

Preparation Route, characterization and Dose measurement of MAl_2O_4 (M=Ba, Ca, Mg) phosphors activated with Dy^{3+}

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The polycrystalline powder samples of $\text{MAl}_2\text{O}_4:\text{Dy}$ (M= Ba, Mg, Ca) phosphor were prepared using urea as fuel by a combustion route. Powder X-ray diffraction confirms the phase and structure. Photoluminescence(PL) emission spectrum showed characteristic emission of Dy doped in the aluminate samples. The ML(mechanoluminescence) and TL(thermoluminescence) intensity increases with increasing gamma ray dose. TL and ML measurements were carried out on Dy^{3+} doped aluminates using gamma irradiation in the dose range 0.2-2.2 kGy. It is observed that MAl_2O_4 (M= Ba, Mg, Ca) doped with Dy phosphors have linear response up to about 1.1 kGy of radiation dose and show low fading(5-6% over the period of 15 days) for ML and TL measurement. The simple glow curve, linear response to gamma ray dose and less fading make the $\text{MgAl}_2\text{O}_4:\text{Dy}$ phosphor a suitable candidate for TL and ML dosimetry.

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1. Introduction

Rare earth doped phosphors have an important role as radiation detectors in various fields like clinical, personal and environmental monitoring of ionizing radiation. Various methods of preparation have also been developed for easy synthesis of these materials to make them available easily. The thermoluminescence (TL) materials have been widely applied to defect studying and dosimetry, such as the detection of ionizing radiation and dating in archaeology [1-3]. Thermoluminescence (TL) dosimetry has been developed to the stage that it now represents a key technique in absorbed dose determination. Of the many materials that have been studied, several are now commonly used as thermoluminescent dosimeters (TLD): a number of reviews concerning the preparation and properties of commercially and home-made thermoluminescent materials have been published during the past several years. Interest in radiation dosimetry by the TL technique has resulted in numerous efforts seeking production of new, high performance TL materials. It is within such a framework that systematic investigation of the Aluminate compound MAl_2O_4 is currently in progress.

Alkaline earth aluminate ceramics are important host materials that have been prepared and studied by several researchers for luminescence applications [4]. Alkaline earth aluminate belongs to the spinel group of minerals (MAl_2O_4) [5] with general chemical composition, AB_2O_4 , where A is a divalent atom such as Mg^{2+} , Sr^{2+} , Ca^{2+} , Fe^{2+} , Mn^{2+} , Zn^{2+} , and B is a trivalent atom such as Fe^{3+} , Al^{3+} .

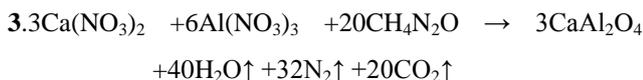
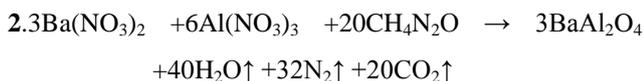
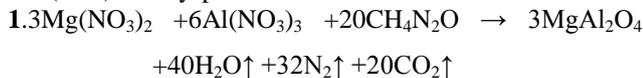
Mechanoluminescence is an interesting phenomenon which is a light emission caused by mechanical stimuli such as grinding, cutting, collision, striking, friction etc [6-8]. Eu doped SrAl_2O_4 was prepared by solution combustion method and its ML dosimetry application is discussed [9]. $\text{BaAl}_2\text{O}_4:\text{Eu}$ phosphor synthesised by combustion method may also be used for dosimetry purpose [10].

Good luminescent materials should have high purity, better chemical homogeneity and high surface area in a rapid, inexpensive single step operation. The MAl_2O_4 (M=Ba, Ca, Mg) offers many advantages, such as high thermal and chemical stability, hydrophobic behaviour, high mechanical resistance, low sintering temperature, and high quantum yields [11].

The present work discusses a straightforward solution combustion synthesis technique to prepare aluminates because of its several advantages like the process yields powder with high purity, better homogeneity and high surface area in a rapid, inexpensive single step operation [12]. Combustion synthesis technique involves the exothermic chemical reaction between metal nitrates and an organic fuel, typically urea. The maximum reaction temperature generated in this process depends on fuel to oxidizer ratio, initial furnace temperature, nature of the fuel and quantity of the initial precursor [13]. In the present research, we firstly provided a direct evidence for the detailed preparation route and then the dose measurement behaviour of such aluminate MAl_2O_4 (M= Ca, Ba, Mg) activated by Dy has been discussed.

2. Experimental Method

The samples were prepared by solution combustion synthesis technique. The ingredients used were $M(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($M = \text{Ba}, \text{Ca}, \text{Mg}$), fuel (urea) and dysprosium nitrate.

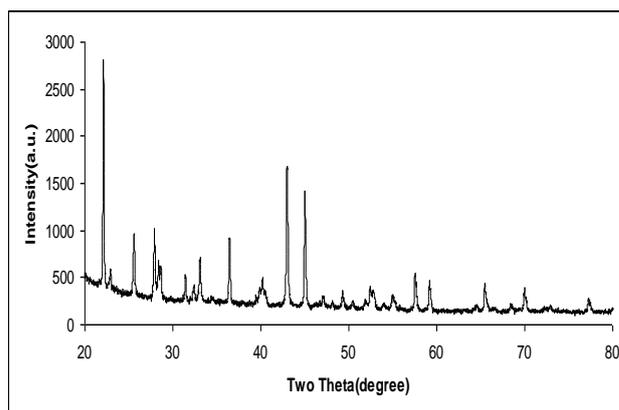


Desired amount of all material were taken in a glass beaker and dissolved in distilled water. The beaker was kept in a furnace set at 280°C . The reaction is self-propagating and is able to sustain this high temperature long enough. The entire combustion process was over in about 5 min. This technique 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 diffractometer (PW-1710). SEM measurement is carried out to observe the surface morphology of MAl_2O_4 : Dy phosphor (Model Hitachi S-3400N). The gamma-ray irradiation was carried out using ^{60}Co source. The rate of exposure of gamma rays was 0.930 kGy/hour . 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. A PC based thermoluminescence analyser system (TL-1009I) was used for recording TL of gamma irradiated sample. In order to confirm the presence and role of Dy^{3+} in MAl_2O_4 ($M = \text{Ca}, \text{Ba}, \text{Mg}$) phosphors, PL of the samples have been recorded by Spectrofluorophotometer (Simadzu RF-5301PC).

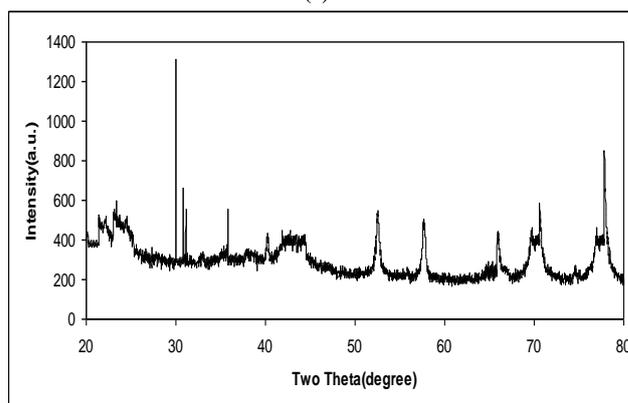
3. Result and Discussion

3.1 Characterization of Phosphor

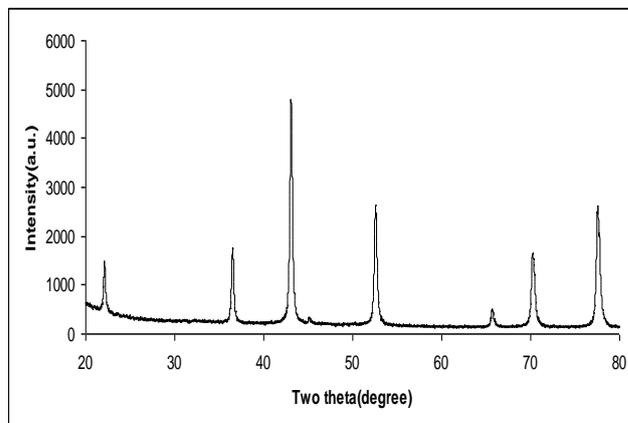
Crystalline phases of the heat-treated powders were characterized using an X-ray diffractometer (PW-1710) and well matched with the JCPDS card Nos. i.e. BaAl_2O_4 JCPDS card No. 73-1333, CaAl_2O_4 JCPDS card no. 83-2025, MgAl_2O_4 JCPDS card no. 75-0905 respectively [fig.1(a),(b),(c)]. Finally the composition and homogeneity of all the doped materials were studied by XRD analysis showing that no structural changes post-doping are detected since XRD patterns of doped materials are identical to the respective hosts used in each preparation.



(a)



(b)



(c)

Fig. 1(a),(b),(c). XRD of BaAl_2O_4 , CaAl_2O_4 , MgAl_2O_4 phosphors.

3.2 SEM Characterization

Fig. 2(a),(b),(c) show that the SEM images of MAl_2O_4 ($M = \text{Ba}, \text{Ca}, \text{Mg}$) phosphors are crystallised and randomly dispersed in the surface. It also shows the uniform crystal morphology and the grains are irregular shaped particles with a size less than $5 \mu\text{m}$, this shows that the combustion reaction of the mixture took place well. The particles possess foamy like morphology formed from highly agglomerated crystallites.

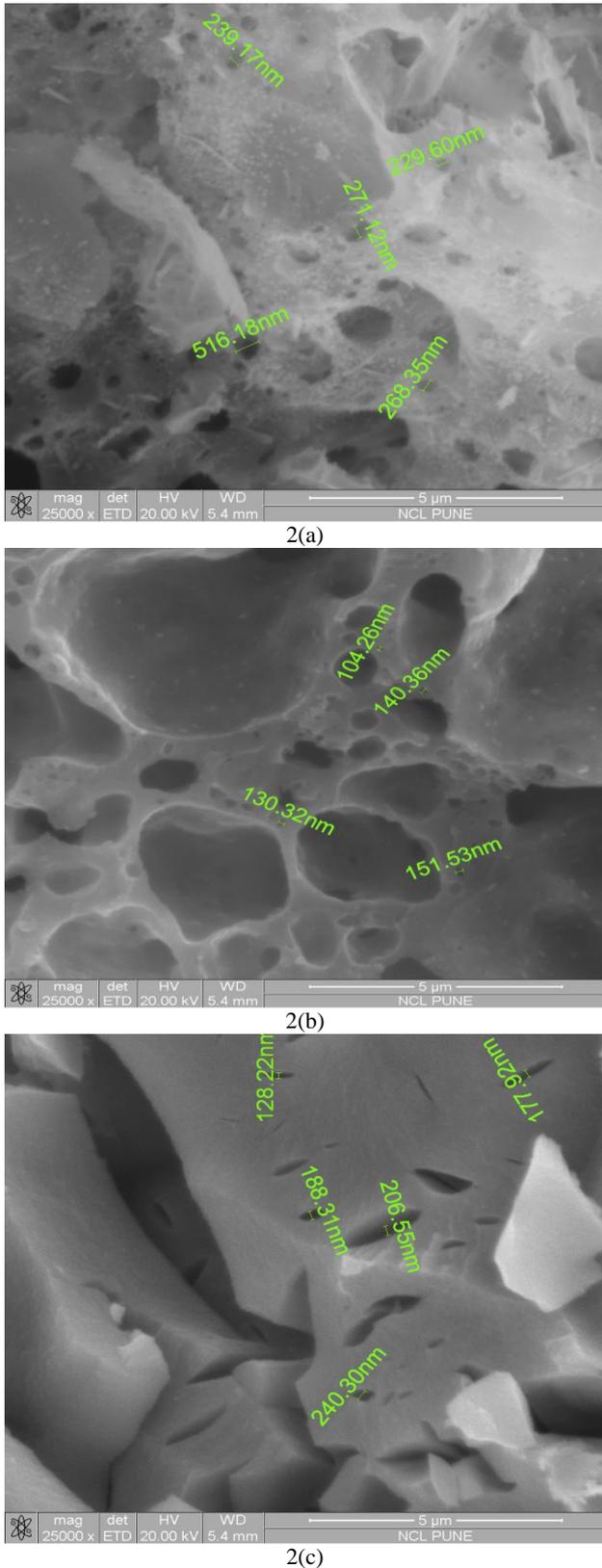


Fig 2 (a),(b),(c) SEM images of BaAl_2O_4 , CaAl_2O_4 , MgAl_2O_4 phosphors.

3.3 PL characterisation

The emission spectra of $\text{MAl}_2\text{O}_4:\text{Dy}$ ($M= \text{Ba}, \text{Ca}, \text{Mg}$,) phosphors for fuel urea is shown in fig 3. Two peaks around 472 nm and 575 nm are observed when phosphor is

excited by the electromagnetic radiation of wavelength 350 nm. Dy^{3+} emits mainly at two points in the visible region, arising from $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (430-500 nm) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (550-600 nm) transitions. The relative intensities of the two bands depend on the local symmetry. When the ratio of blue to green emission is appropriate, one can obtain white emission using Dy^{3+} . This property has generated some interest in Dy^{3+} luminescence. The spectra of the Dy^{3+} ion have been found the same in various samples (i.e. host lattice) only with change in their relative intensities.

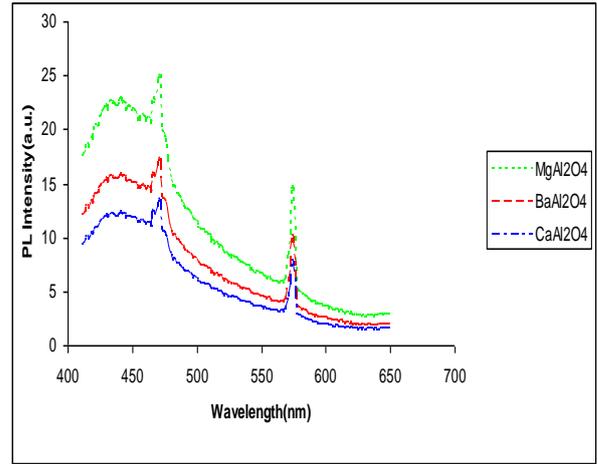


Fig.3. PL spectra of $\text{MAl}_2\text{O}_4:\text{Dy}$ ($M=\text{Ba}, \text{Ca}, \text{Mg}$) phosphors.

3.4 ML characterization

Fig. 4. shows the ML intensity versus time curve of gamma ray irradiated $\text{MAl}_2\text{O}_4:\text{Dy}$ ($M= \text{Ba}, \text{Ca}, \text{Mg}$) phosphors. Two distinct peaks were observed when ML was excited by dropping a load of mass 0.7 kg on to the sample. ML intensity increases linearly with increasing the impact velocity of the piston 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 then decreases and finally disappeared for all the samples MAl_2O_4 ($M= \text{Ca}, \text{Ba}, \text{Mg}$).

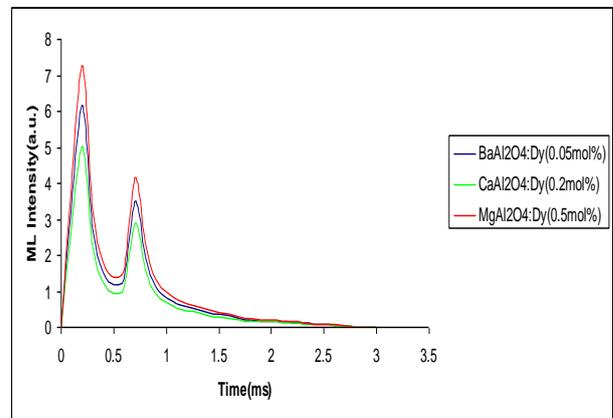


Fig. 4. Dependence of ML intensity on time of $\text{MAl}_2\text{O}_4:\text{Dy}^{3+}$ ($M= \text{Ba}, \text{Ca}, \text{Mg}$) phosphors.

Fig. 5. shows the dependence of ML intensity on γ -ray dose of $MAI_2O_4:Dy$ phosphors. ML intensity increased almost linearly with γ -ray doses given to the samples $MAI_2O_4(M= Ca, Ba, Mg)$.

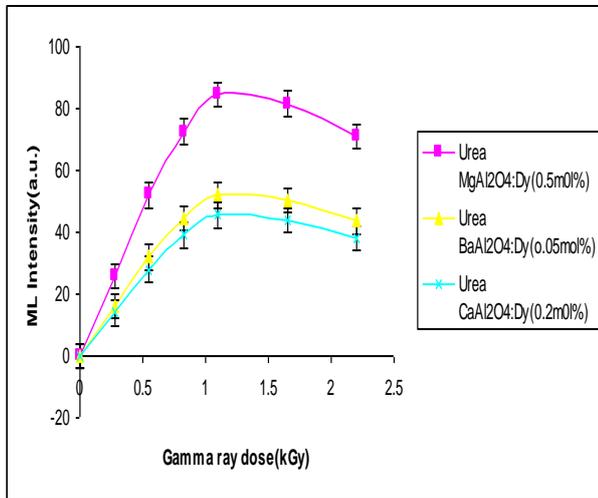


Fig.5. Dependence of gamma ray dose on ML intensity of $MAI_2O_4:Dy^{3+}$ ($M= Ba, Ca, Mg$) phosphors.

Fig. 6. shows low fading of $MAI_2O_4:Dy$ phosphor within 15 days of its irradiation with gamma ray dose. Figure shows only 25-30% fading within observed time.

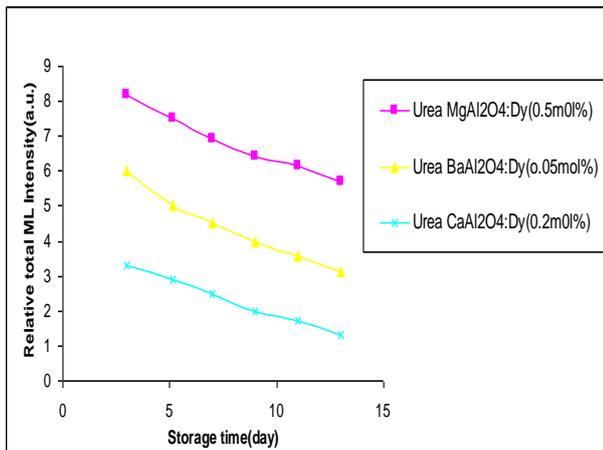


Fig.6. Dependence of relative ML intensity of $MAI_2O_4:Dy^{3+}$ ($M= Ba, Ca, Mg$) on storage time.

Under the exposure to γ -ray, electron hole pairs are created, some of the released electrons are captured by the impurity Dy^{3+} ions reducing these to Dy^{2+} and some of the free holes are captured by the trap levels. When the excitation source is removed, the trapped holes are released thermally to the valence band and migrate to recombine with the metastable state. Therefore, if the load is applied the movement of dislocation set in the motion by applied load. Some of the filled traps can be released, the captured holes and then the released holes can recombine with metastable (Dy^{2+}), transfer as to another metastable (Dy^{3+})* form, finally relax and return to the ground state

accompanying the luminescence. Thus the, ML intensity should be influenced by the amount of filled traps and the depth of the trap levels. The origin of ML may be caused by the holes released due to the movement of dislocation set in motion by the stress on the phosphors.

3.5 TL characterisation

Fig. 7. shows the TL glow curves of $MAI_2O_4:Dy^{3+}$ ($M= Ca, Ba, Mg$) powders at 1.1kGy of gamma ray dose. It shows a significant thermo-luminescence glow peak at about 110-140°C and at around 200°C. The peak indicates the existence of electron and/or hole trapping sites at that temperature in the crystal.

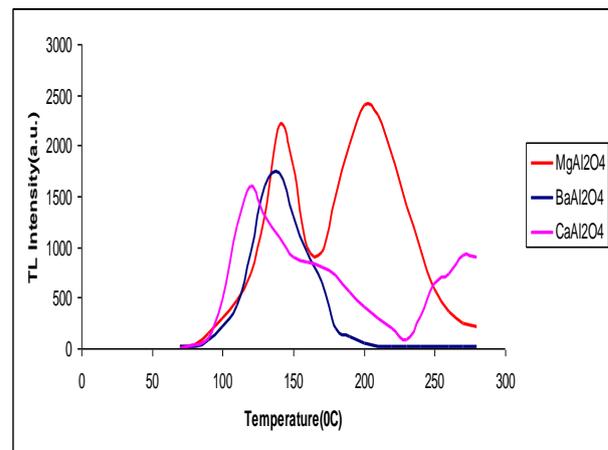


Fig.7. TL glow curve of $BaAl_2O_4:Dy$, $CaAl_2O_4:Dy$, $MgAl_2O_4:Dy$ phosphors.

Fig. 8. show total TL yields as a function of γ -ray doses given to the rare earth doped aluminate based phosphors. It is found that TL intensity increases with increasing the γ -ray doses given to the samples and seem to saturate for higher values of gamma doses.

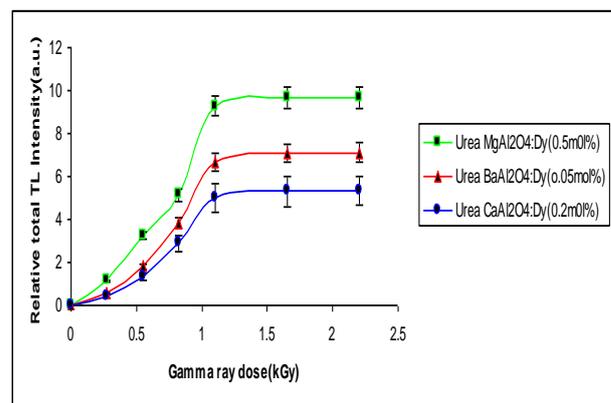


Fig. 8. Dependence of gamma ray dose on TL intensity of $MAI_2O_4:Dy^{3+}$ ($M= Ca, Ba, Mg$) phosphors.

Fig. 9. shows fading of TL over 15 days from gamma-ray irradiation of rare earth doped aluminate based phosphors. Maximum 8% reduction in TL yield was observed.

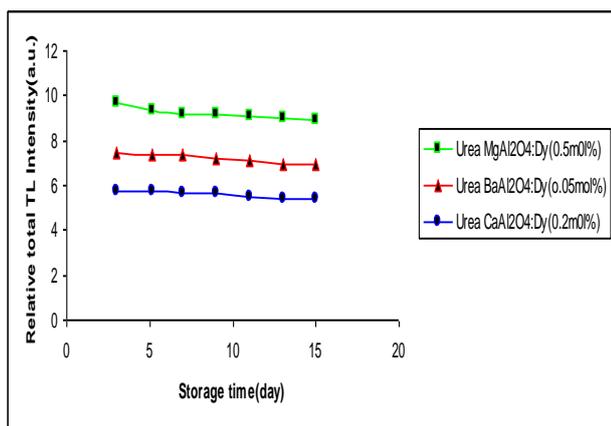


Fig. 9. Dependence of relative TL intensity of $\text{MAl}_2\text{O}_4:\text{Dy}^{3+}$ (M= Ba, Ca, Mg) on storage time.

TL is a phenomenon occurs due to the imperfections. Incorporation of rare earth impurity increases the population of defects present in the host lattice. When the samples were exposed to gamma rays it induces radicals as Al_2O^- , Al_2O_4^- , Al_2O_3^- etc along with conversion of Dy^{3+} into Dy^{2+} . When sample is heated release of electron from traps (V-centre and F-centre) may take place. The subsequent electron hole recombination may release energy. This energy may non-radiatively transfers to Dy^{3+} ions causing their excitation and subsequent de-excitation of excited Dy^{3+} ion may give rise to the characteristic luminescence

4. Conclusion

Well crystallized $\text{MAl}_2\text{O}_4:\text{Dy}^{3+}$ (M= Ba, Ca, Mg) powdered phosphor was obtained by Solution Combustion Technique at around 440°C with golden yellow flame (loss in ignition is only 3%). It was found that ML and TL intensity strongly depends upon gamma ray dose. The TL and ML dosimetric characteristics imply the potential of

$\text{MAl}_2\text{O}_4:\text{Dy}^{3+}$ (M= Ba, Ca, Mg) phosphor as gamma-ray TL and ML materials in the personal protection dosimetry field. They show linear dose simple TL and ML glow curve and less fading. Among three aluminates (CaAl_2O_4 , BaAl_2O_4 and MgAl_2O_4) investigated here, we found that MgAl_2O_4 is a suitable candidate for TL and ML dosimeter.

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