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Short communication

Radiation-induced changes in the optical properties of $NaMgF_3$(Sm): Observation of resettable Sm radio-photoluminescence

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ABSTRACT

Stable radio-photoluminescence (RPL) is observed in $NaMgF_3$(Sm) after X-ray irradiation due to valence conversion of Sm^{3+} to Sm^{2+}. This valence conversion can be reversed by deep UV (254 nm) illumination. It is likely that this reversible process occurs via defects near some of the Sm^{3+} sites that act as hole traps. The ratio of the Sm^{2+}/Sm^{3+} RPL emissions follows an exponential-type curve dependence on X-ray dose where the ratio saturates above ~500 Gy. Optically stimulated luminescence (OSL) is also observed but only from Sm^{3+} and primarily from electrons trapped at *F*-centers. The OSL response is demonstrated to be linear up to 100 Gy. Thus, $NaMgF_3$(Sm) has potential as a dosimeter where individual irradiations can be monitored via OSL and the total cumulative dose via non-destructive RPL readout. The RPL can be optically reset when required.

1. Introduction

The fluoroperovskite $NaMgF_3$ when doped with luminescent ions has been shown to be an excellent material for applications in radiation dosimetry and imaging [1–10]. In many cases the doped compound exhibits optically stimulated luminescence (OSL) [2,3,5,6,10] and thermally stimulated luminescence (TL) [7,8]. These phenomena arise from the trapping of charge in point defects within the compound that can be stimulated into recombination at a luminescent ion with light or heat, respectively. The stimulated luminescence provides a method of measuring radiation doses, as the intensity is proportional to the concentration of trapped charge. OSL has recently found favor over the alternative TL due to the all-optical method of readout, allowing for greater speed and versatility, and leading to the development of new devices [11,12]. The use of optical stimulation also results in improved imaging capabilities and the ability to imbed materials in plastic, allowing for the manufacture of composite detectors [11]. The major drawback of OSL and TL is that readout necessarily erases the stored dose information, as trapped charge must be released for recombination to occur. Room temperature fading of the stored signal can also occur in the case of shallow traps [3,11,13]. It is therefore of interest to develop materials where the dose information can be retained after readout, which can occur in cases of radiation-induced valence conversion [14–18] that is also known as radio-photoluminescence (RPL) [18,19] and the use of stable defect-impurity complexes [2].

In recent years the use of Sm as a dopant has been investigated in many other materials as a tool for radiation monitoring. When fluorophosphate glasses are doped with Sm, both Sm^{2+} and Sm^{3+} are commonly observed and conversion from Sm^{3+} to Sm^{2+} occurs upon exposure to ionizing radiation [14–17]. This can potentially be used to develop high-resolution X-ray imaging plates useful for high-dose microbeam radiation therapy [14–17]. Additional studies have incorporated Sm into different materials in order to investigate TL [20–22] and OSL [13,20,21] properties suitable for dosimetry. $NaMgF_3$ is very promising for medical and radiotherapy dosimetry due to its effective atomic number (Z_{eff} = 10.39) [4] and mass-energy absorption being close to that of human tissue for photon energies above 0.1 MeV [1].

In this paper we present the results of photoluminescence (PL), RPL, OSL and optical absorption measurements on bulk polycrystalline $NaMgF_3$(0.05% Sm) before and after irradiation with X-rays. We show RPL occurs due to Sm^{3+} to Sm^{2+} valence conversion along with Sm^{3+} OSL. These properties can be useful in dosimetry to monitor cumulative doses via RPL and individual doses via OSL.

2. Experimental

A polycrystalline sample of $NaMgF_3$(Sm) with a Sm concentration of 0.05% was prepared by mixing NaF, MgF_2 and SmF_3 in stoichiometric ratios and heating in an RF furnace in an Ar atmosphere. The mixture was heated to 1100 °C and cooled to 1035 °C over 1 h. It was then slow-cooled through the melting point over 15.5 h to 1015 °C before being left to cool to room temperature. This procedure produced a sample with good transparency that was cut into small rectangles with widths

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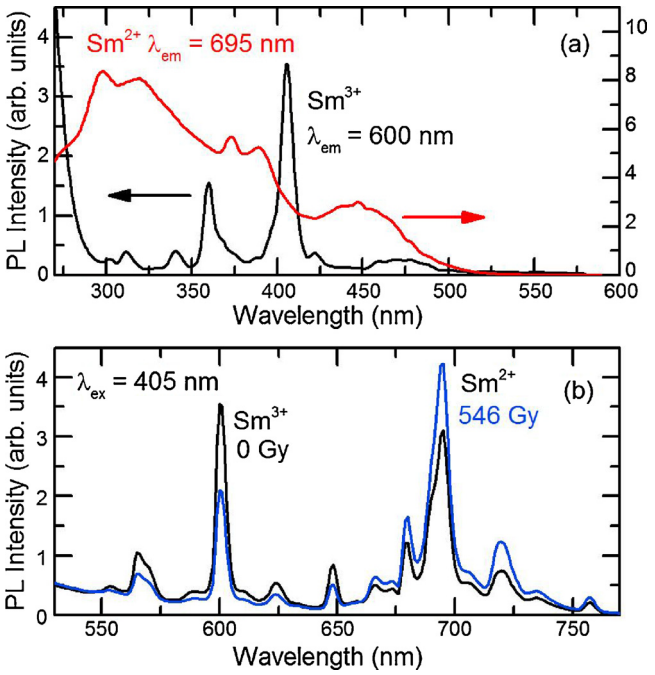

Fig. 1. (a) PL excitation spectra prior to irradiation for Sm^{3+} (black line) where λ_{em} = 600 nm and Sm^{2+} (red line) where λ_{em} = 695 nm. (b) PL emission spectra where λ_{ex} = 405 nm prior to irradiation (black line) and after a 546 Gy cumulative X-ray dose (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

on the order of 1 mm. The samples were polished in order to perform optical transmittance measurements.

PL and OSL measurements were performed using a Jobin-Yvon Fluorolog-3 spectrometer which corrects the data for detector response and lamp intensity. Transmittance data were collected using a Shimadzu UV-2600 spectrophotometer. UV bleaching was performed using an Oliphant UV lamp. X-ray irradiations were performed using a Phillips PW1730 X-ray generator with a tungsten tube. The generator was operated at 40 kV and 20 mA where the dose rate was ~0.1 Gys^{-1} for PL and OSL measurements. Optical absorption measurements were made before and after X-ray irradiation at a closer position to the X-ray tube and where the dose rate was ~1 Gys^{-1}. All measurements were made at room temperature.

3. Results and discussion

We show in Fig. 1 that PL is observed from divalent and trivalent Sm. Sm is expected to substitute for Na^+ on the basis of ionic radii [23]. The excess positive charge introduced by Sm^{2+} and Sm^{3+} needs to be compensated for and this can occur, for example, by Na-vacancies, which are known to occur when Eu^{3+} and Eu^{2+} are substituted onto the Na^+ site. Sm^{3+} has a peak emission at ~600 nm corresponding to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition within the $4f^5$ configuration when excited at 405 nm. The 405 nm Sm^{3+} excitation corresponds to a transition from the $^6H_{5/2}$ ground state to the $^4F_{7/2}$ excited state. All of the Sm^{3+} excitation peaks seen in Fig. 1(a) arise from Sm^{3+} 4f-4f transitions. Sm^{2+} has a peak emission at ~695 nm arising from the $^5D_0 \rightarrow {}^7F_1$ transition [24] when excited at 405 nm. In contrast to the excitation spectrum for Sm^{3+}, distinct Sm^{2+} transitions are not so clear in Fig. 1(a). There are broad excitations attributable to several 4f → 5d absorptions while the low intensity peaks are due to transitions within the $4f^6$ configuration. We observe that the PL emission intensity of Sm^{2+} is approximately double that of Sm^{3+} at their respective peaks. The Sm^{3+} transitions within the $4f^5$ configuration are electric-dipole forbidden and so must be far weaker than the 5d → 4f transitions of Sm^{2+}. The comparable PL intensity of the two valences therefore implies a greater initial concentration of Sm^{3+}.

The PL emission spectrum is plotted in Fig. 1(b) after an X-ray dose of 546 Gy and when exciting at 405 nm. It is apparent that there is an X-ray-induced decrease in the Sm^{3+} PL and an increase in the Sm^{2+} PL. This is due to radiation-induced valence conversion and therefore an RPL effect. As mentioned earlier, this process is also known to occur in Sm-doped fluorophosphate glasses [14–17]. In the case of the glasses, it is believed that this occurs by X-ray irradiation leading to $PO - e^- \rightarrow POHC$ and $Sm^{3+} + e^- \rightarrow Sm^{2+}$, where PO is a phosphate group and POHC is a phosphorous-oxygen hole center located on a phosphate group [14]. Similar Sm valence conversion has also been reported after gamma-ray irradiation of Na_2SO_4 [25], after femtosecond pulsed laser irradiation of Sm doped sodium aluminoborate glass [26], and after X-ray irradiation of nanocrystalline BaFCl(Sm) [27]. The process in the sodium aluminoborate glass is likely to be via multiphoton ionization of oxygen in a borate group and electron transfer to Sm^{3+}. Photoionization of oxygen is also believed to occur for Na_2SO_4. The nature of the hole site was not reported for BaFCl(Sm) but the significant enhancement of the valence conversion in the nanocrystalline material suggests that oxygen at the surfaces could be responsible. In boroaluminosilicate glasses the proportion of converted Sm^{2+} increased with Sm_2O_3 doping and heat treatment in air [28]. Given the role of oxygen in valence conversion in previous studies, it is possible that it also plays a role in $NaMgF_3$(Sm) since a small amount of oxygen is known to be incorporated during synthesis [6,7]. Thus, the Sm^{3+} to Sm^{2+} valence conversion could be $O^{2-} - e^- \rightarrow O^-$ and $Sm^{3+} + e^- \rightarrow Sm^{2+}$, where oxygen is close to Sm^{3+}. We find that this process can be reversed by prolonged optical illumination at 254 nm (4.9 eV). The electron trapped on Sm^{2+} occupies a state within the bandgap (~11 eV [29]), and therefore the reconversion is likely to occur via excitation of the trapped electron into the conduction band and then to the hole trapped on the nearby oxygen. By varying the preparation procedure to introduce additional oxygen sites, for example by doping Sm as Sm_2O_3, we may expect a greater conversion efficiency and therefore improved sensitivity to ionizing radiation.

Sm^{3+} OSL emission is observed after X-ray irradiation and when stimulated at 295 nm as can be seen in Fig. 2(a) after a 120 Gy X-ray dose. There is no evidence for Sm^{2+} OSL. The OSL stimulation is shown in Fig. 2(a) when detecting at 600 nm and after subtracting the Sm^{3+} PL excitation curve before X-ray irradiation. The broad OSL stimulation has a maximum at ~280 nm and this is likely to primarily be due to optical stimulation of trapped electrons in *F*-centers that are known to absorb at 290 nm [30,31]. The absence of OSL from Sm^{2+} suggests that the *F*-centers and holes are trapped near Sm^{3+}. OSL excitation leads to excitation of the electrons from the *F*-type traps and recombination with the nearby hole, resulting in energy transfer to Sm^{3+} and OSL emission.

The existence of *F*-centers is confirmed in Fig. 2(b) where the optical absorption is shown after an X-ray dose of 7.2 kGy. Bleaching of the OSL by continual stimulation at 300 nm leaves a residual absorption from Sm^{2+} transitions (not shown). This residual absorption was subtracted from the absorption after X-ray irradiation to produce the OSL-induced change in the absorption that is plotted in Fig. 2(b). We show in the figure that it can be fitted to a sum of 4 Gaussian curves with peaks at 491 nm (2.53 eV), 412 nm (3.01 eV), 298 nm (4.16 eV), and 222 nm (5.59 eV). From previous studies on pure $NaMgF_3$ after X-ray irradiation, the 290 nm absorption can be attributed to *F*-centers [30,31], the 405 nm absorption to F_2-centres [30,31], and the 490 nm absorption to F_3-centres [31]. The absorption at 230 nm is also reported in irradiated $NaMgF_3$ and has been tentatively assigned to interstitial aggregates e.g. H_2-centres, on account of the absorption intensity being proportional to all *F*-type vacancies [31].

The appearance of OSL means that it can be used to monitor individual radiation doses. A typical OSL decay curve is shown in Fig. 3(a) for an X-ray dose of 50 Gy where the background obtained by fitting has been subtracted. The decay can be fitted to a sum of 3