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Characterisation and luminescence studies of Tm and Na doped magnesium borate phosphors

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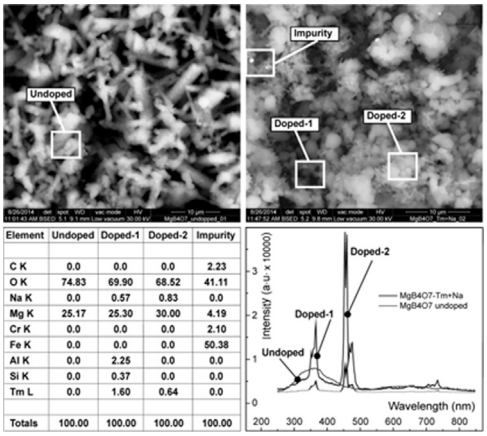
HIGHLIGHTS

- XRD, EDS and ESEM are used for characterizing the samples.
- Broad emission band and Tm^{3+} 4f–4f transition peaks are discussed.
- Charge compensation mechanism of MgB_4O_7:Tm^{3+}, Na^+ are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, structural and luminescence properties of magnesium borate of the form MgB_4O_7 doped with Tm and Na were investigated by X-ray diffraction (XRD), Raman spectroscopy and cathodoluminescence (CL). The morphologies of the synthetised compounds exhibit clustered granules and road-like materials. As doping trivalent ions into a host with divalent cations requires charge compensation, this effect is discussed. The CL spectra of undoped MgB_4O_7 shows a broad band emission centred around 350 nm which is postulated to be produced by self-trapped excitons and some other defects. From the CL emission spectrum, main emission bands centred at 360, 455, 475 nm due to the respective transitions of $^1D_2 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ suggest the presence of Tm^{3+} ion in MgB_4O_7 lattice site. CL mechanism was proposed to explain the observed phenomena which are valuable in possibility of the developing new luminescent materials for different applications. In addition, the experimental Raman spectrum of doped and undoped MgB_4O_7 were reported and discussed.

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1. Introduction

There are various types of metal borates found not only in the nature but also synthetised in the laboratory with many chemical compositions such as MgB_4O_7, $Mg_2B_2O_5$, and $Mg_3B_2O_6$. Valuable feature of borate-based materials such as near tissue-equivalency (Z_{eff} =7.25) makes them very attractive (McKeever et al., 1995).

Many borate-based compounds are found to be promising by many research groups since they have a wide spectral response range from infra-red (IR) wavelength to visible and UV wavelengths (Thakare et al., 2007; Berezovskaya et al., 2007; Sasaki et al., 2000). Moreover, the luminescent characteristics of this compound provide that borates have remarkable potential for many electronic and optoelectronic applications. REE doping is particularly well-suited for the investigation of luminescence properties. Borate-based materials activated with various rare earth (Eu, Dy, Tm, or alkali metals Na, Li) have been widely investigated by many authors in the quest of efficient optoelectronic or dosimetric materials (Türkler Ege et al., 2007; Kawashima et al., 2014; Yukihara et al., 2014; Li et al., 2005; Fukudaan and Takeuchi, 1989).

MgB_4O_7 dosimeters doped with Tm and Dy are especially used for photon, beta and neutron dosimetry. The most important disadvantage of this material is the high rate of thermal and optical fading in terms of radiation dosimetry. Existing the complex nature and various types of defects in MgB_4O_7 doped with RE and transition element inevitably means that identification of all these different configurations are difficult and therefore interpretation of its luminescence emission related to defect model assumptions is problematic. Although many significant empirical studies continue to be conducted in this area, the potential mechanisms behind the luminescence from doped material are not yet fully understood.

Recently, Raman spectroscopy is being used widely to determine local structure of building units that constitutes the borate materials. Although there are few examples in the literature on Raman study of borates crystals there are not yet literature examples on the Raman spectrum of the MgB_4O_7. Borate glasses and borates crystals may exhibit different behaviour on the number of possible vibration modes (Solntsev et al., 2010; Yano et al., 2003).

Herein, we investigate CL properties of undoped MgB_4O_7 and MgB_4O_7:Tm, Na samples in detail. An important factor in our choice for hosting optically active rare earth ion was the ease by which the phosphors can be produced and their prime cost is low. Though the existing literature of using thermoluminescence (TL) to study phosphor materials has established, there is no study concerning the detailed CL investigation of Na and Tm doped MgB_4O_7 phosphor. Hence, we sought to obtain further understanding of the nature and the interaction between the host material and the activator ions. This is fundamentally important phenomenon for key technological challenges. In addition, Raman spectra of undoped MgB_4O_7 and MgB_4O_7:Tm,Na were recorded at the room temperature and the assignments of the possible vibrations modes were determined according to the previous works.

The presence of RE ions in borate material provides a bright phosphor for luminescence applications; therefore, these phosphors have been intensively studied since the development of phosphors. Many volume of published literature exists on the role of RE ions in wide band gap insulators but the actual details of the operating mechanisms remain only partially understood. There are not any data from this kind of study in the literature for MgB_4O_7 material, although it has been in application for many years.

2. Materials and method

Undoped, rare earth (Thulium, Tm) and Na doped magnesium borate samples, MgB_4O_7 were developed and prepared by Dr. Prokic, at the Institute of Nuclear Sciences, Belgrade. MgB_4O_7 was prepared by mixing $MgCO_3$ and H_3BO_3 in stoichiometric proportion. MgB_4O_7:Tm, Na phosphors were prepared by a sintering technique by adding Tm_2O_3 and Na_2SO_4 to the above stoichiometric mixture (Prokic 1980, 1986). Powder samples have been cold pressed with a thickness of ~1 mm and radius of ~4.5 mm. Undoped and doped samples were subjected to furnace heat treatment at 550 °C for 4 h with a 5 °C/min heating rate for sintering under atmospheric conditions to modify the distribution of clusters sizes within the lattice, and then allowed to quench on a metal plate. An undoped MgB_4O_7 sample was also studied in order to assess the host emission and the influence of doping.

Tm^{3+} may not be suitable doping agent for magnesium borate since there is a big difference between the ionic radii of Tm^{3+} ions and Mg^{2+} in which it substitutes. The inclusion of Tm^{3+} to act as efficient luminescence sites distorts the host lattice and charge balance. Therefore the sites often require secondary impurity to offer local charge compensation. The charge compensation from the local defect sites gives rise to lattice deformation which is not desirable. It is more convenient to provide a charge compensating ions in order to form a stable compound. The alkali metals like K, Li, Na etc. are found to be the best candidates in this regard. Therefore, for Tm doped sample, a second dopant Na was added for charge compensation.

The XRD analyses of Na and Tm doped MgB_4O_7 phosphors were carried out using Philips X'Pert MPD diffractometer. The experimental conditions were conducted using CuKα radiation line (λ=1.5418 Å) with a Ni filter at a scan angle of 0.5 °/min in the range from 5° to 70°.

ESEM INSPECT S microscope of FEI Company having a chemical EDS probe and a MONOCL3 Gatan probe was used to examine surface elemental composition of the phosphor materials and to record CL spectra, respectively. The blue-sensitive PMT covers the 250 to 850 nm range. Excitation voltage of 25 kV and beam current of 100 μA were used for the CL measurements. The wavelength calibration was based on a standard mercury lamp.

The micro-Raman spectrum of the spot sample was conducted in a Thermo-Fischer DXR Raman Microscope. The light at 532 nm of a frequency doubled Nd:YVO_4 DPSS solid laser (maximum power 10 mW) was used for excitation. The average spectral resolution in the Raman shift ranging from 100 to 3600 cm^{-1} was 4 cm^{-1}, i.e., grating 900 lines/mm and 2 μm spot sizes.

3. Results and discussion

3.1. XRD and ESEM-EDS

The phase purity and crystal structure of the products were firstly identified by using X-ray powder diffraction (XRD). Typical XRD patterns of undoped MgB_4O_7, MgB_4O_7:Tm, Na and from the International Centre for Diffraction Data (ICDD) recorded at 300 K are shown in Fig. 1. XRD patterns clearly indicate that the crystallographic structure of the product is an orthorhombic system whose space group is *Pbca* and lattice parameters a=8.596, b=13.72 and c=7.956. The peaks observed in the diffraction patterns match with the JCDPS card No:31-0787. From the XRD pattern, the lattice parameter appears insensitive to co-doping by Na^+ and Tm^{3+} ions, which indicates that the structure is not significantly affected and the Mg^{2+} ions of the host lattice get cooperatively replaced by both Na^+ and Tm^{3+}.

The samples were analysed by environmental scanning electron microscope (ESEM) in order to observe the morphologies of the products (Fig. 2a and b). In all cases, the images were recorded with backscattered electron detector. It is concluded that the