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Synthesis and investigations on correlation between EPR and optical properties of Fe doped Li_2SiO_3

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ABSTRACT

Iron doped lithium metasilicate sample was synthesized using a combustion technique and characterized by XRD (X ray diffraction), SEM (scanning electron microscopy), FTIR (Fourier transform infrared spectroscopy), optical, and EPR (electron paramagnetic resonance) analyses. The phase purity of the combustion synthesized products was confirmed by XRD analysis. SEM data suggested the formation of a porous compound by virtue of the entrapment of the gases that evolved during the sample synthesis. FTIR data confirmed the formation of Si—O bonds in the system. Optical data confirmed the existence of both divalent and trivalent iron in the system. Characteristic absorption bands in the region 215–270 nm and 535–620 nm were observed due to the presence of Fe^{3+} in Oh and Td geometry respectively. On the other hand, the presence of bands at 967 and 1442 nm suggested the stabilisation of Fe^{2+} also in both Oh and Td geometries, respectively. The divalent iron being a non-Kramer ion, could not be observed by EPR. However, strong temperature-dependent EPR signals were observed in the sample owing to Fe^{3+}. By analyzing the EPR data, super-paramagnetic type of behaviour was observed in the system. Furthermore, the relaxation times along with other EPR spectroscopic parameters were estimated for the system.

1. Introduction

In recent years, alkali silicates have been widely studied due to their potential application as electrical, thermal, and optical materials [1–3]. Lithium metasilicate (Li_2SiO_3) is a promising material for the construction of solid tritium breeders due to its excellent properties such as tritium solubility; compatibility with other blanket and structural materials; thermo-physical, chemical, and mechanical stability at higher temperatures; and favorable irradiation behaviour [4–7]. Also, it is a technologically important ceramic system for applications in electronic devices such as the in-battery functionality and ceramics of low thermal expansion glass (that are used in ceramic bobs) [8–11]. A significant amount of research has been carried out in recent years on its application as a carbon dioxide (CO_2) sorbent material as per the following reaction: $Li_2SiO_3 + CO_2 \leftrightarrow$ silicon dioxide (SiO_2) + lithium carbonate (Li_2CO_3) [12]. Li_2SiO_3 is a member of the family of iso-structural compounds with the general formula A_2BO_3 [13]. Its polar orthorhombic symmetry is with the *mm2* point group suggesting that the material is useful for piezoelectric, pyroelectric, and electro-optic applications. Most of its properties such as the dielectric constant and conductivity depend on the composition and microstructure of the material.

A number of techniques have been reported for the synthesis of lithium (Li) silicate compounds such as the solid-state reaction [14], microemulsion [15], sol–gel method [16], hydrothermal [17] and combustion synthesis [18]. Cruz et al. [19] studied the effects of temperature on the Li_2SiO_3 phase using a modified combustion method for which lithium hydroxide (LiOH) and silicic acid (H_2SiO_3) served as the precursors. They had prepared the Li_2SiO_3 phase with a few impurities ($Li_2Si_2O_5$, SiO_2) at 450 °C and pure Li_2SiO_3 at 650 °C. Zhang et al. [16] had prepared Li_2SiO_3 powder at 450 °C using a sol–gel method. However, it was thermally unstable and transformed completely to lithium disilicate ($Li_2Si_2O_5$) at higher temperatures (≥ 900 °C).

A lack of information exists regarding the exploration of the optical properties of Li_2SiO_3 as a phosphor material. In general, an inorganic host matrix that shows phosphorescence or fluorescence (photoluminescence) is known as a phosphor material. Only a number of reports have been published in the scientific literature to the best of our

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knowledge regarding this aspect of the material. Naik et al. [20] reported the photoluminescence properties of a rare-earth-doped (Ce^{3+}, Eu^{3+}, Tb^{3+}) Li silicate. Sabikoglu et al. [21] investigated the photoluminescence properties of the Li_2SiO_3:Ln (Ln = Er^{3+}, Eu^{3+}, Dy^{3+}, and Sm^{3+}) phosphor. Singh et al. [18] studied the radiation-induced defects in Li_2SiO_3:Sm phosphor.

Electron paramagnetic resonance (EPR) spectroscopy is a powerful technique that can provide valuable information regarding any paramagnetic species present in a matrix. EPR properties of Fe^{3+} doped host materials have been investigated widely. To the best of the authors' knowledge, however, the reports on the EPR and optical properties of Fe^{3+} doped Li_2SiO_3 have been hardly studied as compared to other hosts.

In the present work, we discuss the synthesis of Fe^{3+} doped Li_2SiO_3 via a solution-combustion method using glycine as a fuel. The synthesized product was further characterized for their physical, optical and EPR using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible (UV–Vis) spectrometry, and EPR techniques. This was done in order to get a structure-property correlation of the Fe^{3+} ions in the Li_2SiO_3 matrix.

2. Material preparation and analysis

Powder sample of Li_2SiO_3:Fe^{3+} phosphor was synthesized via a combustion route for which a fuel and an oxidizer are required. The basic condition for the solution combustion reaction was carried out as follows: The host to fuel ratio was calculated using the total oxidizing (O) and reducing valences (F) based on the concept of propellant chemistry. Akin to a typical synthesis, $LiNO_3$, SiO_2, $Fe(NO_3)_3{\cdot}9H_2O$ and glycine ($C_2H_5NO_2$) served as the precursor materials for a dissolution in minimum quantities of deionised water in a 150-ml glass beaker to obtain a homogeneous solution. The beaker was then transferred into a furnace that had been preheated to 550 °C. The combustion occurred with the introduction of the solution along with the evolution of the gases. The solution frothed and swelled, forming foam that ruptured with a flame that lasted for several seconds. The product-formation reaction was self-propagating that maintained a high temperature for 1–5 s. Then, the beaker was immediately removed from the muffle furnace. After the reaction, the materials were crushed with a mortar and pestle and then placed in 50-ml alumina crucibles for a 980-°C heat treatment that lasted for 7 h. The resultant powder was used for a further characterization.

The crystal phase of the prepared phosphor was analyzed using an XRD pattern that had been measured using the X'Pert PRO-MRD device (PAN analytical, The Netherlands). The vibrational modes of the prepared phosphor were studied using FTIR spectrum that was measured using the Rx1 instrument (Perkin Elmer, U.S.A.) in the range from 4000 to 400 cm^{-1}. The morphology was analyzed using the S-4300 SEM (Hitachi, Japan). The UV–Vis-near infrared (NIR) absorption of the samples was measured at room temperature (RT) using diffuse-reflectance spectroscopy for which the Cary Instruments 6000i UV–Vis-NIR spectrophotometer (Agilent Technologies, Inc., U.S.A.), equipped with an integrating sphere, was utilized. A powdered sample was taken in a quartz tube for the EPR measurements. The temperature dependence of the EPR spectra was studied using the FE1X EPR spectrometer (JEOL, Japan) operated in the X-band frequency with a field modulation of 100 kHz.

3. Results and discussion

3.1. Powder XRD: structural studies

The XRD pattern of the Li_2SiO_3:Fe^{3+} synthesized using the solution-combustion method is shown in Fig. 1 (a). All of the observed diffraction peaks for the sample were well matched with the standard powder diffraction pattern (JCPDS) Card No.-70-0330 as shown in Fig. 1 (b). It was observed that the system crystallized in an orthorhombic phase with end centered lattice formation having space group $C_{mc}21$. From the observed pattern the approximate lattice parameters were evaluated as follows: a = 9.390, b = 5.40 and c = 4.66 Å. The XRD parameters including the peak positions and their assigned planes for the synthesized sample are listed in Table 1. There was no signature of impurity peaks (due to Fe^{3+} ion) at the current doping levels. The average crystallite size could be estimated from the 100% (most intense) peak using the following Scherrer equation:

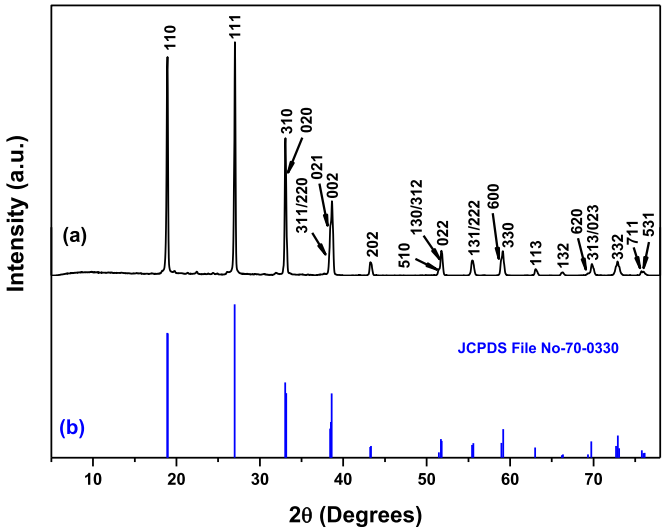

Fig. 1. Black lines at the top show the XRD pattern of the synthesized Fe doped lithium metasilicate (Li_2SiO_3) sample. Blue lines at the bottom show the standard XRD peaks taken from the International Centre for Diffraction Data (JCPDS Card No.-70-0330) database for the orthorhombic Li_2SiO_3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$D = 0.9\,\lambda/\beta\cos\theta \quad (1)$$

Here λ is the wavelength of the incident X-ray, θ is the corresponding Bragg's diffraction angle, and β is the full width at half maximum (FWHM) of the (111) peak. Using the above equation the average crystallite size was calculated to be 48.92 nm.

3.2. SEM: morphological studies

Fig. 2 (A) and (B) shows the SEM micrographs of the sample with two

Table 1
XRD parameters of the Fe doped Li_2SiO_3 sample.

2θ values	Intensity (relative values)	*h k l*
26.98	100	1 1 1
18.88	81.3	2 0 0
18.95	80.9	1 1 0
33.05	49	3 1 0
33.17	42	0 2 0
38.61	41.9	0 0 2
38.52	23.2	0 2 1
38.41	19	3 1 1
		2 2 0
59.19	18.6	3 3 0
72.92	14.5	3 3 2
		0 4 1
51.71	12.1	1 3 0
		3 1 2
51.80	11	0 2 2
69.74	10.7	3 1 3
		0 2 3