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# Samarium-doped oxyfluoride borophosphate glasses for x-ray dosimetry in Microbeam Radiation Therapy

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ABSTRACT

One of the key parameters and most difficult challenges related to Microbeam Radiation Therapy (MRT) is the exact measurement of radiation dose delivered. The approach presented here is based on the conversion of the oxidation state of samarium ions (embedded in a suitable glass host) upon exposure to high energy radiation. The conversion from $Sm^{3+}$ to $Sm^{2+}$ under the effect of high x-ray irradiation doses has been studied in four oxyfluoride glasses based on Ca, Mg, Sr and Ba. These glasses can easily be prepared in air, contrary to pure fluoride glasses. They provide good transparency in the visible range, essential for analysis by confocal microscopy. Only the Mg-based glasses exhibited a clear conversion of $Sm^{3+}$ to $Sm^{2+}$ under x-ray exposure; and hence show potential for use as MRT dosimetry. The conversion did not saturate even up to ~20 kGy (dose in air at the sample surface) under a 50 keV synchrotron beam. Further, we were able to determine the spatial dose profile of the x-ray beam through confocal fluoroscopic microscopy; and the dose profile matched closely that from the Monte Carlo simulation.



## 1. Introduction

Microbeam Radiation Therapy (MRT) is an experimental radiation therapy for the treatment of many types of cancer. This synchrotron-based technique has the potential to improve the efficiency of the treatment compared to broad-beam radiation treatment [1,2]. It involves the irradiation of the tumor by parallel x-ray planes with thickness ranging from 20–80 μm, spaced uniformly in the range of 100–400 μm [3] as illustrated in Fig. 1. One of the challenges related to this technique is the accurate irradiation-dose measurement. This includes a measurement of the total x-ray dose as well as the peak-to-valley ratio. X-ray doses required by MRT can reach 1000 Gy and more. Therefore, the detector has to be able to measure high x-ray doses and also to be sensitive enough to low x-ray doses (valley doses). Furthermore the glass should allow a high spatial resolution to provide an accurate dose profile of the irradiation used to calculate the x-ray doses. The reduction of $Sm^{3+}$ to $Sm^{2+}$ under the effect of x-ray irradiation has been considered in different Sm-doped fluoride glasses [4]. So far, Sm-doped fluorophosphate and fluoroaluminate glasses have shown good potential for use up to the kiloGray regime [5]. $Sm^{3+}$ and $Sm^{2+}$ ions provide intense photoluminescence emission bands in the red region when suitably excited with a blue or UV light [6]. The $Sm^{2+}$ photoluminescence emission spectrum has only small overlap with that from $Sm^{3+}$. This provides an easy detection and quantification of each ion, which can then be related to the incident x-ray dose. Our goal is to find a host material that allows the conversion from $Sm^{3+}$ to $Sm^{2+}$ and the stabilization of the oxidation state (+II) for high irradiation doses. To minimize its cost in term of production, it has to be prepared under normal atmosphere, i.e. without any need for an $O_2$-free or reducing atmosphere. Oxide glasses do not seem to provide an ideal environment for the conversion of $Sm^{3+}$ to $Sm^{2+}$ under MRT's experimental conditions. However, samarium in its oxidation state (+II) can be found in some oxide crystals. The most interesting case is the strontium tetraborate crystal $SrB_4O_7$ which hosts only $Sm^{2+}$ even when it is synthesized from $Sm_2O_3$ in air [7,8]. In this crystal, the samarium is surrounded by 15 oxygen atoms located at distances ranging from 2.52 to 3.20 Å [9]. At low samarium content, the $Sm^{2+}$ ion is also found in $MBPO_5$:Sm crystals (M = Ca, Sr, and Ba) and in $M_{1-x}Sm_xSO_4$ (M = Ba, Sr) in addition to $Sm^{3+}$ [7,10]. Borophosphate glasses can provide a high amount of non-bridging oxygens that are apparently necessary to stabilize $Sm^{2+}$, brought by tetrahedral boron and phosphorus species. Furthermore, borophosphate glasses are able to provide good chemical durability [11–16]. Given the above observations, we have decided to synthesize four types of Sm-doped oxyfluoride glasses that can potentially allow the conversion of $Sm^{3+}$ to $Sm^{2+}$ upon irradiation with x-rays. These glasses are Mg-, Ca-, Sr- and Ba-based oxyfluoride borophosphate glasses, doped by the addition of $SmF_3$. Following synthesis, the above glasses were exposed to a high dose radiation at the

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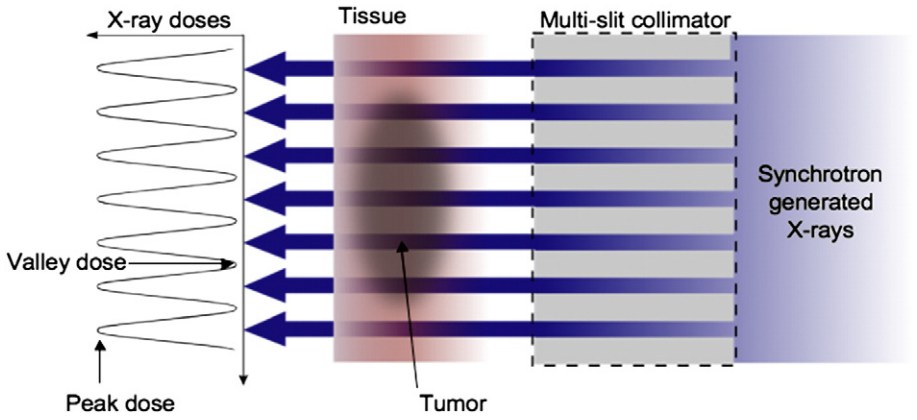


**Fig. 1.** Illustration of the principle of Micribeam Radiation Therapy (MRT). Synchrotron generated x-rays are sent through a multi-slit collimator to create a micro-layers pattern, then these planes irradiate the tumor. The total x-ray dose as well as the valley and peak doses have to be accurately determine for a successful therapy.

Canadian Synchrotron (CLS) up to several thousand Grays. Then photoluminescence experiments were carried out to examine the $Sm^{3+}$ to $Sm^{2+}$ conversion. Further, a microbeam was also used to examine the spatial resolution that is achievable with these Sm-doped glasses under confocal fluoroscopic readout of the $Sm^{2+}$ luminescence. The results indicate that Sm-doped Mg-based glasses show good potential for use in high-dose high-resolution dosimetry.

## 2. Experiment

The glasses were all prepared from the same nominal composition:

$$18.6\,MF_2-18.6\,MO-37.4\,P_2O_5-24.9\,B_2O_3-0.5\,SmF_3$$

with M = Mg, Ca, Sr, and Ba.

The glasses were prepared from $(NH_4)_2HPO_4$ (Alfa Aesar, 98%), $B_2O_3$ (Alfa Aesar, 99%), $SmF_3$ (Alfa Aesar, 99.99%), $MgF_2$ (Balzers), MgO (Puratronic, grade 1), $CaF_2$ (ESPI), CaO (Alfa Aesar, 99.95%), $SrF_2$ (Alfa Aesar, 99%) and $SrCO_3$ (Alfa Aesar, 99%, 1% Ba), $BaF_2$ (Alfa Aesar, 99%), and $BaCO_3$ (Alfa Aesar, tech.). All syntheses were prepared following the same procedure. First, the oxides and carbonates were mixed in an alumina crucible, heated for 4 h at 600 °C then at 1300 °C for 1 h. Each sample was annealed at a temperature 15 °C below its respective $T_g$ for 4 h. Afterward, the melt was quenched at room temperature on a brass plate. The obtained oxide glass was grounded in thin powder into a ceramic mortar and placed back into the same crucible. The fluorides were added and the mixture was heated at 1300°C for 1 h and quenched at room temperature. Each sample was annealed at a temperature 15 °C below its respective $T_g$ for 4 h. The prepared samples were cut and polished, and then irradiated with x-rays at the CLS on the Biomedical Imaging Therapy beamline. The peak energy of the x-ray beam was 50 keV (used in MRT). The dose rate was experimentally estimated to be approximately 0.0064 Gy $s^{-1}$ $mA^{-1}$ at 250 mA of the storage ring current. The reported dose values correspond to dose in air at the sample surface. Several pieces of each sample were irradiated for different doses from 0.5 to 20,000 Gy, and then they were wrapped with aluminum foil and stored until the photoluminescence response measurements were carried out. A piece of Mg-based glass was also irradiated with a microbeam at a total dose of 10,000 Gy. The size of the slit in the multi-slit collimator was 50 μm wide and the slits were separated by a distance of 400 μm center-to-center. The distance between the collimator and the sample was 1 m. The depth of measurement from the surface of the sample was 20 μm. The response of a sample upon x-ray irradiation was readout using a confocal microscopic technique. We used a 473 nm diode-pumped solid-state laser as the excitation source, and the consequent photoluminescence signals from $Sm^{3+}$ and $Sm^{2+}$ were measured by two separate photomultiplier tubes (PMT) in order to measure the response as:

$$R=\frac{PL_{(Sm^{2+})}}{PL_{(Sm^{3+})}}=\left(\frac{I_{PMT(2+)}}{I_{PMT(3+)}}\right)_{irradiated}-\left(\frac{I_{PMT(2+)}}{I_{PMT(3+)}}\right)_{non-irradiated} \quad (1)$$

where $I_{PMT(2+)}$ and $I_{PMT(3+)}$ are measured PMT signals. These are integrated photoluminescent signals over the ranges of 570 to 650 nm and 660 to 800 nm, respectively. The first term takes the signal values for irradiated samples; while, the second term is those for non-irradiated samples, which subtracts the contribution of typical $^4G_{5/2}\rightarrow{}^6H_{11/2}$ emission of $Sm^{3+}$ to the $I_{PMT(2+)}$ signal, hence the response value without irradiation is zero. Fig. 2 shows the emission peak from the photo-excitation of $Sm^{3+}$ and $Sm^{2+}$ before and after irradiation for the Mg-based glass. The value given by Eq. (1) is the relative intensity of the photoluminescence generated by the $Sm^{2+}$ created by irradiation. It is an indicator of the $Sm^{3+}\rightarrow Sm^{2+}$ conversion.

The thermal analysis of the samples were performed using a Seratam TG-DSC 111 from room temperature to 800 °C. Prior to analysis, the samples were ground to powder in a ceramic mortar.

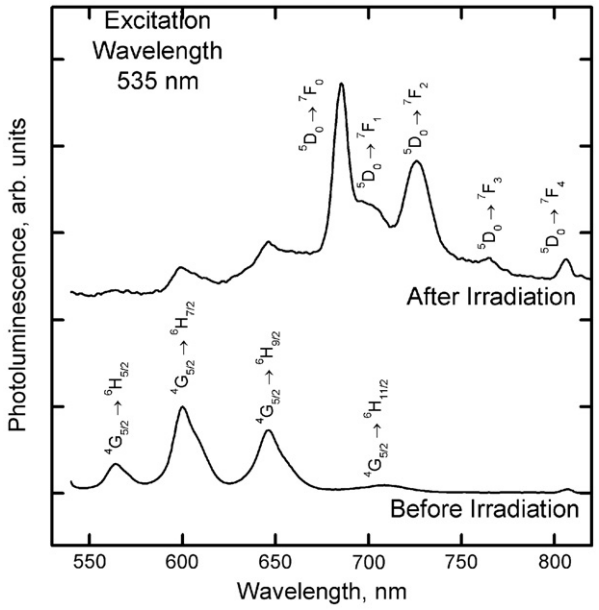


**Fig. 2.** Example of the photoluminescence peaks of $Sm^{3+}$ and $Sm^{2+}$ before and after irradiation for the Mg-based glass.