



Structural Characterization and Optical Properties of Monoclinic Ba₂MgSi₂O₇ (BMS) Phosphor

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ABSTRACT

Pure Ba₂MgSi₂O₇ (BMS) white light emitting phosphor was synthesized by high temperature solid-state reaction route. The phase identification of the prepared phosphor was done with the help of XRD technique. Actual phase formation and functional group identification of this phosphor was confirmed through Fourier Transform Infra-red Spectroscopy (FTIR) and Photoluminescence properties including with excitation and emission spectra were also studied. Ba₂MgSi₂O₇ (BMS) phosphor revealed its monoclinic crystal symmetry with a space group C2/c. observed that the XRD pattern well matched JCPDS file No.23-0842. The average crystallite size was calculated as 29.46nm and strain as 0.30. The prepared phosphor was excited from 337nm and their corresponding emission spectra were recorded at blue (459nm) region. In this present investigation, XRD, FTIR and Photoluminescence characteristics of these phosphors are also reported.

Keywords: Solid-state reaction; X-ray diffraction (XRD); Photoluminescence (PL), Ba₂MgSi₂O₇ (BMS).

1. Introduction

In the present scenario, phosphor-based luminescent materials are broadly utilized as applications in technical fields likewise CRT (Cathode Ray Tube), PDP (Plasma Display Panel) and phosphorescent paint [1]. In some research literatures, persistence alkaline earth (i.e. Ca, Ba, Sr) silicate phosphors synthesized through conventional solid-state reaction route were recently reported [2, 3], because this technique requires high temperature [10]. It has often been observed that alkaline earth (i.e. Ca, Ba, Sr) silicates have relatively remarkable stability of physical and chemical features, as well as crystalline structure. Due to which they lend themselves as luminescent hosts. In addition, they are easily synthesized [4-7]. In addition to having a monoclinic crystal structure, Ba₂MgSi₂O₇ exhibits 1D (one dimensional) layer structure, similarly. Thus, Ba²⁺ site is coordinated with eight oxide ions of SiO₄ and MgO₄ units [8, 9]. In this study, Di barium magnesium di silicate (BMS) phosphor was prepared via conventional solid-state reaction method. The structural characterization such as XRD, FTIR and optical properties like photoluminescence characteristics were discussed in detail.

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2. Experimental Studies

2.1 Sample Preparation

The phosphor as a host was successfully synthesized through solid-state reaction route. This technique is one of the best synthesize methods as compared to other techniques [10]. All starting raw reagents employed in this experiment were BaCO₃ (AR), MgO (AR), SiO₂*H₂O (AR), and also used 0.1 mol % H₃BO₃ (AR) as a flux. The starting materials were weighed stoichiometric ratio and mixed homogeneously through using acetone (CH₃COCH₃) and grinded thoroughly for 2 hour using the agate mortar and pestle in clock wise direction. After crushed sample was transferred in an alumina crucible. Sample was kept in programmable muffle furnace and then sintered at 1100⁰C for approximately 3h. The heating as well as the cooling rate of the furnace were set at 5°C per minute. Final Ba₂MgSi₂O₇ phosphor (white powder) was obtained after additional grinding up to 1 hour. The resulting sample was restored in airtight bottle for further studies. Figure 1 displays the pure BMS phosphor.

The reagents reaction process is given as follows:



2.2 Sample Characterization

X-ray diffraction (XRD) measurements were recorded with the help of Bruker D8 Advance X-ray diffractometer with Cu-K_α radiation (λ = 1.5406 Å, 40 kV, 40 mA) at room temperature. FTIR measurements of synthesized phosphor via mixing the sample with KBr (AR) pallet preparation have been performed using Bruker Alpha (transmission unit) Fourier Transform Infrared Spectroscopy for functional group identification. The photoluminescence (PL) data were collected by using a SHIMADZU, RF-5301 PC spectro-fluorophotometer provided. While performing the studies excitation and emission slit width were fixed at 3 nm. All experiments were performed in identical conditions and it was observed that the results were reproducible.

3. Result and Discussion

3.1 X-Ray Diffraction (XRD)

3.1.1 Crystal Structure Analysis

Phase identification of pure Ba₂MgSi₂O₇ (BMS) phosphor was done by XRD technique. Its data recorded in the range (10⁰2θ\80⁰). Figure 2 shows the XRD pattern of pure BMS phosphor. XRD pattern of monoclinic crystal structure with a chemical formation of standard Ba₂MgSi₂O₇ is determined to be well matched with the standard data (JCPDS file No. 23-0842) [11]. The cell volume V= 711 (Å)³ and the following lattice parameters: a = 8.4128 Å, b = 10.7101 Å, c = 8.4387 Å, and β = 110.71° were also observed [12]. All parameters of this phosphor shown in Table no. 1. M. Shimizu et al. reported that when the pure Ba₂MgSi₂O₇ crystal structure was investigated through single crystal X-ray investigation, it was revealed that its structure was demonstrated an akermanite-type structure with the tetragonal space group [13]. After a few years, some surprising results came out about this structure. Kenji Toda and his co-workers also reported that un-doped Ba₂MgSi₂O₇ phosphor; also completely different from the tetragonal crystal symmetry. Namely, this structure confirmed the monoclinic crystal structure [14]. Based on our result, we can clearly say that this structure shows monoclinic crystal structure with space group C2/c.



Fig: 1. Pure Ba₂MgSi₂O₇ Phosphor

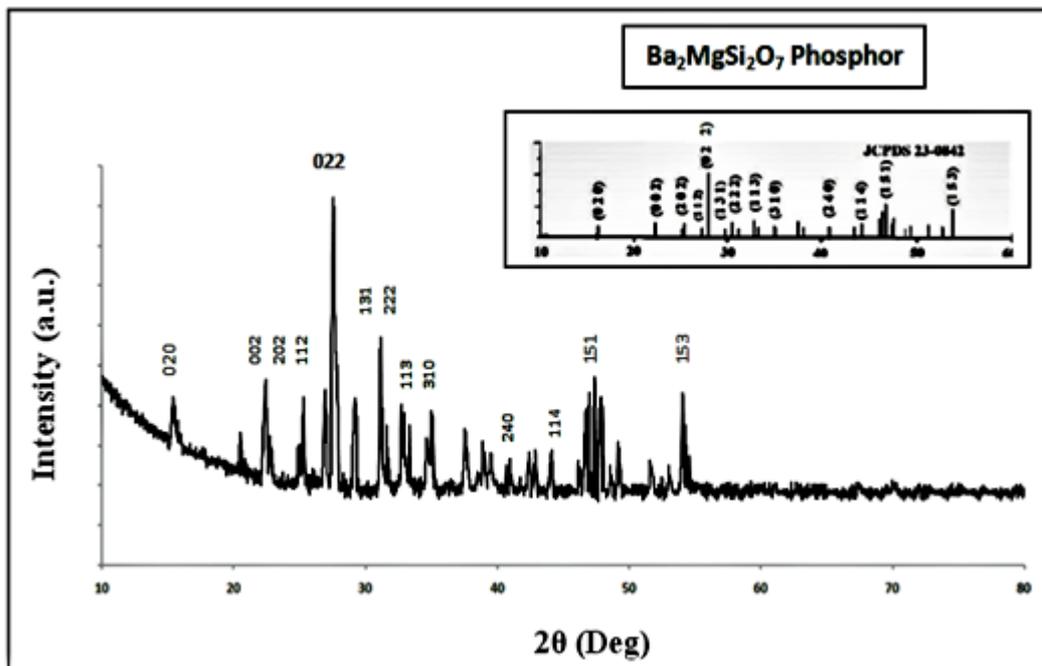


Fig. 2. XRD Pattern of Un-doped $\text{Ba}_2\text{MgSi}_2\text{O}_7$ Phosphor

3.1.2 Debye–Scherrer Formula

The calculation of average crystallite size (D), with the help of Debye–Scherrer formula, for prominent peak (022) of the $\text{Ba}_2\text{MgSi}_2\text{O}_7$ phosphor showed in table: 1.

Debye–Scherrer formula is demonstrated as follows:

$$D = K\lambda / \beta \cos\theta \quad (3)$$

Where K is the Scherrer constant having value 0.94, λ is wavelength of incident X-ray ($\lambda = 1.5406 \text{ \AA}$), β is the FWHM (Full width half maximum) of the peaks and θ is the corresponding Bragg's diffraction angle.

Table: (1) According to the highest peak (022), position of the peak of the XRD patterns and the calculation values of the parameters.

NO	Parameters	$\text{Ba}_2\text{MgSi}_2\text{O}_7$ Phosphor
1.	Crystal Structure	Monoclinic
2.	Space Group	C2/c
3.	Lattice Parameters	a= 8.4128 \AA b= 10.7101 \AA & c= 8.4387 \AA $\beta=110.71^\circ$
4.	Crystalline Size D (nm)	29.46nm
5.	2 θ (deg)	27.51
6.	Cell Volume	711 (\AA) ³
7.	Crystal plane Space	3.2396 (\AA)
8.	Strain	0.30

3.1.3 Strain Determination by Uniform Deformation Model (UDM)

The strain induced broadening in the powder sample was calculated via the following mathematical relation:

$$\varepsilon = \beta/4\tan\theta \quad (4)$$

3.2 FTIR Spectra

3.2.1 KBr Pallet Preparation

The KBr pallet is displayed in fig. 3(a) and 3(b). Before recording the FTIR spectra of a synthesized sample, it is very essential to mix the synthesized sample with KBr (IR Grade) powder and grind it. After applying with hydraulic pressure to form a thin pallet. It is important to be note that KBr powder and sample should be in very little quantities. In this way, FTIR spectra and reading are obtained very clearly.



Fig: 3(a) Hydraulic Pressure Equipment, Fig: 3(b) KBr-BMS Pallet

The FTIR spectrum of this pure BMS sample has been showed in fig: 3(c). FTIR spectra were recorded in the range of (4000 cm^{-1} to 400 cm^{-1}). The band, centred at 485.72 , 564.13 , 618.43 , 672.35 , 836.63 , 921.56 and 1025.28 cm^{-1} can be allocated to the existence of SiO_4 functional group. In addition, considering the absorption bands, validated at 672.35 cm^{-1} and 564.13 cm^{-1} , respectively could be responsible to the existence of SiO_4 group [15]. Thus observed, the absorption bands of silicate groups were clearly evident in the (IR) infra-red spectrum.

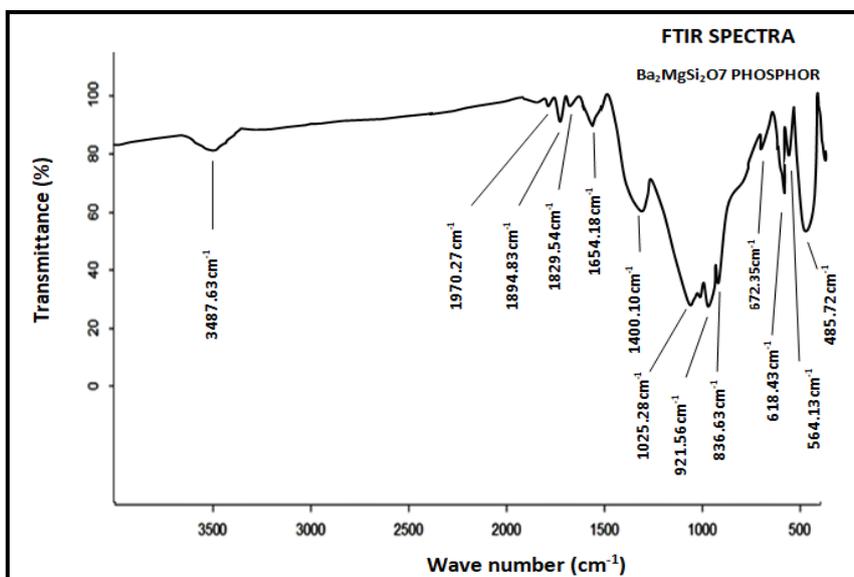


Fig: 3(c) FTIR Spectra of Pure BMS Phosphor

The sharp band centered at 836.63 , 921.56 and 1025.28 cm^{-1} was allocated to the Si-O-Si asymmetric stretch. The bands at 672.35 and 618.43 cm^{-1} may be

responsible to the Si-O symmetric stretch and Ba-O bending vibrations. The bands bending at 564.13 and 485.72 cm^{-1} are allocated to the Si-O-Si vibrational mode. The Peak centered at 836 cm^{-1} may be responsible to Mg-O bending vibrations. The free carbonate $[\text{CO}_3^{2-}]$ ion has a D3h symmetry 69 (trigonal planar) and the band (asymmetric stretching) on its spectrum dominates at 1654.18 cm^{-1} . The bands centered at 1829.54, 1894.83 and 1970.27 cm^{-1} are responsible due to carbonation reaction mechanism. This can be lead to distortion in the lattice resulting in 1400.10 and 1654.18 cm^{-1} vibration modes allocated to vibration in divalent barium ion $[\text{Ba}^{2+}]$ and divalent magnesium ion $[\text{Mg}^{2+}]$ respectively. Various peaks in the range of 1800-1900 cm^{-1} are possibly cause by Ba-O stretching. The peak centered at 3487.63 cm^{-1} are visible due to O-H stretching this indicates the existence of moisture in the sample [16-22].

3.3 Photoluminescence (PL) Spectra

The photoluminescence characteristics of this un-doped BMS phosphor are determined in the basis of excitation and emission spectra also displayed in fig. 4 respectively. We see that a series of lines are obtained in the range (300nm–700nm) with the strongest peak at 337nm and some other line at 352nm in the excitation spectra. Simultaneously, the strongest peak in blue region at 459nm in the emission spectra. On the basis of this PL results, we can say that the un-doped BMS phosphor showed excitation and emission spectra on very low relative PL intensity.

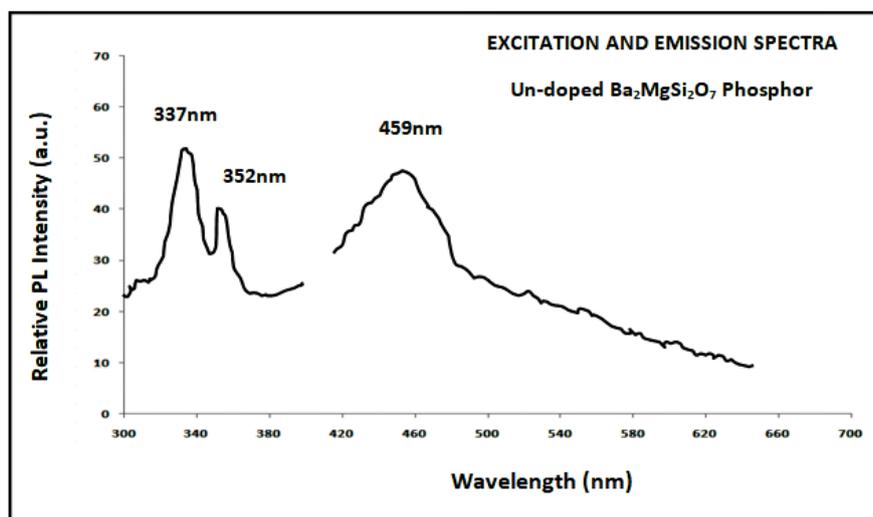


Fig: 4. Excitation and Emission Spectra of BMS Phosphor

Conclusion

In brief, $\text{Ba}_2\text{MgSi}_2\text{O}_7$ phosphor was successfully synthesized via traditional high temperature solid-state reaction synthesis. The XRD spectra displayed that the standard pattern of the obtained phosphor were well matched through JCPDS file. The sharp crystalline features and homogeneity of the phosphor is much better in the micro range Actual phase formation and functional group identification was confirmed via FTIR spectroscopy. The BMS phosphor as a host showed the very poor PL emission intensity obtained in blue region at 459 nm wavelength. Based on our result, we can clearly say that this structure shows confirmed monoclinic crystal structure with space group C2/c.

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