Available online at www.sciencedirect.com

ScienceDirect

Current Applied Physics 8 (2008) 420–424

Current Applied Physics
An official journal of the KPS

www.elsevier.com/locate/cap
www.kps.or.kr

Photostimulated luminescence and thermoluminescence in europium-doped barium magnesium fluoride

J.W. Quilty [a,*], A. Edgar [a,b], G. Schierning [c]

[a] School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand
[b] MacDiarmid Institute, School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand
[c] Institute for Nanotechnology, Forschungszentrum Karlsruhe, Postfach 3640, 76021 Karlsruhe, Germany

Abstract

We present the results of thermoluminescence and photostimulated luminescence measurements of $BaMgF_4$, a ferroelectric material which, when doped with divalent europium, can function as an efficient X-ray storage phosphor. While only a broad and largely structureless peak in the photostimulated luminescence excitation spectrum is observed, several trap centres are identifiable in thermoluminescence spectra. The broad peak in the photostimulated luminescence excitation spectrum is deduced to be an R centre and responsible for the observed storage phosphor effect. Madelung energy calculations of the fluorine site potentials in the $BaMgF_4$ crystal structure were performed and indicate that three of the four distinct fluorine sites, F(2)–F(4), are energetically preferred for site vacancies, consistent with the assignment of the electron trap as an R centre.

PACS: 74.25.Gz; 74.25.Jb; 74.70.Ad; 78.30.Er

Keywords: $BaMgF_4$; Photostimulated luminescence; Thermoluminescence

1. Introduction

X-ray storage phosphors are used for recording radiographic X-ray images based on the photostimulated luminescence mechanism [1]. This mechanism involves the generation of electron–hole pairs by the incident X-ray radiation, local trapping of the electrons, and subsequent electron–hole recombination when stimulated by incident light. The electron–hole recombination energy is transferred to a luminescent ion, and the spatial variation of this photostimulated luminescence constitutes the X-ray image.

The key process in image formation is that of electron trapping, but the Coulomb attraction between electrons and holes means that a large fraction of the electron–hole pairs form either free or bound excitons and thus are not available for local trapping [2]. It has been suggested [3] that the fraction of trapped electrons and holes could be changed in a ferroelectric material, as the strong internal electric field may promote charge separation.

$BaMgF_4$ is one member of the isostructural family of materials $BaMF_4$, $M =$ Mg, Mn, Fe, Co, Ni and Zn. These materials crystallise in an orthorhombic unit cell with space group $Cmc2_1$ [4], shown in Fig. 1 for $BaMgF_4$. The Mg cation is octahedrally coordinated to the fluorine anions to form distorted octahedra which are alternately rotated around the *a*-axis (Fig. 1). There are four crystallographically distinct fluorine sites. Structural and electronic calculations indicate the octahedral distortion arises because the undistorted unit cell is unable to accommodate the energetically preferred Mg–F(1) bond lengths, forcing the F(1) anion outward to attain the favoured separation [5]. This distortion and rotation gives rise to the ferroelectric spontaneous polarisation, directed along the *c*-axis, observed in this family of materials [6–8].

---

[*] Corresponding author.
E-mail address: J.Quilty@irl.cri.nz (J.W. Quilty).

1567-1739/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2007.10.027

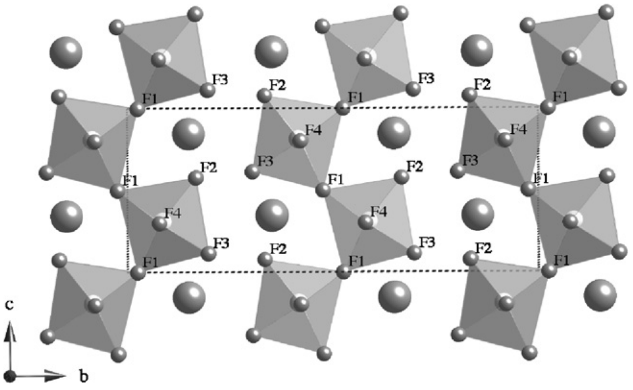

Fig. 1. The $BaMgF_4$ unit cell. The Ba atoms (large spheres) lie at the same level as the apical F(4) atoms, while the Mg (light spheres) and F(1)–F(3) atoms form distorted octahedral sheets in the *bc*-plane.

Electron traps in halide materials, often called colour centres, are usually associated with a single electron trapped at a simple anion vacancy — the F centre. Clusters of two and three F centres, the M centre and R centre (sometimes denoted as F_2 and F_3), can also trap electrons and have lower photoionization energies than the simple F centre. Fluorine site vacancies in $BaMgF_4$ are known to act as electron trap centres [9].

When doped with a luminescent ion such as europium, $BaMgF_4$:Eu shows an emission peak in the violet region of the spectrum at around 400–420 nm under UV excitation [10–12]. Europium doping is particularly attractive as, due to compatible ionic radii, it substitutes only on the single crystallographic Ba site as Eu^{2+} [13]. The Eu^{2+} ion may also act as a relatively efficient hole trap [11] and in many X-ray storage phosphors the electron–hole recombination energy is transferred to the luminescent ion. We are thus motivated to investigate $BaMgF_4$ as a potential ferroelectric X-ray storage phosphor, to our knowledge the first study of this effect in $BaMgF_4$.

2. Experiment

Polycrystalline samples of $BaMgF_4$ were prepared from precursor powders of BaF_2, MgF_2 and EuF_2 mixed in a nitrogen atmosphere. Europium concentrations subsequently quoted are mol.%. The mixed powders were heated in glassy carbon crucibles in argon past the $BaMgF_4$ melting point of 920 °C [14]. The resulting melt was cooled slowly through 920 °C and then rapidly cooled to room temperature.

Photoluminescence and photostimulated luminescence spectra were measured at room temperature with a Perkin-Elmer LS-55 luminescence spectrometer, and the samples were X-irradiated with a Philips PW 1720 X-ray generator using a tungsten tube at 50 kV/20 mA. Thermoluminescence spectra were measured with custom-built apparatus with a temperature range from room temperature to 400 °C [15]. A photomultiplier tube, with broad band-pass filter around the 420 nm europium luminescence wavelength, was used to detect the thermoluminescence. X-ray powder diffraction patterns were measured on a Philips PW3719 diffractometer with a Cu tube and showed good agreement with $BaMgF_4$ patterns from the literature [4].

3. Results and discussion

Luminescence measurements of $BaMgF_4$:Eu 0.2% are shown in Fig. 2. The broad emission line centred at 415 nm (black curve) is characteristic of the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} and is consistent with previous measurements of $BaMgF_4$:Eu at significantly higher europium concentrations [10–13,16]. A much sharper and weaker peak at 363 nm is the $4f^7\,(^6P_{7/2}) \rightarrow 4f^7\,(^8S_{7/2})$ transition [10]. The excitation spectrum (grey curve) exhibits a broad peak at 290 nm superimposed on a broader background, the latter extending to more than 375 nm. This structure is due to the allowed 5d–4f transitions of Eu^{2+} with the $5d^1$ state split by a low symmetry crystal field and broadened by $4f^6$ multiplet coupling. [10,12,13]. There was no indication of emission lines in the vicinity of 590–615 nm due to the f–f transitions of Eu^{3+} [12] in longer wavelength scans (not shown).

Photostimulated luminescence decay curves were measured for a set of polycrystal $BaMgF_4$:Eu samples with europium concentrations from 0.05% to 1.00% and from a sample of a commercial imaging plate, the Agfa MD30, which is composed of iodine-doped $BaFBr:Eu^{2+}$. From these curves, conversion efficiencies and stimulation energies [17] to the $1/e$ point were measured for the $BaMgF_4$:Eu samples relative to the commercial imaging plate conversion efficiency of 20.4 $pJ/mm^2/mR$ and stimulation energy of 150 $\mu J/mm^2$ [18]. These results show a stimulation energy similar to that of the commercial plate for 0.1% Eu and a maximum conversion efficiency 4% of the commercial plate for 0.2% Eu. The photostimulated luminescence excitation

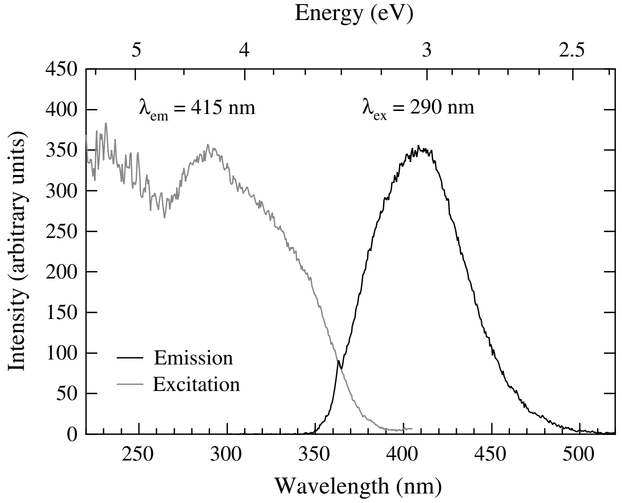

Fig. 2. Emission (black) and excitation (grey) luminescence spectra of a $BaMgF_4$:Eu 0.2% polycrystal at room temperature, showing the characteristic broad europium emission line at 415 nm.