

THE LOCAL STRUCTURE OF PHOSPHOR MATERIAL, $\text{Sr}_2\text{MgSi}_2\text{O}_7$ AND $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ BY INFRARED SPECTROSCOPY

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ABSTRACT

The structure of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7$ doped with Eu^{2+} were presented in this paper. The samples have been prepared using solid state reaction, whereas it has been sintered at 1350°C for 3 hour in air and 1350°C for 3 hour in a weakly reductive atmosphere of 10% H_2 -90% N_2 respectively. The obtained samples were characterized using EDAX, X-ray Diffraction (XRD) and Infrared Spectroscopy. X-ray diffraction pattern shown that the single crystalline phase obtain was contained $\text{Sr}_2\text{MgSi}_2\text{O}_7$ for both doped and undoped sample. The structure features of both samples base on silicate tetrahedral were obtained by infrared spectroscopy. Vibration band at 1638 cm^{-1} and 1474 cm^{-1} in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ doped with Eu^{2+} represent Mg^{2+} and Sr^{2+} respectively. Majority vibration mode was shifted to high frequency when doping Eu^{2+} in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ sample.

INTRODUCTION

Materials that generate luminescence are called phosphors. A phosphor is a substance that exhibits the phenomenon of phosphorescence (sustained glowing after exposure to energized particles such as electrons). Phosphors are transition metal compounds or rare earth compounds of various types. Almost all good inorganic phosphors consist of a crystalline “host material” in which small amount of certain impurities, the “activators” are dissolved [1]. The host materials are typically oxides, sulfides, selenides, halides or silicates of zinc, cadmium, manganese, aluminum, silicon, or various rare earth metals. Silicate host is characteristic with chemical and physical stability, easy preparation and low cost. Therefore the silicate host is attracting more intention in the application of long afterglow [2-4].

Recently, Eu^{2+} doped alkaline earth magnesium disilicates ($\text{M}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, $\text{M}=\text{Ca}$, Sr , Ba) have been found to show persistent luminescence probably strong and long enough to attract commercial interest [5,6]. A lot of reports have been published focus on luminescent properties of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ phosphor compare to local structure of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ or another phosphor material. However Y.-I. Kim *et. al* has been study

about crystal structural of refinement of $\text{CaMgSi}_2\text{O}_6$: Eu^{2+} using X-ray powder diffraction data [7].

From Jong Hyuk Kang *et. al* 2005 was reported that structure of the sample can affect the luminescent properties of phosphor material entitled that the correlation of PL properties of $(\text{Y, Ln})\text{V}^{4+}:\text{Eu}^{3+}$ ($\text{Ln}=\text{Gd}$ and La) phosphor with their crystal structure [8]. The microscopic and even nanoscale structure of distrontium magnesium disilicates doped with Eu^{2+} and co-doping Dy^{3+} ($\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: $\text{Eu}^{2+}\text{Dy}^{3+}$) was studied by high-resolution transmission electron microscopy (TEM) to find lattice defect [9].

In the present work, $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} phosphor was prepared by solid state reaction method. The influence of doping content Eu^{2+} in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host and their structural and behavior of vibration was investigated by infrared spectroscopy.

EXPERIMENTAL

SiO_2 , SrCO_3 , MgO , Eu_2O_3 were employed as the raw materials. Small quantities of B_2O_3 (about 5% mol) were added as a flux. The raw material were mixed homogeneously by the ball mill for 2 h, and pre-fired at 900°C for 2 h in air. Then the product was reground and pressed into pallets, finally sintered at 1350°C for 3 h with a weak reductive atmosphere of flowing 10% H_2 -90% N_2 gas. The composition of the sample was measured by EDAX.

Phase identification of the synthesized phosphors was performed using X-ray diffraction method, using powders form. The XRD measurements were carried out with $\text{CuK}\alpha$ radiation operating at 40 kV, 30 mA at room temperature using Siemens Diffractometer D5000, equipped with diffraction software analysis. Diffraction patterns were collected in the 2-theta (2θ) range from 10° to 80° , in steps of 0.04° and 1s counting time per step.

The samples were prepared prior for infrared excitation using the potassium bromide (KBr) pellet method on powdered samples. The IR spectra were measured, where at least 10 scans were recorded at a resolution of 4 cm^{-1} . The IR spectra dispersed in the samples were recorded in the range $400\text{--}2000\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Figure 1 shows the phosphor powder material obtained in this study. In Figure 1(a) show the powder sample of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ did not doped with Eu^{2+} and (b) show a phosphor powder product $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} after irradiated by UV light for 10 minutes. The powder emitted blue light color in visible range and it able to glowing in the dark after about 5 minutes. This powder glows due to the absence of doping material, Eu^{2+} . The same doping material has been used to explain the luminescence of Eu^{2+} in $\text{Sr}_2\text{SiO}_3\text{Cl}_2$ [10]. Rare-earth elements are dopants donating interesting and often useful

properties to host crystals. In many cases, such as in optical absorption or light emission, there exists a direct relation to the energies in ground and excited states of the electron system [11].

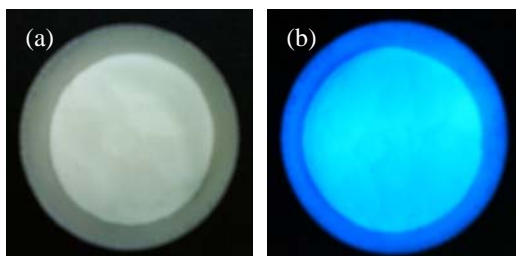


Figure 1: Powder sample (a) $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and (b) $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}$ after irradiated by UV light.

Figure 2(a) and (b) shows the X-ray diffraction (XRD) patterns of doped Eu^{2+} and undoped $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host respectively. The position and intensity of diffraction peaks of the polycrystalline powder doped and undoped $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host are consistent with that of the powder diffraction file (ICDD: 75-1736). The $\text{Sr}_2\text{MgSi}_2\text{O}_7$ crystalline phase is the same with the lattice parameters are $a=b=7.99570 \text{ \AA}$, $c=5.15210 \text{ \AA}$. Its symmetry is tetragonal with the type P_{421m} (113 space number and D_{2d}^3 space group) and has akermanite structure [12]. From the analysis of XRD, it was revealed that the doping of Eu^{2+} did not influence the crystal structure of phosphor host matrix due to cannot detect doping material which is less than 5 mol %. The composition of the powder sample has been measured using EDAX. The result of the EDAX analysis is shown in Figure 3, which is representing the composition of the powder sample studies.

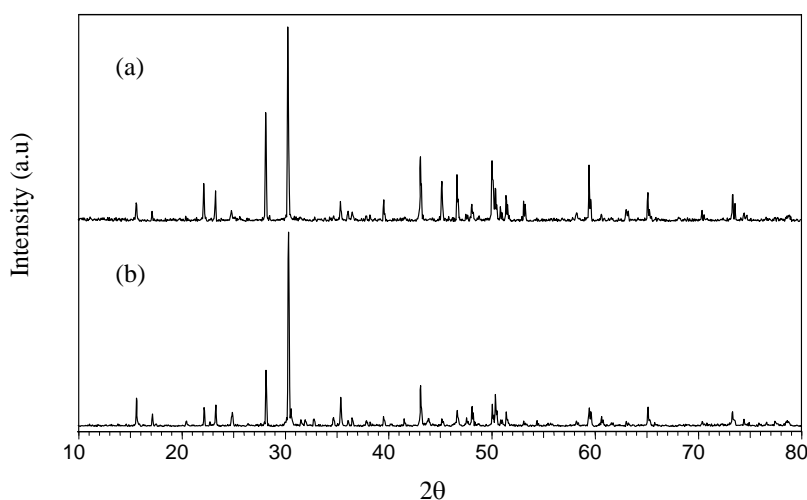


Figure 2: X-ray Diffraction of (a) $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}$ and (b) $\text{Sr}_2\text{MgSi}_2\text{O}_7$

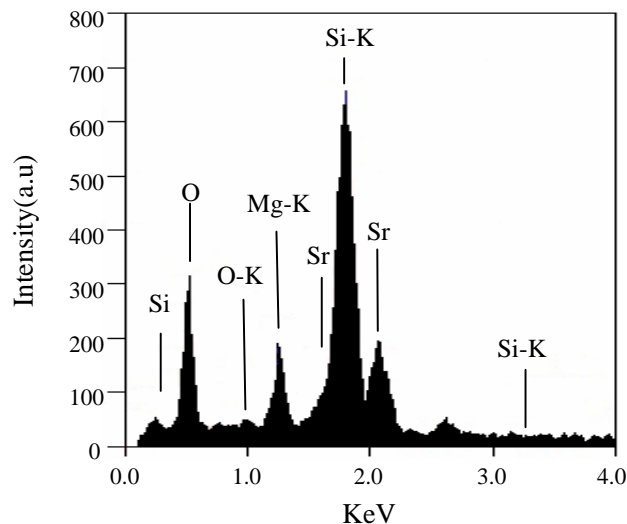


Figure 3: EDAX analysis

The infrared spectra of undoped and doped Eu^{2+} $\text{Sr}_2\text{MgSi}_2\text{O}_7$, SiO_2 , SrCO_3 , MgO , and Eu_2O_3 in the range of $400\text{-}2000\text{ cm}^{-1}$ are shown in the Figure 4. The vibration bands are listed in the Table 1. Vibration mode for deformation of SiO_2 at 458 and 509 cm^{-1} and tetrahedral Si^{4+} are 693 , 777 , 794 , 1082 cm^{-1} . Tetrahedral Si^{4+} site change to Si^{6+} site when modifier (SrCO_3 and MgO) was added in the host material (SiO_2) with vibration mode at 668 , 704 , 839 , 923 , 965 , 1004 cm^{-1} which characterize the vibrations of non-bridging oxygen at Si^{4+} tetrahedral. Beside that, the vibration mode of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} was shifted from $\text{Sr}_2\text{MgSi}_2\text{O}_7$ in the range $440\text{-}1004\text{ cm}^{-1}$ to $470\text{-}1110\text{ cm}^{-1}$.

The typical feature of the infrared spectrum in this work is influence of vibration from doping material, Eu^{2+} in $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host structure. The spectrum of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} shows the vibration band at 1638 cm^{-1} and 1474 cm^{-1} which influence from Eu^{2+} . Eu^{2+} ions is expected to replace Sr^{2+} in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host since the ionic radius of the eight coordinated species of Eu^{2+} and Sr^{2+} are close to a perfect match 1.25 \AA and 1.26 \AA respectively [13]. Eu^{2+} does not replace Mg^{2+} site due to ionic radius of Mg^{2+} (0.57 \AA) is smallest than Eu^{2+} [9]. The vibration mode at 1638 cm^{-1} and 1474 cm^{-1} represent the vibration mode of Mg^{2+} and Sr^{2+} respectively 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 [14]. Original position of Sr^{2+} was replaced by Eu^{2+} and the original of Sr^{2+} located at somewhere. Therefore the vibration mode of Sr^{2+} at 1474 cm^{-1} is clearly observed from $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} . Vibration mode of Mg^{2+} was observed at 1638 cm^{-1} because of the same of distortion in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host crystal lattice.

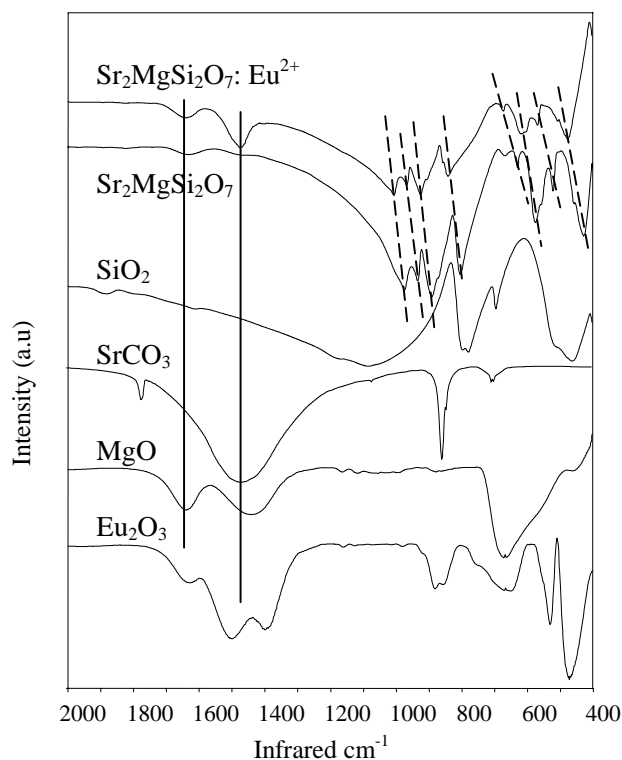


Figure 4: Infrared spectra of powder sample.

Table 1: Infrared bands of powder $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, SiO_2 , SrCO_3 , MgO , and Eu_2O_3

	Infrared frequencies observed															
$\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$	1638	1474	1110	1010	966	928	912	846	765	670	614	600	566	539	504	473
$\text{Sr}_2\text{MgSi}_2\text{O}_7$	1641	1497	1110	1004	960	923	904	839	704	668	615	601	565	497	440	
SiO_2	1616			1082			900	794	777	693				509	458	
SrCO_3	1597	1465	1303	1071				855	702							
MgO	1639	1434	1160	1116			875			671	657		560			458
Eu_2O_3	1634	1503	1399	1161	979		879	854	755	707	672	647		529		471

CONCLUSION

$\text{Sr}_2\text{MgSi}_2\text{O}_7$ host and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors were prepared by solid-state reaction in weak reductive atmosphere. From the sample powder, $\text{Sr}_2\text{MgSi}_2\text{O}_7$ crystal phase was identify by X-ray diffraction. In this study, we have investigated the influence doping material in the host crystal lattice using infrared spectroscopy. Consequently, it was found that Eu^{2+} ions affected the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host crystal lattice when vibration mode was shifted to high frequency when doping Eu^{2+} in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ sample and new vibration mode clearly at 1474 and 1638 cm^{-1} observed to identify of Sr^{2+} and Mg^{2+} . This study shows that infrared spectroscopy can be used as local probe of doping rare earth in the host material.

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