Chem Sci Trans., 2013, **2(4),** 1262-1267
DOI:10.7598/cst2013.510

Chemical Science Transactions
ISSN/E-ISSN: 2278-3458/2278-3318

RESEARCH ARTICLE

Effect of the Fuels on the Luminescence Characterisation of Tb Doped $MgAl_2O_4$ Phosphors

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Received 4 January 2013 / Accepted 14 February 2013

Abstract: There are number of factors beside the physical state of the sample, the nature of excitation radiation and types of the impurity ions in a phosphor. Less attention has been paid to the effect of fuels on host preparation in its final performance. Tb(0.5mol%) doped $MgAl_2O_4$ phosphors have been synthesised by solution combustion technique by using different fuel like carbohydrazide, hydrazine and urea and their photoluminescence (PL), thermoluminescence (TL) and mechanoluminescence (ML) properties have been studied. XRD result confirms formation of the phosphor. ML has been excited impulsively by dropping a load of mass 0.7 kg on to the phosphors from various heights. As the piston is dropped on to the sample, ML intensity initially increased with time attained an optimum value for a particular time then decreased again increases to a value than decreases and finally disappeared for all the samples. ML intensity increased with gamma doses given to the sample. PL emission spectrum showed characteristic emission of Tb^{3+} ions. Two distinct peaks were observed at around 140 °C and 300 °C in TL glow curve of all the samples. It is observed that urea enhances the luminescence properties of the $MgAl_2O_4$:Tb phosphor.

Keywords: Photoluminescence, Mechanoluminescence, Thermoluminescence, Defects, Dislocations

Introduction

Mechanoluminescence (ML), also known as triboluminescence or fractoluminescence, is light emission induced as a result of a mechanical action on a solid[1]. Although ML has been known of for at least 400 years, interest in ML compounds has almost exclusively been academic in nature and no practical applications have been established due to the weakness of the ML intensity. The ML intensity depends on the technique used for deformation. ML generated simply by grinding, cleaving or scratching produces a very dim ML. Recently, it has been shown that a high-intensity ultrasound in liquid slurries of sugar and other organic crystals could produce a 1000 times more intense ML than grinding[2] and ML materials with a high intensity have been developed, showing promising applications of this phenomenon in advance stress sensing techniques, including no contact, full-field sensing and self-diagnosis structures[3–5]. In order to confirm the presence and role of rare earth ions in aluminate based phosphors photoluminescence (PL) of the samples have been recorded by spectrofluorophotometer. The spectrofluorophotometer irradiates a sample with excitation light and measures the fluorescence emitted from the irradiated sample to perform a qualitative or quantitative analysis. Good luminescent materials should have high purity, better chemical homogeneity and high surface area in a rapid, inexpensive single step operation. The magnesium aluminate spinel ($MgAl_2O_4$) offers many advantages, such as high thermal, chemical and mechanical stability, high hardness and low electrical loss. As such, it is currently utilized as a refractory for furnace walls and firebricks and also has the potential for application as environment humidity sensors, laser materials, substrate in integrated electronics and a candidate material for fusion reactor application. It has the cubic space group Fd3m[6-14]. Rare earth doped $MgAl_2O_4$ phosphor are reported to be used in colour display devices and LED devices. Various TL studies have also been carried out to find the defect centres in TL peaks[15-16].

Solution combustion process is being considered to be a promising method to obtain phosphors because of its several advantages. The method involves a high level of molecular mixing of the components in solution leading to improved chemical homogeneity of the synthesized powder. Further, the process yields powder with high purity, better homogeneity and high surface area in a rapid, inexpensive single step operation[17]. The maximum reaction temperature generated in this process depends on fuel to oxidizer ratio, initial furnace temperature, nature of the fuel[18]. The objective of this work is to study the effect of fuel on luminescence characterisation of $MgAl_2O_4$ phosphor through solution combustion process.

Experimental

The samples were prepared by solution combustion synthesis technique. The ingredients used were $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, fuel and terbium nitrate. Desired amount of all material were taken in a glass beaker and dissolved in distilled water. The beaker was kept in a furnace set at 280 °C. The reaction is self-propagating and is able to sustain this high temperature long enough. The entire combustion process was over in about 5 min. This technique can produce a homogeneous product in a short amount of time without the use of an expensive high-temperature furnace. Formations of the samples were confirmed by XRD pattern recorded by X-ray defractometer (PW-1710). The gamma-ray-irradiation was carried out using ^{60}Co source. ML was excited impulsively by dropping a load on the sample placed on a Lucite plate with different impact velocities. The luminescence was monitored by a 931A photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope (SM-340). All ML measurements were carried out after gamma irradiation. To confirm the presence of rare earth ions in aluminate based phosphors photoluminescence (PL) of the samples have been recorded by spectrofluorophotometer. A PC based thermo luminescence analyser system (TL-1009I) was used for recording TL of gamma irradiated sample.

Results and Discussion

XRD Characterisation

XRD pattern of the $MgAl_2O_4$ phosphors by using urea, carbohydrazide and hydrazine as fuels is shown in Figure 1. XRD pattern obtained is almost similar to the JCPDS card No. 75-0905 and it may be concluded that small amount of impurity doped in the host material does not affect the XRD pattern. It is observed that ratio of peak intensities of all prepared sample were not the same. Comparing the XRD spectra with the fuels used for preparation, it is observed that more intense peak is observed for the fuel urea.

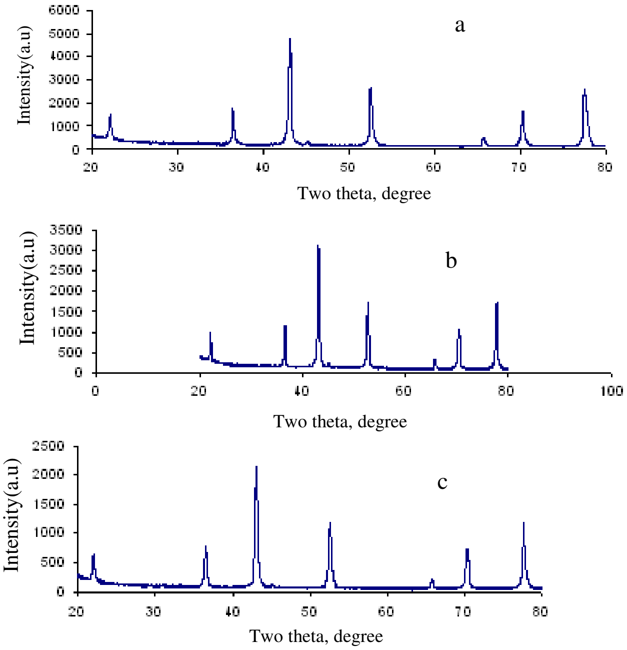

Figure 2. XRD pattern of $MgAl_2O_4$:Tb phosphors. (*a:Urea, b:Hydrazine, c:Carbohydrazide*)

Mechanoluminescence study

ML glow curve, spectra and gamma dose response can be viewed in Figures 2, 3 and 5 respectively. Figure 2 shows the ML intensity versus time curve of gamma ray irradiated $MgAl_2O_4$:Tb phosphors for different fuel. Two distinct peaks were observed when ML was excited by dropping a load of mass 0.7 kg on to it for all the sample. ML intensity initially increased with time attained an optimum value for a particular time then decreased again increases to a value than decreases and finally disappeared for all the samples. ML intensity is observed maximum for fuel urea. Figure 3 shows PL emission spectra of $MgAl_2O_4$:Tb (0.5 mol%) phosphors for different fuel. Tb^{3+} doped γ-irradiated $MgAl_2O_4$ phosphor show two prominent peaks one at around 495 nm and another at around 550 nm corresponding to transitions $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$. Peak around 550 nm is greater than the 495 nm peak. Dependence of ML intensity on γ-ray dose of $MgAl_2O_4$:Tb phosphor is shown in Figure 5. ML intensity increased almost linearly with γ-ray doses given to the samples.

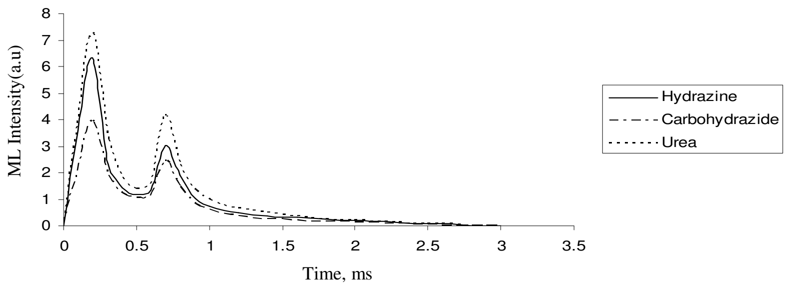

Figure 2. Time dependence of ML intensity of $MgAl_2O_4$:Tb(0.5 mol %) phosphors. γ-dose 1.1kGy

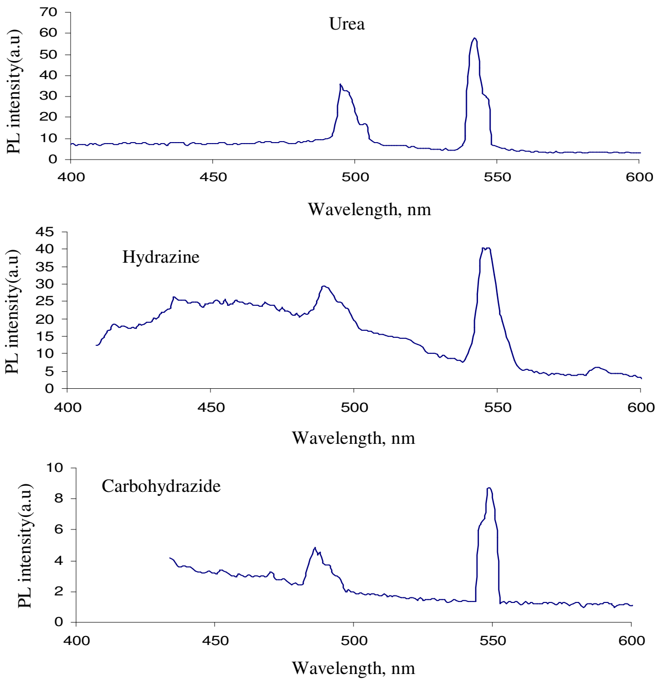

Figure 3. PL emission spectra of $MgAl_2O_4$:Tb(0.5mol%) phosphors for different fuel

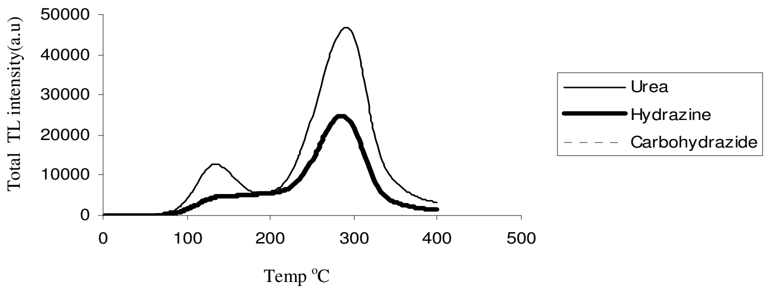

Figure 4. TL glow curve of $MgAl_2O_4$:Tb(0.5mol%) phosphors for different fuel

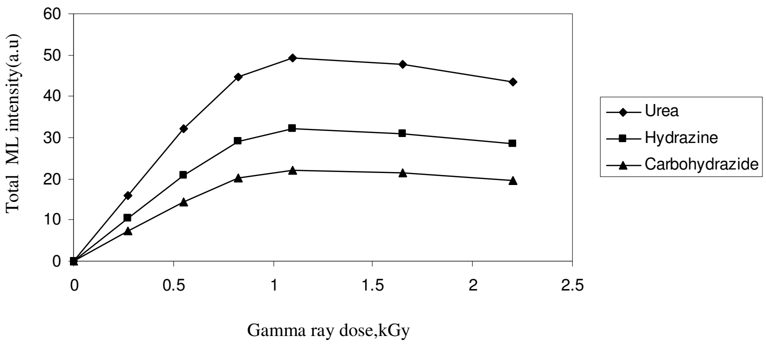

Figure 5. Dependence of ML intensity on γ-ray dose of $MgAl_2O_4$:Tb phosphors for different fuels

Some intermediate states are responsible for ML emission in this system. The origin of light emission are not due to the separation of the charges on the fracturing surfaces and piezoelectricity as the particle size is very small observed in XRD and $MgAl_2O_4$ has a centrosymmetric structure (Fd3m). Therefore it is suggested that ML of $MgAl_2O_4:Tb^{3+}$ is strongly related to the movement of dislocations and the recombination of activated electrons and holes. The movement of dislocations excites carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centres. When the electrons captured by moving dislocations are picked up by holes, deep traps and other compatible traps, then deformation bleaching occurs. At the same time, radiative recombination of dislocation captured electrons with the holes gives rise to the mechanoluminescence. On increasing the γ-dose, the density of defect centres increases and when a sample of a given mass is deformed at a given impact velocity, I_m and I_T should increase with the density of defect centres.

Thermoluminescence study

Thermally stimulated characterisation are discussed for $MgAl_2O_4$:Tb phosphor. The TL glow curve and gamma dose response are visualised in Figure 4 and 6 respectively. Figure 4 shows TL glow curve of $MgAl_2O_4$:Tb(0.5mol%) phosphors for different fuel. TL peaks at around 140 and 300 °C are observed for all the samples. Tb^{3+} doped γ-irradiated $MgAl_2O_4$ phosphor for fuel urea show optimum intensity than other fuel. The dependence of TL intensity on γ-ray dose of $MgAl_2O_4$:Tb phosphors is shown in Figure 6. TL intensity increased almost linearly with γ-ray doses given to the samples. In $MgAl_2O_4:Tb^{3+}$, the most probable centres which can be observed are the V centres (a hole trapped at a cation vacancy) and F centres (an electron trapped at an anion vacancy). It is known that the cation disorder and non-stoichiometric of aluminates like $MgAl_2O_4$ provide a large number of lattice defects, which may serve as trapping centres.

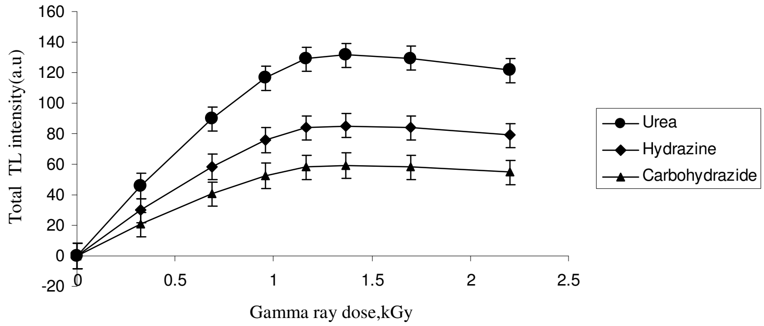

Figure 6. Dependence of TL intensity on γ-ray dose of $MgAl_2O_4$:Tb phosphors for different fuels.

It is observed from the above discussion that ML, TL and PL of $MgAl_2O_4:Tb^{3+}$ phosphor is more for urea. Urea concentration and combustion temperature in the combustion technology greatly influenced the crystalline structure and optical properties of the products. The flame temperature during combustion is 436 °C with urea. The flame temperature and the amount of gaseous product released during combustion are key factors in determining the ML, TL and PL properties of synthesised phosphors.

Conclusion

$MgAl_2O_4:Tb^{3+}$ was synthesized via a solution combustion process from metal nitrates and organic fuel. Well crystallized powders were obtained at 436 °C within 5 min. The ML technique is good one as it provides the actual time information and the ML intensity *versus* time curve gives the information about the time dependence of the compression and contact area therefore this work might be important in developing new luminescent devices applicable for ML sensors. The luminescence decay characteristics indicated that the material shows mechano and thermoluminescence. Since ML and TL increases with gamma ray dose it may be use as ML and TL dosimetry. In the future, the preparation conditions and the dopant/co-dopant content need further studies to optimize the luminescence performance of $MgAl_2O_4:Tb^{3+}$.

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