Investigations on europium doped alumino-silicate xerogel incorporated in micro-channel glass and porous silicon

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ABSTRACT

Porous materials in general have received great attention from the last century. The development of new porous materials and the preparation of new composites based on porous materials is a subject of interest. The development of porous silicon based optical composite materials opened up new ways of incorporating optically active sol-gel materials into porous silicon. High purity silica optical fibres allow the most rapid and efficient data transmission. The objective of this work is to develop micro-channel glass / porous silicon – rare earth doped xerogel and glass composites, which would serve as compact optical amplifiers and delay line devices. Micro-channel glass / porous silicon - xerogel composites have been prepared by incorporation of sol-gel prepared from tetraethoxysilane, aluminium iso-propoxide and europium chloride into the porous matrix. Both xerogel and glass composites have been studied by various techniques such as FTIR, micro-Raman, photoluminescence spectroscopy, EDX and Scanning Electron Microscopy (SEM).

Keywords: Porous Silicon, Micro-channel glass, Sol-gel.

1. INTRODUCTION

Porous materials with their excellent property to host sol-gel materials are important for developing new composite materials. Porous silicon (PS) has gained attention as an important optical material after the discovery of its visible room temperature photoluminescence in 1990.[1] Porous silicon has shown to be a promising host for rare earths because it has large surface area allowing the easy infiltration of the ions into matrix.[2] There are various reports on the incorporation of rare earth ions into porous matrix like ion implantation,[3] electrochemical migration,[4] or spin-on technique.[5] Compared to other techniques, sol-gel method attracts much attention as an alternative low cost technology for fabrication of a variety of materials. The technique is not a new one, but the preparation of xerogel of high purity and homogeneity for various photonics applications is relatively new.[6] Rare earth ions doped into thin films, glasses and porous materials via sol-gel process make the efficient way of designing photonics materials. Emission from lanthanide ions has high efficiency, low temperature quenching, sharp spectral bands and high coherence.[7] Europium is widely used for fabrication of red-emitting materials.[8] The incorporation of rare earth ions into micro-channel glass is less studied compared to that of porous silicon. In the present work we are reporting on a new technique of incorporating europium ions in porous matrix by vacuum filtration method, which is also an efficient method of introducing the ions into the matrix. The prepared composite material has been studied by various spectroscopic techniques like FTIR, micro-Raman, PL and Scanning Electron Microscopy.

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2. EXPERIMENTAL

2.1. Sample preparation:

A set of porous silicon samples has been fabricated through the electrochemical etching in HF based electrolyte. Single crystal (100)-oriented, Cz-grown, *p*-type Si wafers of resistivity, $\rho = 10\ \Omega$ cm have been used for the present investigations. Galvanostatic anodic etching was performed under a high current density of 6 mA/cm^2 for 3 hours and the electrolyte used for the etching process was 4% HF in DMF. The micro-channel glass was received from State Optical Institute, St. Petersburg. The channel glasses were having pore size of 7µm and a thickness of about 0.05cm.

The preparation of rare-earth doped alumino-silicate xerogel and that of composite based on micro-channel glass / porous silicon (PS) is presented schematically in figure 1. In brief, the dopants (rare earths ions) were added to the alumino-silicate sol and gelation was controlled by acid-ethanol mixture. The composites were prepared by controlled vacuum filtration of the sol into the micro-channel glass and by controlled gelation of the sol inside the pores of silicon by introducing the hydroxylated porous silicon into the europium doped alumino-silicate sol before gelation.

2.2. FTIR spectroscopy

Fourier transform infrared (FTIR) measurements were performed in transmission mode using a Digilab FTS-6000 spectrometer. The sample was placed either in the main chamber of spectrometer, using a Perkin-Elmer micro-sampling attachment, or on the positional stage of a UMA 500 IR microscope. For measurements in the main chamber a wide band MCT detector in the wavenumber range of 450-6000 cm^{-1} with a resolution of 2 cm^{-1} and 8 cm^{-1} was used. A narrow band MCT detector with a spectral range of 4500-750 cm^{-1} was used in a UMA 500 IR microscope. A total of 128 scans were summed to increase the signal-to-noise ratio in both cases.

2.3. Photoluminescence spectroscopy

Room temperature photoluminescence (PL) spectra were measured with a Renishaw 1000 micro-Raman system. The excitation wavelengths were 514.5 nm from an Ar^+ laser (Laser Physics Reliant 150 Select Multi-Line) and 633 nm from a HeNe laser. The 50x magnifying objective of the Leica microscope focused the beam into a spot of about 1 µm in diameter. Typically PL spectra were measured from a few different spots on the external surface of as received micro-channel glass or porous silicon sample.

2.4. SEM characterisation

The SEM equipment used was an S-3500N variable pressure scanning electron microscope (Hitachi, Japan.) with a resolution of 3.5nm at 20 kV. The samples were coated with gold to increase the electrical conductivity of the specimen.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterisation of rare earth doped xerogel / micro-channel glass composite material

The rare earth (Eu^{3+}) doped alumino-silicate xerogel was introduced to micro-channel glass matrix according to the scheme shown in figure 1. The method of incorporation of xerogel inside the glass matrix was performed under the vacuum. The pores of the micro-channel glass are uniformly filled by europium-doped xerogel as can be seen from the SEM images (figure 2a and b). The enlarged image of the filled pores (figure 2b) shows cylindrical shaped xerogel confined well inside the pores. The reduction in size of these cylindrical xerogel can be attributed to the drying effects, as it is well known that xerogel will shrink in size upon drying.[9] The rare earth doped xerogel – micro-channel glass composite were subjected to heat treatment at 500°C holding the sample at the same temperature for two hours. The SEM images of the annealed samples were presented in figure 3(a) and 3(b). The samples showed the total shrinkage of the xerogel at higher temperature and it is

revealed that the shrinkage leads to thin films of glass inside the micro-channel glass matrix. An EDX analyses of the rare earth doped alumino-silicate xerogel and the glass inside the micro-channel glass matrix showed the presence of silicon and aluminium.

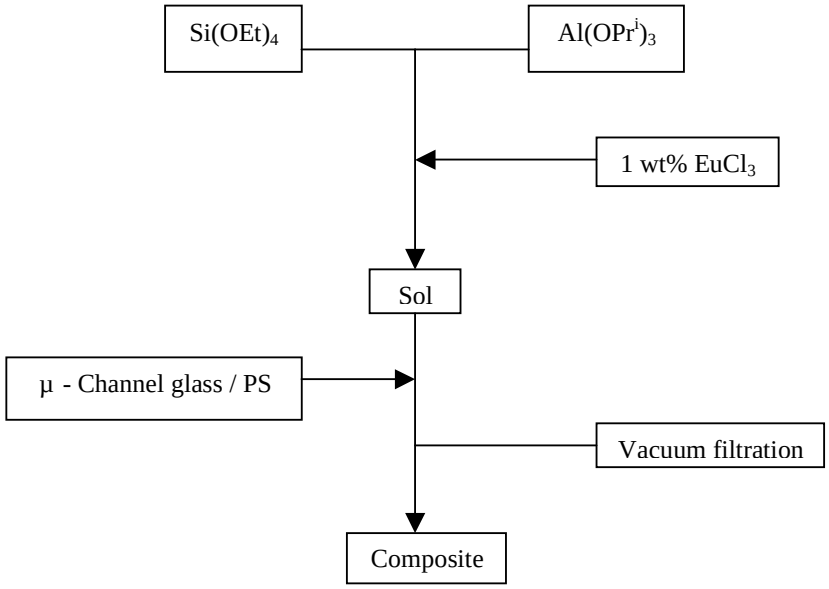
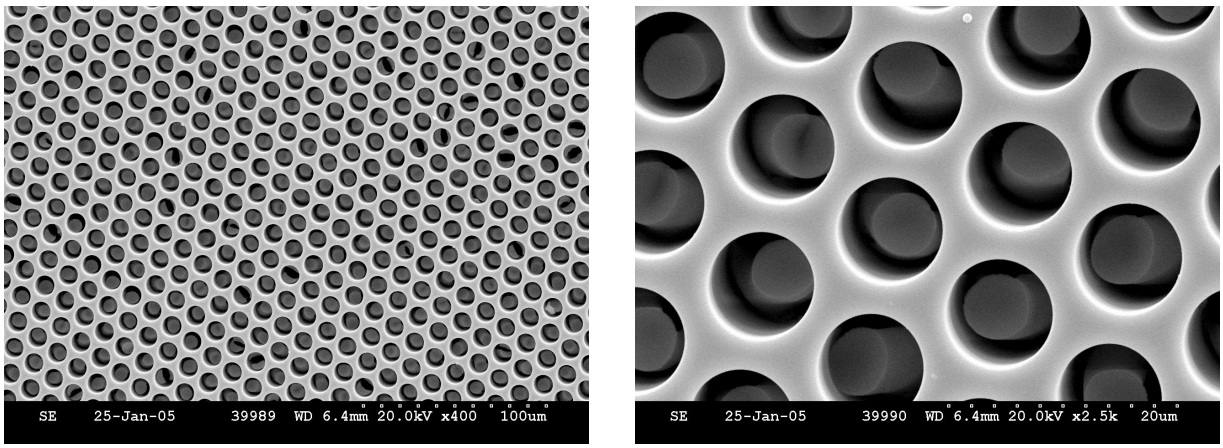
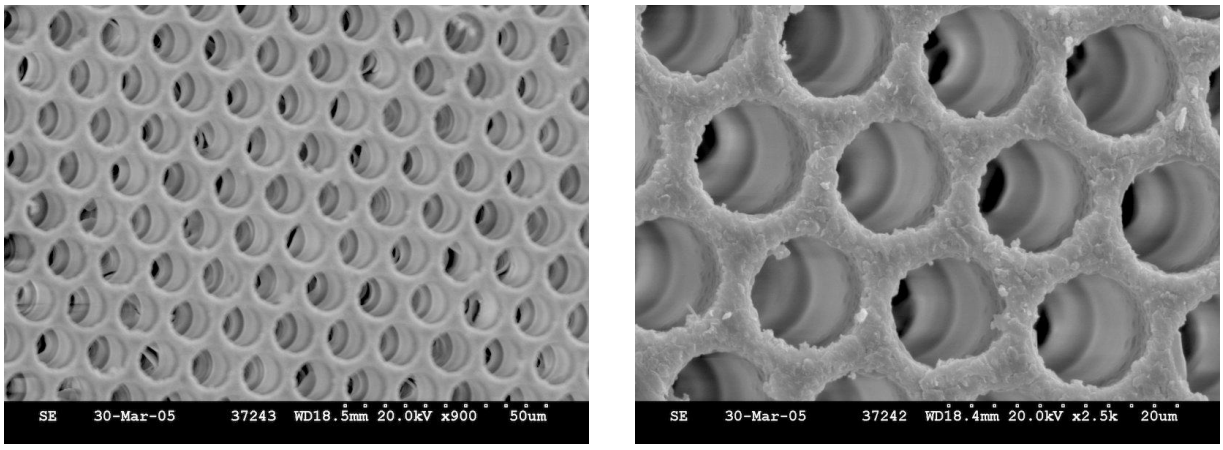


Figure 1. Schematic representation of the preparation of µ - channel glass / PS – rare earth doped xerogel composite.



(a) (b)

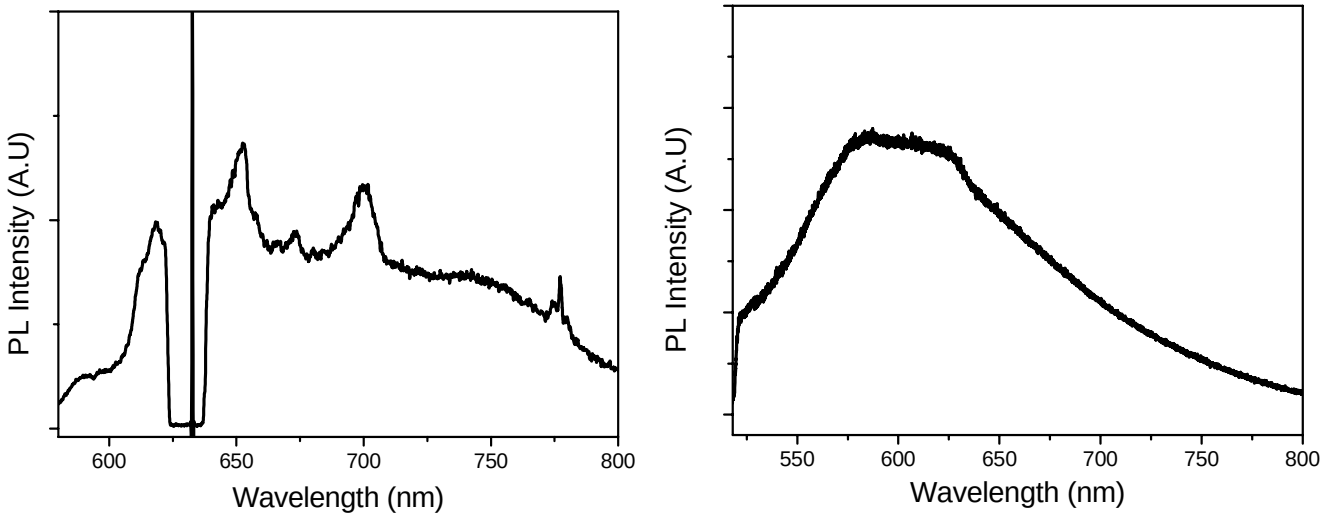
Figure 2 (a & b) SEM images of µ - channel glass – rare earth doped xerogel composite before heat treatment.



(a) (b)

Figure 3 (a & b) SEM images of μ - channel glass – rare earth doped glass composite after heat treatment at 500°C for 2 hours.

The luminescence studies carried out in the micro-channel – xerogel composite showed the PL spectra from europium containing xerogel registered at room temperature. Figure 4a depicts the PL spectrum of rare earth doped xerogel inside the pores from freshly prepared sample. The excitation wavelength of 633 nm was used in this PL measurement. The optical bands centred at 595, 618, 653, 700 nm originating from the electronic transitions between the levels of trivalent europium ion $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ respectively.[7] The figure 4b shows PL spectrum for the rare earth doped xerogel sample (same sample used for 633nm excitation) after a period of three weeks. The broad band may be due to the adsorbed water showing the disordered nature.



(a) (b)

Figure 4 (a) Room temperature PL spectra of europium – containing alumino-silicate xerogel inside the pores of μ - channel glass (b) after a period of three weeks.

The optical image on the cross-section of μ - channel glass shows the xerogel fibre inside the pores as depicted in figure 4. This image again confirms the cylindrical nature of the fibre inside the pore.

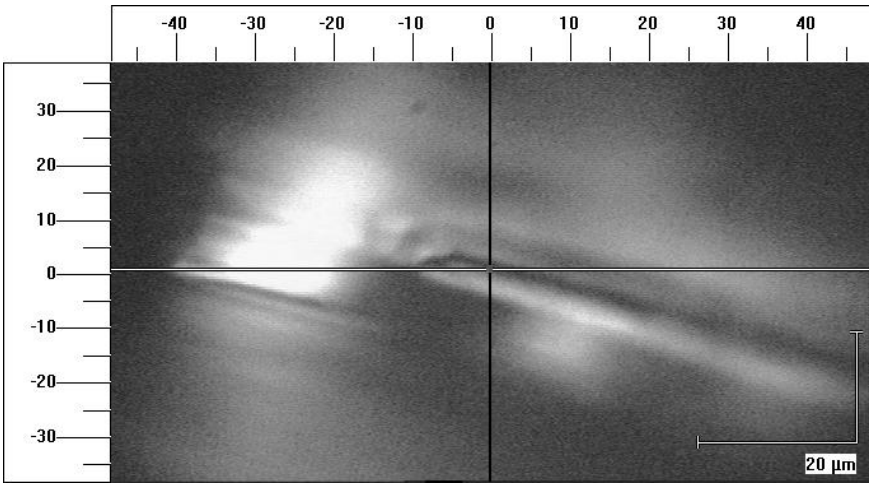
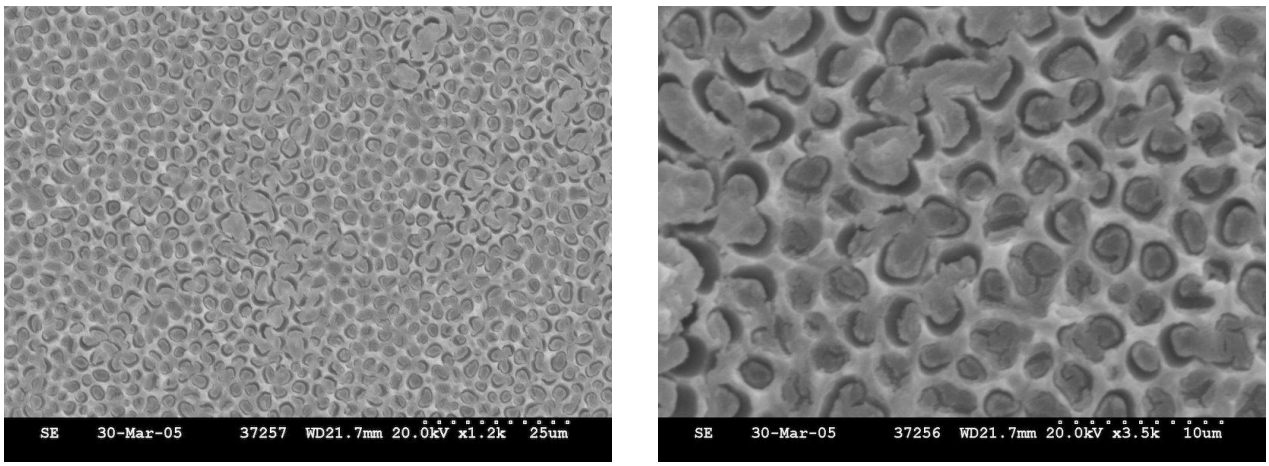


Figure 4 Optical image of europium – containing alumino-silicate xerogel fibre inside the pores of μ - channel glass.

3.2. Preparation and characterisation of xerogel / porous silicon composite material

The method of preparation of porous silicon – europium doped alumino-silicate xerogel is same as that of been explained for micro-channel glass composite (as shown in the scheme 1). The xerogel infiltrated into the pores of silicon is presented in the SEM images 5(a) and 5(b) with different magnification. As can be seen from these images, the pores are uniformly filled with europium doped alumino-silicate xerogel. The macroporous silicon samples (as shown here) are suitable for hosting the sol-gel materials compared to the microporous silicon (pore size less than 10 nm) samples, as the diameter of the pores in microporous samples are insufficient for penetration of the sol through the channels of the pores.[10]



(a) (b)

Figure 5(a & b) SEM images of porous silicon – europium doped xerogel composite.

The PL spectrum of the europium doped alumino-silicate glass – porous silicon composite sintered at 800°C for two hours is presented in figure 6. The observed luminescence bands correspond to the optical transitions of Eu^{3+} ions in the porous silicon matrix.

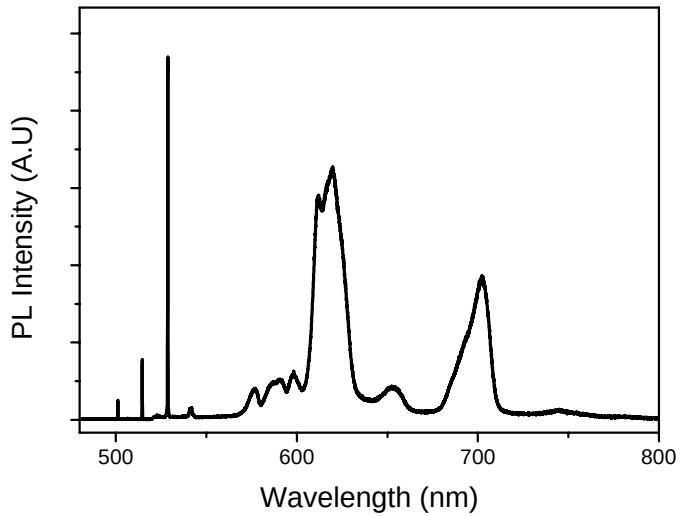


Figure 6 PL spectrum of porous silicon – europium doped alumino-silicate glass composite sintered at 800°C for two hours.

An FTIR study on the xerogel – porous silicon is presented in figure 7. The IR spectrum revealed bands associated with network vibrational modes centred around 800, 930, 1071, 1647 and 3423 cm^{-1}. The broad band at 3423 cm^{-1} corresponds to the fundamental stretching vibrations of –OH groups and reveals the presence of hydroxyl groups in the glass. A band at 1647 cm^{-1} is assigned to the bending mode of water molecules and indicates the presence of adsorbed water molecules. The presence of Si-O-Si asymmetric stretch is revealed from the strong band at 1071 cm^{-1}. The small bands observed at 930 and 800 cm^{-1} are assigned to Si-OH stretching and Si-O-Si symmetric stretching or vibrational modes of ring structure.[11,12]

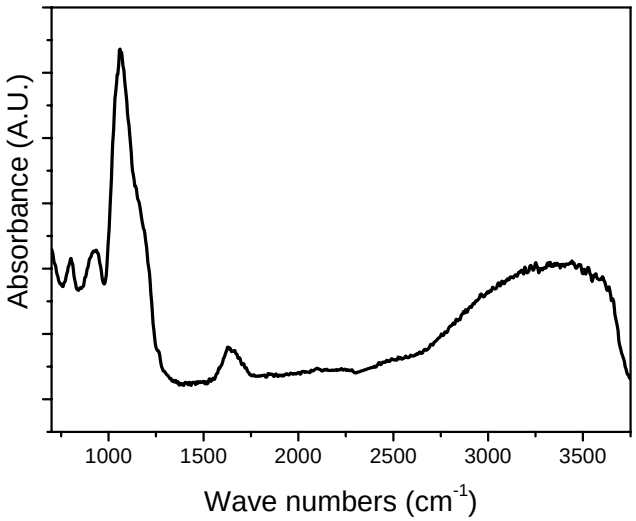


Fig. 7. FTIR spectrum of europium doped xerogel –porous silicon composite.

Thus the results revealed the possibility of the preparation of micro-channel glass / porous silicon – rare earth doped xerogel or glass composite. The method of preparation of such a composite is reported here for the first time.

4. CONCLUSIONS

Thus we have demonstrated that europium doped xerogel – micro-channel glass / porous silicon composites can be effectively prepared using standard sol-gel processing. Porous materials are good matrix for the preparation of composites based on rare earths. Also, we showed the formation of rare earth doped xerogel fibres, which can have potential application in the area of photonics.

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