

MECHANOLUMINESCENCE PROPERTIES OF EUROPIUM DOPED DI-STRONTIUM MAGNESIUM DI-SILICATE PHOSPHOR

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ABSTRACT

Europium doped di-strontium Magnesium di-Silicate ($\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$) phosphor was prepared by the solid state reaction method and its mechanoluminescence (ML) characteristic was investigated. The obtained phosphor was characterized using powder X-ray diffraction (XRD) analysis. The formation of phosphor was confirmed by XRD. The crystal structure of prepared $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor was akermanite type structure which belongs to the tetragonal crystallography with space group $P4_21m$, this structure is a member of the melilite group and forms layered compound. The ML intensity of prepared phosphor was increases linearly with the increasing of mechanical load. Decay rates for different impact velocities were also calculated using curve-fitting techniques. The time of the peak ML and the rate of decay did not change significantly with respect to increasing impact velocity of the moving piston and peak ML intensity varied linearly.

Keywords: $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$; XRD; Akermanite; Melilite; Mechanoluminescence.

INTRODUCTION

Luminescence induced during any mechanical action on materials is known as mechanoluminescence (ML). ML can be excited either by grinding, rubbing, cutting, cleaving, shaking, scratching, crushing, compressing, or by impulsive deformation of solids. ML has been observed in insulators, semiconductors as well as in conductors. This phenomenon has been observed in many kinds of solids including ionic crystals, semiconductors, metals, glasses and organic crystals (Vij, 1998). In the present ML studies, an impulsive deformation technique has been used. During the deformation of a solid, a great number of physical processes may occur within very short time intervals, which may excite or stimulate the process of photon emission. When a moving piston is applied to the phosphor, initially the ML intensity increases with time, attains a peak value and then decreases with time. Such a curve between the ML intensity and deformation time of phosphors is known as the ML glow curve (Chandra et al. 2010). ML has found various important applications such as impact sensors in spacecrafts (the emission intensity can be used to determine the kinetic energy of impact), fracture sensor, damage sensor, stress sensor for the visualizations of stress field near the crack-tip, stress distribution in the solids, and quasidynamic crack-propagation in solids etc. Thus, many researchers have been focused on the investigation of phosphors with high ML (Sahu et al. 2014a). Until now, some phosphors with high ML, such as red phosphors $\text{BaTiO}_3\text{-CaTiO}_3:\text{Pr}$, (Xu et al. 1999) green phosphors $\text{SrAl}_2\text{O}_4:\text{Eu}$, (Xu et al. 1999) yellow phosphors $\text{ZnS}:\text{Mn}$, (Xu et al. 1999) and blue phosphor $\text{CaYAl}_3\text{O}_7:\text{Eu}$ etc., (Xu et al. 2000) have been developed. However, the requirement of application for ML sensors still is not satisfied with the development of ML materials. At the same time, the high stabilities, such as resistance of water, thermal stability are also very important for the application of ML. More ML phosphors with strong ML intensity and high stability are needed.

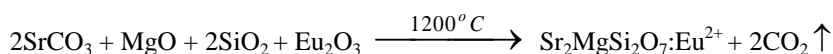
In this paper, silicate was chosen as a host due to its special properties, such as low cost, easy preparation, excellent thermal and chemical stabilities, and especially the strong absorption in the near-UV region. Therefore, in this paper, we investigate the structural characterization and luminescence properties of europium doped di-strontium Magnesium di-Silicate ($\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$) phosphor by the solid state reaction method. The

crystal structure was analyzed by X-ray diffractometer (XRD) The luminescence properties were also investigated on the basis of ML and ML decay.

EXPERIMENTAL

Phosphor Synthesis and Measurement techniques

The powder samples of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor was prepared by the high temperature solid state reaction method and 0.1 mole % of boric acid [H_3BO_3 (99.90%)] was added as flux. The raw materials are SrCO_3 (99.90%), MgO (99.90%), SiO_2 (99.99%) and Eu_2O_3 (99.99%) all of analytical grade, were employed in this experiment. Initially, the raw powders were weighed according to the nominal compositions of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor, then the powders were mixed and milled thoroughly for 2 hour using the mortar and pestle. The chemical reaction used for stoichiometric calculation is:



The grinded sample were placed in an alumina crucible and subsequently fired at 1200°C for 3 hours in a weak reducing atmosphere. The weak reducing atmospheres are generated with the help of activated charcoal.

The powder X-ray diffraction pattern has been obtained from Bruker D8 advanced x-ray powder diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.540 \text{ nm}$) and data were collected over the 2θ range 10° - 80° . The experimental set up used for the impulsive deformation of ML was shown in Fig.1. A load (moving piston) of particular mass and shape was dropped from different heights [different impact velocities (v_0)] for striking the prepared $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor. In this experiment, the mass of the dropping load was 400 g and shape of the load was cylindrical. The phosphor under study was placed on the upper surface of a transparent lucite plate and it was then covered with a thin aluminum foil and fixed with an adhesive tape. The foil reflects light and prevents scattering of the fragments during the impact of a moving piston onto the prepared phosphor. This arrangement eliminates the error in the ML measurement due to the scattering of the crystallite fragments during the impact of the load onto the phosphor. The housing is made up of thick soft iron to provide shielding from light and magnetic field. The slit arrangement at the window is provided to adjust the size of the window according to the incident beam. When the phosphor placed on the lucite plate was crushed by impact of the moving piston, light is emitted (Sahu et al. 2014b).

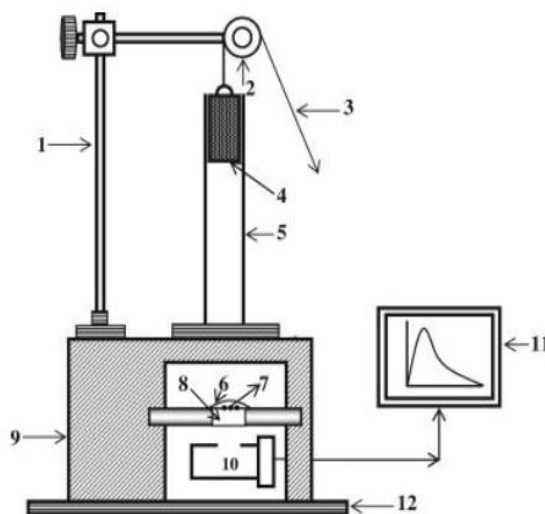


Fig. 1 Schematic diagram of the experimental setup for ML measurement

In the Fig.1, **1** - Stand; **2** - Pulley; **3** - Metallic wire; **4** - Load; **5** - Guiding cylinder; **6** - Aluminium foil; **7** - Phosphor; **8** - Transparent Lucite plate; **9** - Wooden block; **10** - Photomultiplier tube (PMT); **11** - Storage oscilloscope; **12** - Iron base mounted on a table. By changing the distance between the moving piston to be dropped and the sample placed on the lucite plate, the impact velocity of the load, could be changed from 198 cm/s to 313 cm/s (20 to 50 cm height). Since the pulley and the guiding cylinder used were of negligible friction, the impact velocity was taken as $\sqrt{2gh}$, where “g” is the acceleration due to gravity and “h” is the height through which the moving piston is dropped freely. An RCA 931A photomultiplier tube (PMT) was placed below the transparent lucite plate. The PMT was run at 750 Volts. The output of photomultiplier tube was connected to the phosphorescent screen oscilloscope (Scientific 300 MHz, SM 340). The ML glow curve can be plotted with the help of SM-340 application software installed in a computer attached with the storage oscilloscope (Sahu et al. 2014c). All measurements were carried out at a room temperature.

RESULTS AND DISCUSSION

XRD analysis

The crystal structure of the sintered phosphor was analyzed by the XRD. The typical XRD patterns of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor with the standard XRD pattern is shown in Fig. 2. The position and intensity of diffraction peaks of the prepared $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor were matched and found to be consistent with the standard XRD pattern (COD card No. 96-431-7124) by MATCH 2 software. The figure of merit (FOM) while matching these was 0.9566 (96%), which illustrates that the phase of the prepared sample agrees with the standard XRD patterns. In Fig. 2, it can be concluded that prepared phosphor was chemically and structurally $\text{Sr}_2\text{MgSi}_2\text{O}_7$ phosphor. The crystal structure of the $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor was an akermanite type structure which belongs to the tetragonal crystallography with space group $P4_2/m$, this structure is a member of the melilite group and forms a layered compound.

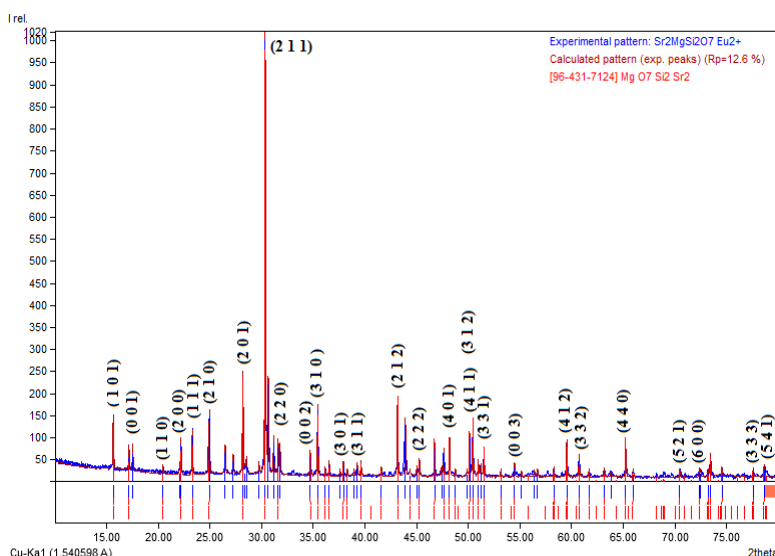


Fig. 2 XRD patterns of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor

Mechanoluminescence (ML)

Fig. 3 shows that the characteristics curve between ML intensity versus time for different heights ($h = 20, 30, 40, 50$ cm). The phosphor was fracture via dropping a load [moving piston] of particular mass (400 g) and cylindrical shape on the $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor. The velocity of the moving piston, holding the impact mass, could be changed, by changing the height through which it was dropped. Every time for the ML measurement, the quantity of

$\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor was kept constant (8 mg). When the moving piston is dropped onto the prepared phosphor at different height, light is emitted. The photon emission time is nearly 2 ms, when prepared $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor fractures. In these ML measurements, maximum ML intensity has been obtained for the 50 cm dropping height and ML intensity increases linearly with the increases the falling height of the moving piston. The sintered $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor was not irradiated by any excitation source (Sahu et al. 2015 a). Fig. 3 (inset) shows the characteristics curve of ML intensity versus impact velocities for $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor. It is seen that, ML intensity increases linearly with increasing impact velocity [$\sqrt{2gh}$, (where “g” is the acceleration due to gravity and “h” is the height through which the load is dropped freely)] of the moving piston. The ML intensity of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor increases linearly with increasing the mechanical stress (Zhang et al. 2009c).

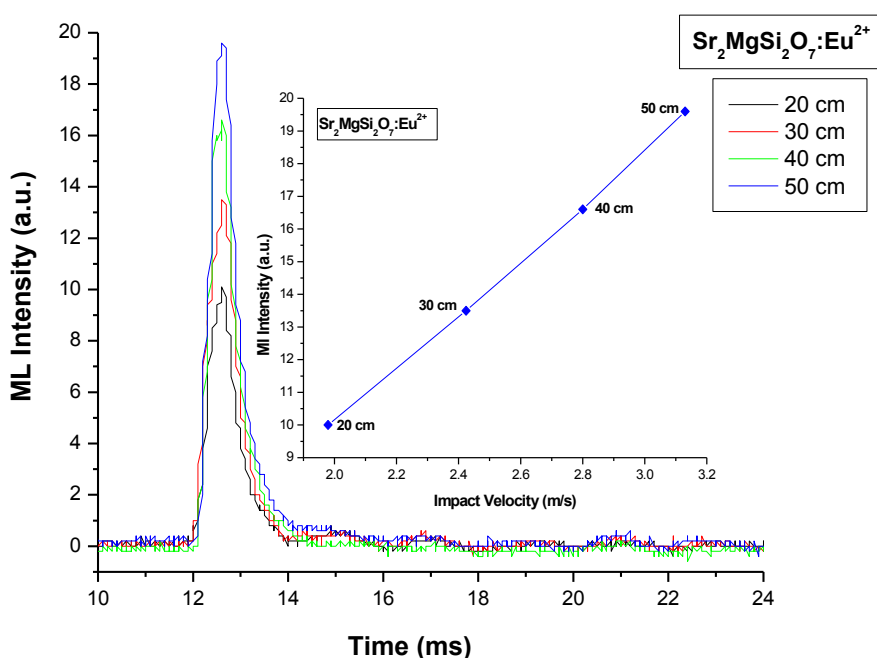


Fig. 3 ML intensity versus time curve of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor

(Inset - ML intensity versus impact velocity curve of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor)

When the load or piston makes an impact on the crystal with an initial velocity v_0 , the former decelerates and after a particular time its velocity becomes zero. The time dependence of the velocity of the piston may be written as

$$v = v_0 \exp(-\beta v_0 t) \quad (1)$$

Where β is a constant, equation (1) can be written as

$$\frac{dx}{dt} = v_0 \exp(-\beta v_0 t) \quad (2)$$

Where dx is the compression of the crystal during the time interval dt .

Integrating equation (2), we have

$$x = \frac{1}{\beta} \exp(-\beta v_0 t) + C \quad (3)$$

$x=0$ for $t=0$, therefore, equation (3) may be written as

$$x = \frac{1}{\beta} [1 - \exp(-\beta v_o t)] \tag{4}$$

The phosphor is in powder form and the impact velocities compress it to a certain extent, but this does not change significantly with increasing impact velocity. Equation (4) shows that impact time remains mostly unchanged with increasing impact velocity because there is no significant change in compression, which is expressed by ‘x’ in equation (4). This may be one possible reason why the time that corresponds to the peak ML intensity does not change significantly with increasing impact velocity (Sahu et al. 2015b).. Fig. 4 shows the time corresponds to ML signal peak with impact velocity of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor.

The relationship between semi-log plot of ML intensity versus $(t-t_m)$ for $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor is shown in Fig. 5, and the lines were fitted using the following equation (5) with Origin Pro 8.0

$$\tau = \frac{1}{\text{slop of straight line}} \tag{5}$$

Curve fitting results show that decay constant (τ) varies from 0.87 to 0.94 ms. The ML decay constant value is increases with the impact velocities, and maximum for the maximum impact velocities (See table 1) (Sahu et al. 2015c).

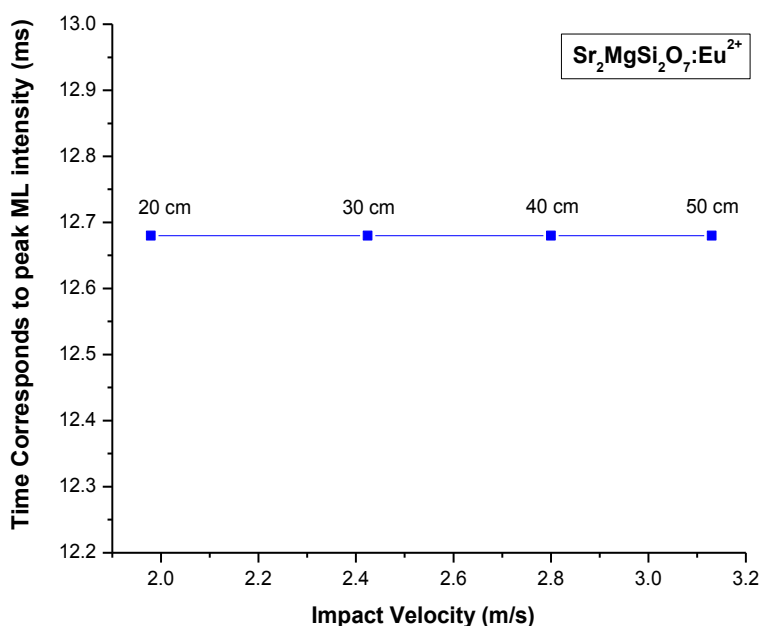


Fig. 4 Time corresponds to ML signal peak with impact velocity of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor

When a mechanical stress, such as compress, friction, and striking, and so on, was applied on the sintered $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors, piezo-electric field can be produced. Therefore, in such phosphor the ML excitation may be caused by the local piezoelectric field near the impurities and defects in the crystals. During the impact on the

material, one of its newly created surfaces gets positively charged and the other surface of the crack gets negatively charged. Thus, an intense electric field of the order of $10^6 - 10^7$ Volt cm^{-1} is produced (Chandra et al. 1995). Under such order of electric field, the ejected electrons from the negatively charged surface may be accelerated and subsequently their impact on the positively charged surfaces may excite the luminescence center such as Eu^{2+} . Subsequently, the de-excitation of excited Eu^{2+} ions may give rise to the light emission due to the transition from excited state to ground state (Zhang et al. 2009a). As the impact velocity increases, the impact pressure also increases leading to the increase in the electric field at local region which causes the decrease in trap depth. Hence the probability of de-trapping increases. From Fig. 3 (inset), it can be seen that with increasing impact velocity, ML intensity also increases linearly i.e., the ML intensity of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor are linearly proportional to the magnitude of the impact velocity, which suggests that this phosphor can be used as sensors to detect the stress of an object (Zhang et al. 2009a).

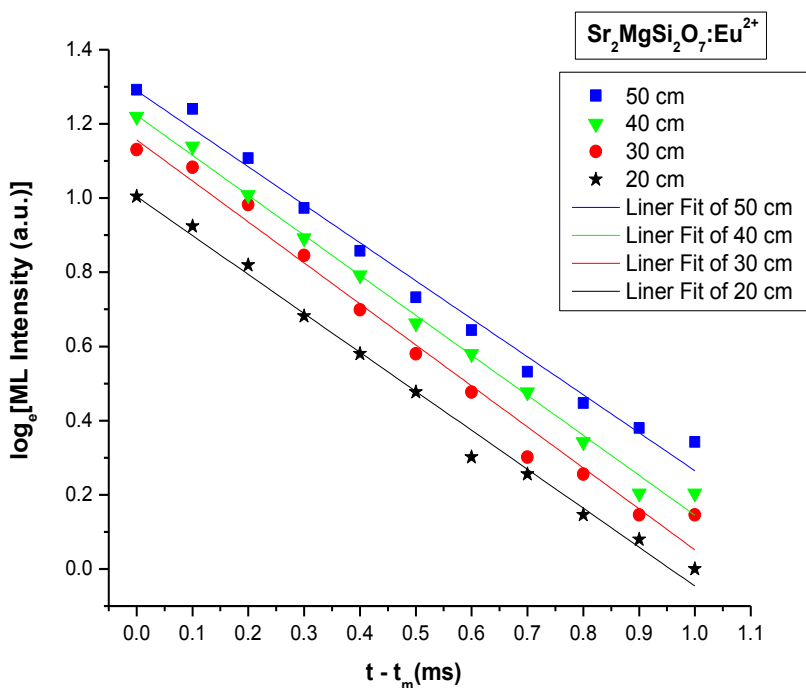


Fig. 5 Semi-log plot of ML intensity versus $(t - t_m)$ for $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor

Table 1 Calculation of ML decay constant

Impact velocity	20 cm	30 cm	40 cm	50 cm
□ □ Decay constant (ms)	0.87	0.88	0.90	0.94

CONCLUSIONS

In Summary, europium doped di-strontium magnesium di-silicate phosphor namely $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ are prepared by the solid state reaction method. The radius of Eu^{2+} (1.12\AA) is close to that of Sr^{2+} (about 1.12\AA) rather than Mg^{2+} (0.65\AA) and Si^{4+} (0.41\AA). Therefore, the Eu^{2+} ions are expected to occupy the Sr^{2+} sites in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host.

When Eu^{2+} enters the lattice, it will replace the Sr^{2+} in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host and occupy Sr^{2+} lattice sites due to distortion in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host crystal lattice. Decay rates for different impact velocities were also calculated using curve-fitting techniques. The time of the peak ML and the rate of decay did not change significantly with respect to increasing impact velocity of the moving piston and peak ML intensity varied linearly. It is worthy to note that the dependence between ML intensity of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor to the impact velocity is close to linearity, which suggests that these phosphors can be used as sensors to detect the stress of an object. Thus, the solid state reaction method furnishes a simple method for preparing silicate based phosphor.

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