Ce^{3+}-doped fibres for remote radiation dosimetry

A. Vedda, N. Chiodini, D. Di Martino, M. Fasoli, S. Keffer, A. Lauria, M. Martini, F. Moretti, G. Spinolo*

Department of Materials Science and INFM/CNR, University of Milano-Bicocca, Via Cozzi 53, I-20125 Milano, Italy

M. Nikl

Institute of Physics ASCR, Cukrovarnicka 10, 16253 Prague (Czech Republic)

G. Brambilla

Optoelectronics Research Centre, University of Southampton, Southampton, S0171BJ,U. K.

ABSTRACT

A new radio-luminescent dosimetric system, based on a SiO_2 optical fibre with the core doped by Ce^{3+} ions as luminescent activators has been investigated. The structural and optical properties of the luminescent fibre have been studied by raman spectroscopy, refractive index measurements, radio-luminescence and scintillation time decay, and compared to those of the parent bulk material. The RL response of a composite fibre made of a short portion of active Ce-doped fibre coupled to a long commercial fibre have been investigated in the presence of 20 kV and 32 kV x-ray radiation fields. A linear RL intensity increase was found in the dose rate interval $7x10^{-3}$ - 4.8 mGy/s together with a good radiation hardness, suggesting possible application in low dose monitoring.

*Corresponding author. Tel.: 39-02-64485162; Fax: 39-02-64485400 E-mail: Anna.Vedda@mater.unimib.it

Remote optical fibre dosimetry allows radiation monitoring in areas of difficult or dangerous access and so it can be useful in high radiation fields like for example close to nuclear reactors. Particularly interesting application can be found also in diagnostic or radiotherapy irradiations for a careful control of the dose imparted to the patient. Optical fibre dosimeters are presently being intensively investigated, and recently a few systems were proposed based on different physical radiation effects in radiation sensitive glass fibres, suitable to be exploited for dosimetric purposes [1]. Besides "all glass" systems, the coupling between crystalline dosimeters with commercial fibres was also considered [2, 3].

Dosimetry can be based on the formation of radiation induced defects giving rise to glass coloration [4,5], or on the filling of pre-existing traps, measured by thermally stimulated luminescence (TSL) [6] or optically stimulated luminescence (OSL) [7]. These systems monitor the total imparted dose after irradiation is completed. Alternatively, the prompt luminescence emitted during irradiation (radio-luminescence, RL) can be measured, which allows "in vivo" dose rate monitoring, and so it is able to detect variations of irradiation intensity; total dose evaluation can be achieved by integration of the RL signal over irradiation time, or by performing parallel TSL or OSL measurements [1, 2, 8]. In this work, we specifically focused on the properties of a new RL dosimetric system, based on a SiO_2 optical fibre with the core doped by Ce^{3+} ions as luminescent activators. The structural and optical properties of the active fibre have been investigated, and compared to those of the parent bulk material which was the subject also of previous investigations [9-11]. The RL response of a composite fibre, made of a short portion of active fibre coupled to a long commercial fibre, in the presence of an x-ray radiation field is presented. A very good sensitivity of the system

was found, together with a good radiation hardness, suggesting possible application in low dose monitoring.

The preparation of optical fibres was performed by "powder in tube" method. In the method adopted to produce Ce^{3+}-doped SiO_2 in powder form the sol solution was obtained with the following composition: 18 ml ethanol 99.9%; 6 ml tetraethoxysilane (TEOS); $Ce(NO_3)_3$*12 H_2O solution in ethanol (10 mg/ml) in the amount to obtain doping of 600 mol% Ce in SiO_2; 3.6 ml of water. The sol-gel transition was reached after several days in thermostatic chamber at 40 °C. Rapid drying in rotating evaporator and further grinding in agate mortar allowed to obtain xerogel powder. Slow sintering up to 1100 °C under oxidizing (O_2) atmosphere in a quartz chamber gave the final glass powder; in detail, a first ramp of 10 °C/h up to 450 °C was followed by a stasis of 24 hours; a second ramp of 6 to 10 °C/h was used to reach the final temperature of 1100 °C. The powder was subsequently introduced in a quartz tube under vacuum condition (10^{-4}-10^{-5} mbar) and voids were eliminated by compaction and using an ultrasonic bath. For pre-form preparation, a high temperature (1500-1600 °C) treatment (rapid thermal treatment - RTT) for some minutes was applied, in order to improve the rare earth scintillation efficiency and eventually remove the OH content excess. During this treatment, the temperature was monitored by an optical pyrometer (Impac IE 120) working at 514 μm emission. The tube was vacuum-sealed and then inserted in a furnace at 2100 °C. The fibre diameter was changed by changing the pulling speed between a minimum of 100 and a maximum of 660 μm. The device prototypes were obtained by fusion-splicing a ~220 μm fibre (with core of ~175 μm) to commercial optical fibres. We used 3M commercial fibres, with numerical aperture equal to 0.48, hard clad multimode, whose silica core was ~200 μm in diameter (~225 μm considering

the cladding). For comparison, a 0.05mol%Ce-doped bulk glass was also considered: it was prepared by the sol-gel method using tetraethoxysilane (TEOS) and Ce (III) nitrate as precursors. The sol composition was obtained with a TEOS:H_2O:ETOH volume ratio of 1:0.6:3. The obtained sol, after gelation and subsequent drying in a thermostatic chamber at 35 °C, gave rise to a xerogel monolith, which was densified up to 1050 °C. A similar sample was further subjected to a RTT up to 1800 °C in air after densification to 1050°C.

Raman spectra were obtained by using a Dilor Raman spectrometer (excitation by a He-Ne laser at 632.8 nm). The fibre refractive index profile was analyzed in a fibre with ~105 μm diameter (core dimension ~80 μm) using a YORK Instruments S14 analyzer. RL measurements were performed by using a home made apparatus working in the 10-320 K temperature range; the detection system was a CCD (Jobin-Yvon Spectrum One 3000) coupled to a monochromator operating in the 210-780 nm range. RL excitation was obtained by x-irradiation through a Be window, using a Philips 2274 x-ray tube operated at 20 kV. The data were corrected for the spectral response of the detection system. RL measurements were also performed on scintillating fibres at different radiation fields, using a Machlett OEG 50 x-ray tube operated at 20 kV and at 32 kV; the emitted light was collected by an EMI 9635 QB photomultiplier. Finally, scintillation decays were measured in single photon counting mode by a spectrofluorometer (Edinburgh Instruments 199S) equipped with a ^{22}Na radioisotope (511 keV photons) excitation source with a repetition rate of 20 kHz. They were obtained on a small piece (3 mm diameter, 2.5 mm thickness) of molten pre-form, remained at the end of the fibre drawing process.

In Fig. 1 are reported RT Raman spectra of a 220 μm Ce-doped fibre, compared with those of a bulk SiO_2: 0.05mol%Ce sample before and after RTT. In all cases, intrinsic Raman features of SiO_2 are observed at about 440, 800 and 1060 cm^{-1} (ω_1, ω_3, and ω_4 respectively) [12], together with D_1 and D_2 peaks at 490 cm^{-1} and 610 cm^{-1} assigned to symmetric stretching modes of four-fold and three-fold rings of SiO_2 tetrahedra [13]. It can be noted that the intensity of D_1 and D_2 peaks is increased in bulk sample after RTT and in the fibre with respect to the bulk glass before RTT. This is in accordance with what observed on silica samples subjected to different fictive temperatures T_F, where the formation of four-fold and three-fold rings of SiO_2 tetrahedra increased exponentially by T_F increasing [14]. The relevant result of these Raman measurements is that, similarly to what observed in bulk material with a low Ce concentration, no evidence of any crystalline aggregate was obtained in the fibre; this indicates that the fibre drawing process maintained the amorphous character of the network and a good rare-earth ion dispersion.

The optical properties of the fibre were then investigated. First of all, no difference between the core and the cladding refractive indexes was found, and thus the modification to the silica refractive index induced by the small concentration of dopant is negligible; the guiding effect is given by the silica/air interface that has a numerical aperture ~1. Concerning luminescence properties, in Fig. 2A we report RT radio-luminescence spectra of a 220 μm fibre compared to those obtained on bulk sample and on the powder used for the pre-form preparation. For the fibre measurement, a few 5 mm pieces were placed horizontally on the sample holder. The emission peaking at about 2.75 eV and related to 5d-4f Ce^{3+} emission [9], which dominates the spectrum of both bulk and powder samples, is detected also in the fibre. However, in this case other

high energy components are also present at about 2.9 eV and 3.2 eV. From a careful spectral analysis performed on several measurements, the parameters of the three components turned out to be 2.78 eV, 2.88 eV, 3.22 eV with full widths at half maximum of 0.90 eV, 0.39 eV and 0.36 eV respectively. The error on parameters is approximately 0.05 eV. The origins of such high energy components are matter of debate: emission from Ce^{3+} ions in different surrounding configurations created by fibre drawing can be possibly suggested; alternatively, a role of intrinsic defects of the host matrix induced or increased by fibre drawing can be proposed. As a support to the first hypothesis, we remark that RL measurements performed on pure sol gel silica after a melting process carried on in our laboratories did not reveal any significant emission; conversely, melted Ce-doped silica displayed a more composite spectrum with respect to that of samples normally densified at 1050 °C, featuring components at about 2.7 eV, 2.8 eV and 3.1 eV. On the other hand, a weak RL emission at about 3.2 eV was detected by measuring the quartz glass tube used for the pre-form preparation, constituting the thin fibre cladding, so that a minor contribution of the fibre RL from the cladding cannot be excluded. Additional information on the emission process was provided by scintillation time decay measurements; these could no the performed directly on the fibre due to its small dimensions; however they were obtained on a small piece of molten pre-form, remained at the end of the fibre drawing process. The scintillation time decay measurement is shown in Fig. 3; in spite of the low signal level, a numerical fit could be performed with a single exponential function whose decay time turned out to be τ 110 ns. This value is about twice that obtained on the bulk material [10], possibly due to the presence of different Ce^{3+} configurations and of optically active defects.

Finally, the RL intensity of a composite fibre was measured. As above described, the composite fibre was made by a small portion (1 cm) of 220 μm Ce^{3+}-doped "active" fibre, coupled to a 1 m long 3M commercial fibre. The active portion was irradiated with 20 kV and 32 kV x-rays at different dose rates, and the RL signal was monitored at the commercial fibre end. The results are shown in Fig. 4. Due to the characteristics of the x-ray tube used and of the irradiation geometry, dose rates in the intervals $7x10^{-3}$ - 1.5 mGy/s and $6x10^{-2}$ – 4.8 mGy/s were investigated for 20 kV and 32 kV respectively. A very good linearity of the RL intensity was noticed. On the other hand, no luminescence was monitored by irradiating the commercial fibre end. Moreover, we remark that no significant differences were noticed by comparing subsequent RL measurements performed after several 32 kV x-ray irradiations up to 10^3 Gy, indicating a good stability and radiation hardness of the device.

In conclusion, the reported data have demonstrated that intense and fast luminescence is emitted by Ce^{3+}-doped silica fibres, whose structural and refractive index properties are very close to those of pure SiO_2. Easy coupling can be made between active luminescent fibres and commercial ones, so to realize a composite fibre for remote dosimetry. The radio-luminescence tests performed until now with low energy x-rays demonstrated a very good linearity in an extended dose rate interval and sensitivity to dose rates below 10^{-2} mGy/s, suggesting that application could be found in the medical field both for diagnostics and therapy radiation monitoring.

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FIGURE CAPTIONS

Fig. 1: RT Raman spectra of 220 μm diameter 0.06 mol%Ce-doped fibre, and of bulk SiO_2:0.05 mol%Ce before and after RTT.

Fig. 2: (A) RT radio-luminescence spectrum of 220 μm diameter 0.06 mol%Ce-doped fibre. Continuous line, experimental data; short dashed line, spectral components; long dashed line, numerical fit. (B) RT radio-luminescence spectra of bulk SiO_2:0.05 mol%Ce and of SiO_2:0.06 mol%Ce powder.

Fig. 3: RT scintillation time decay of 0.06 mol%Ce-doped molten preform excited by ^{22}Na source. Filled circles, experimental data; continuous line, numerical fit based on the deconvolution of the scintillation pulse and a single exponential function.

Fig. 4: RT radio-luminescence intensity of a composite fibre (obtained by fusion splicing about 1 cm of 220 μm diameter 0.06 mol%Ce-doped fibre with 1m long commercial 3M hard clad multimode fibre) versus x-ray dose rate. The x-ray dose is evaluated in air. Open circles and open squares, experimental data at 20 and 32 kV, respectively. Continuous lines, linear fits to the data.

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