\text{Ce}^{3+}$  emission but a relatively large amount of  $\text{Tb}^{3+}$  was required for complete quenching of  $\text{Ce}^{3+}$  emission [17]. Further work on these lines is in progress which may explain the charge transfer between terbium and cerium, and also cross relaxation processes.

#### 4. Conclusion

$\text{Tb}^{3+}$  ions are effectively doped into the MgO matrix well below the melting temperature of MgO in the presence of  $[\text{Mg}(\text{NO}_3)_2]$  as a flux. Six peaks observed

in the emission spectra of MgO:Tb correspond to  $^5D_4 \rightarrow ^7F_{4,5}$  transitions of  $Tb^{3+}$  and are concentration dependent. The present results indicate that MgO activated with  $Tb^{3+}$  and  $Ce^{3+}$  can be used in trichromatic lamp phosphors as a green component.

### Acknowledgement

This research was supported by grants from the NSERCC.

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Received 2 September  
and accepted 16 December 1991