OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 10, October 2010, p. 1620 - 1623

Investigations of the neodymium doped quartz glasses obtained by the hybrid sol-gel method

H. NICIU[a,*], C. VASILIU[b], A. MANEA[a], D. RADU[c], M. SECU[a], C. ONOSE[c], L. GHERVASE[b], D. NICIU[a], I. D. FERARU[b], C. E. A. GRIGORESCU[b]
[a]*National Institute R&D Materials Physics, P.O. Box MG- 7, 077125, Magurele, Romania*
[b]*National Institute R&D Optoelectronics INOE2000, P.O. Box MG-5,077125, Magurele, Romania*
[c]*University Politehnica of Bucharest, 313 Splaiul Independentei Str., Bucharest, Romania*

Undoped and neodymium doped quartz glasses were obtained by the hybrid sol-gel method. The vitrification was performed in He atmosphere. The Nd^{3+}characteristic absorption bands in the UV and VIS were put into evidence. Investigations in the NIR range revealed a small amount (86 ppm) of OH^- in the vitreous matrix. FTIR and Raman spectra exhibit the SiO_2 glass characteristic vibrations and also the characteristic vibrations of Si-OH and Si-Cl bonds. The photoluminescence peaks at 640, 920 and 1080 nm belonging to the Nd^{3+} doped quartz glass were evidenced.

(Received September 28, 2010; accepted October 14, 2010)

Keywords: Nd:Silica glass, Hybrid sol-gel method, Photoluminescence

1. Introduction

In comparison with most usual laser glasses [1] quartz glass exhibits a high transition temperature, a low expansion coefficient (5×10^{-7}/K) and a low nonlinear refractive index thus being very attractive as a host for neodymium ions [2]. Neodymium doped quartz glass has potential applications in the field of laser glasses and optical fiber amplifier [3].

Special properties are required for a high quality laser glass: homogeneous distribution of the lanthanide ions in the host lattice, low hydroxyl content and the largest possible transparency degree. These characteristics are taken into consideration when Nd_2O_3 doping is chosen. The hybrid sol-gel method, employed usually to obtain bi-component powders from pseudo-homogeneous sols, leads to less versatile gels than those obtained from alkoxides. Those powders need higher vitrification temperatures because of their large pores. However, the quite straightforward doping process, the possibility of reducing the amount of OH^- content and also the shortening of production cycle make some advantages of the hybrid sol-gel technique .

2. Experimental

The synthesis was done using $SiCl_4$:C_2H_5OH:H_2O in a molar ratio of 0.004:0.087:0.909. Through the hydrolysis of $SiCl_4$ in ethyl alcohol 95,57% a sol is formed and further gelified. Furteher adding of $SiCl_4$ and H_2O rapidly destabilizes the sol because of the high excess of HCl released through the hydrolysis reaction. The precipitate obtained was impregnated with a solution of $NdCl_3$*$6H_2O$, 99,999 %, in a molar ratio SiO_2:$NdCl_3$ of 0,998:0,002. The doped SiO_2 gel was thermally annealed for drying and densification. The densification thermal treatment is carried out at la 900 °C for 8 hours. The doped vitreous silica powder was thermally treated at high temperature in He: Cl_2 (3:1 vol.) atmosphere at 950 °C, for 4 hours. This temperature was experimentally chosen. At higher temperatures the pores tend to close and embed the volatile components, with negative effects on the final product, which would then hold gas inclusions. The vitrification thermal treatment was carried out at 1750 ^{0}C for 2 hours in He at 20 atm. The high pressure of He helps to remove the gas inclusions from the material. The glass thus obtained is transparent and shows the characteristic colour of Nd-doped glasses. Undoped transparent, colourless quartz glass samples were obtained using the same preparation process.

UV-VIS-NIR transmission investigations were carried out with a UV/VIS/NIR Lambda 1050 spectrophotometer. FTIR analyses of the samples were run with a Perkin Elmer SPECTRUM 100 spectrophotometer in the range of 550-4000 cm^{-1}. Raman spectra were taken with a micro-Raman LabRamHR 800 (Horiba Jobin Yvon) spectrometer with 633 nm laser excitation.

The photoluminescence analyses of neodymium doped quartz glass over the range 605 to 900 nm were performed using a FLS-920 Edinburgh Instruments Spectrofluorimeter, equipped with a 450 Watt lamp and double monochromators for both excitation and emission. To put into evidence the photoluminescence in the range 850-1200 nm we used the "lock-in" technique with the aid of a standard measuring set-up built of two monochromators (one for excitation and the second for emission) a laser diode (P=10mW) with centre wavelength at 535 nm as a excitation source and a photomultiplier sensitive up to 1200 nm.

3. Results

Fig. 1(a) shows the transmission spectra of undoped quartz glass synthesized by the hybrid sol-gel method described above. The sample has a continuous range of transmission between 200 and 850 nm.

The Fig. 1(b) presents the transmission spectra of doped quartz glass. The UV transmission range is limited at 220 nm. The Nd^{3+} characteristic absorption bands appear at the wavelengths of 365, 535, 580, 750, 810 nm and are due to the transitions from the ground state $^4I_{9/2}$ to the excited states $^4D_{3/2}+^4D_{5/2}+^2I_{11/2}$, $^2K_{13/2}+^4G_{7/2}+^4G_{9/2}$, $^4G_{5/2}+^2G(1)_{7/2}$, $^4F_{7/2}+^4S_{3/2}$, $^4F_{5/2}+^2H(2)_{9/2}$ [2]. The strongest absorption band is observed at 590 nm in agreement with usual Nd^{3+} ion transition for laser vitreous host materials.

A high content of hydroxyl groups in the glass makes impossible the obtaining of optical amplifiers using the Nd^{3+} transition $^4F_{3/2}\rightarrow^4I_{13/2}$. D. M. Dood and D. B. Fraser [4] proposed a method to directly determine the content of hydroxyl groups from the transmission spectra. It consists in the analysis of the OH^- groups' concentration at 2740 nm with an error of $\pm$ 4%. NIR transmission spectrum of our synthesized doped glass is presented in Fig. 2 showing 86 ppm OH^-. The quartz glass may contain up to 1200 ppm OH^- groups [5], which leads to absorptions in the NIR range at 1385, 2220 and 2740 nm.

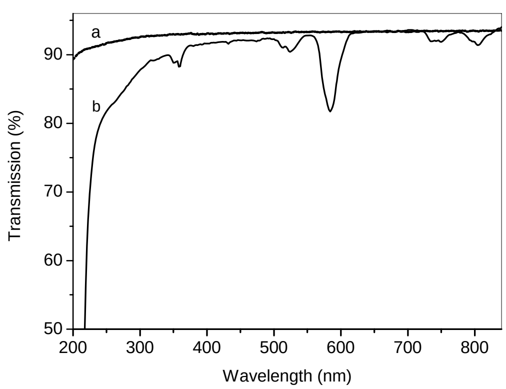

Fig. 1. UV-VIS transmission spectra: a) SiO_2, 1.25 mm thickness; b)SiO_2:Nd^{3+}, 2.15 mm thickness.

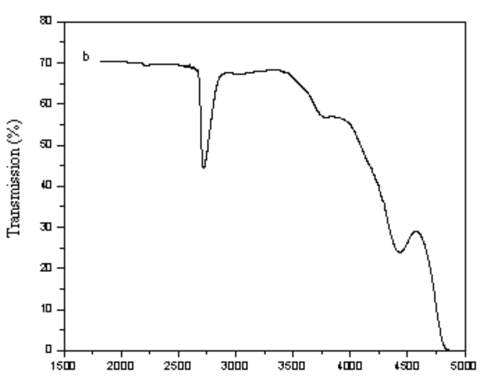

Fig. 2. NIR transmission spectrum, SiO_2:Nd^{3+}, 2.15 mm thickness.

FTIR spectra in Fig. 3 present the absorption bands at ~1040 and ~1145 cm^{-1} corresponding to the stretching vibrations of Si-O-Si, and the absorption bands at ~788 and ~966 cm^{-1} assigned to the stretching vibrations of terminal Si-O groups [6, 7]. For the doped quartz glass (Fig. 3(b)) the absorption bands are more intense and slightly shifted towards lower wave numbers. This effect is associated with $Nd3^+$ doping. Also, the shoulder at 610 cm^{-1} indicates the presence of Si-O-Nd bonds [8].

FTIR spectra in Fig. 4 present the absorption bands at 1650 and ~3300 cm^{-1}, which correspond to the stretching vibrations of SiO-H and Si-OH.

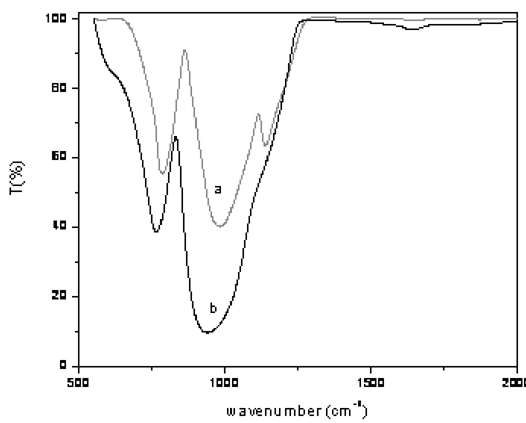

Fig. 3. FTIR transmission spectra: a) SiO_2, 1.25 mm thickness; b)SiO_2:Nd^{3+}, 2.15 mm thickness, 500-4000 cm^{-1}.

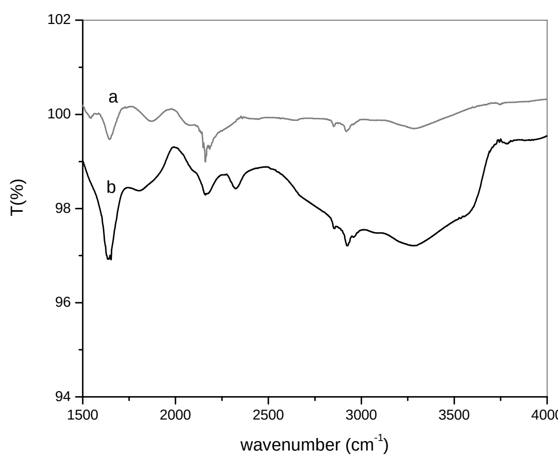

Fig. 4. FTIR transmission spectra: a) SiO_2, 1.25 mm thickness; b)SiO_2:Nd^{3+}, 2.15 mm thickness, 1500-4000 cm^{-1}.

The Fig. 5 shows the Raman spectra of synthesized quartz glass. Both undoped, (Fig. 5(a)), and doped quartz glass (Fig. 5(b)), exhibit the quartz glass characteristic symmetric and asymmetric bending vibrations of Si-O, at

300-500 cm^{-1}, and at 400-600 cm^{-1}, respectively. The characteristic asymmetric and symmetric stretching vibrations of Si-O-Si, were noticed at 850-1200 cm^{-1} and at 800-950 cm^{-1} respectively [9]. The bending vibrations at 1636 cm^{-1} correspond to Si-OH bonds. The stretching vibrations of Si-Cl bonds were noticed at 597 cm^{-1} [10]. In the Raman spectra of Nd^{3+} doped quartz glass are shown in Fig. 5(b). The peak at 1882 cm^{-1} is assigned to the stretching vibrations of Al-H [11]. The results of Raman investigations are in good agreement with the FTIR ones.

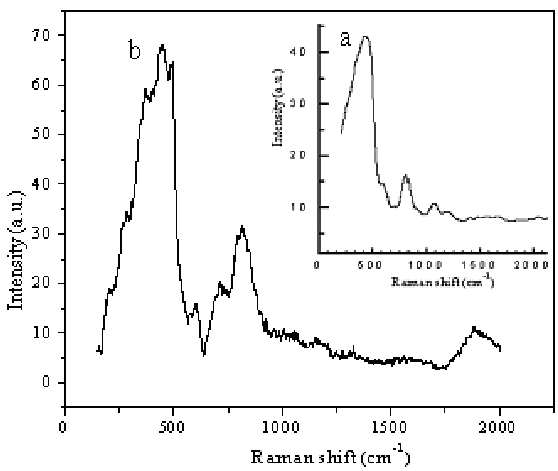

Fig. 5. Raman spectra of synthesized quartz glass: a) SiO_2; b)SiO_2:Nd^{3+}.

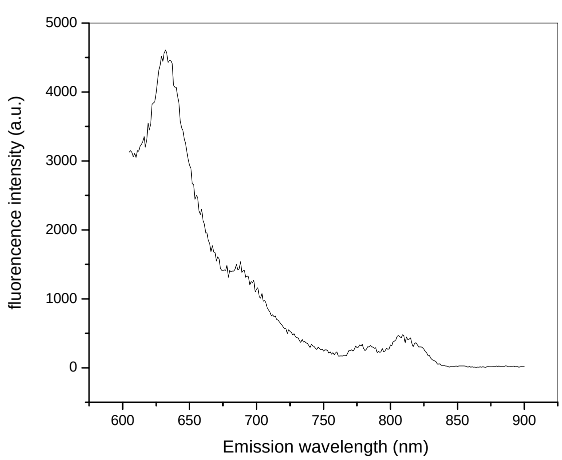

Fig. 6. Photoluminescence spectrum of SiO_2:Nd^{3+} - excitation at 585 nm.

By an excitation at 585 nm (Fig. 6), the photoluminescence at 640 nm due to the Nd^{3+}: $^4G_{9/2} \rightarrow {}^4I_{15/2}$ transition was put into evidence [1, 12, 13].

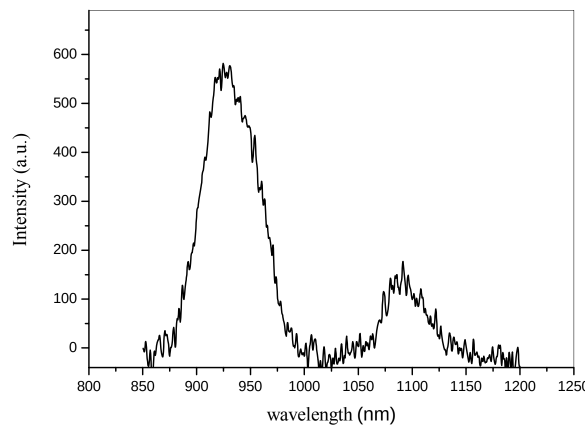

Fig. 7. Photoluminescence of SiO_2:Nd^{3+}, excitation at 535 nm, P = 10 mW.

The photoluminescence spectrum of synthesized Nd^{3+} doped quartz glasses was obtained through laser diode excitation (P=10 mW) with λ = 535 nm. The investigation was done in the range of 850-1200 nm. The photoluminescence was put into evidence at approx. 920 and 1080 nm, which correspond to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions of Nd^{3+} ion [1, 12, 13].

5. Conclusions

Quartz glasses (either undoped or doped) with low OH^- contents were synthesised by the hybrid sol-gel method from multicomponent powders, followed by vitrification in helium atmosphere.

The results of Raman and FTIR investigations are supporting each other and confirm the quartz glass structure and also the low impurity levels of Cl^-, OH^-.

The photoluminescence of the Nd^{3+} doped quartz glass shows the specific transitions of Nd^{3+} ions: $^4G_{9/2} \rightarrow {}^4I_{15/2}$,$^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$.

Future work will be devoted to synthesis and characterisation of quartz glass doped with different lanthanide ions.

Acknowledgements

This work has been carried out in the frame of the 2nd National Plan for Research, Development & Innovation (2007-2013)/ Project No.11-053 / 2007.

References

[1] I. K. Battisha, Egypt, J. Sol. **24**(1), 51 (2001).
[2] Takahiro Sato, Yasushi Fujimoto, Hajime Okada, Hidetsugu Yoshida, Masahiro Nakatsuka, Appl. Phys. Lett. **90**, 221108 (2007).
[3] K. Patek, „Glass Lasers”, J. G. Edwards, Ed., Iliffe Books, London (1970).
[4] D. M. Dood, D. B. Fraser, J. Appl. Phys. **37**(10),

3911 (1966).
[5] P. F. McMillan, R. L. Remmele Jr., American Mineralogist, **71**, 772-778 (1986).
[6] M. Zaharescu, O. C. Mocioiu, C. Andronescu, J. Optoelectron. Adv. Mater. **10**(6), 1315 (2008).
[7] A. Miella, M. Creatore, M. C. M. Van de Sanden, N. Tomozeiu, J. Optoelectron. Adv. Mater. **8**(6), 2003 (2006).
[8] S. Devi, S. Kumar, S. Duhan, Int. J. of Electronics Engineering, **2**(1), 205 (2010).
[9] K. Nakamoto, „Infrared and Raman spectra of Inorganic and Coordination Compounds", 484, Wiley-Interscience, New York, 1986.
[10] K. Sera, K. Suehiro, M. Hayashi, H. Murata**,** Bulletin of the Chemical Society of Japan, **49**(1), 29 (1976).
[11] A. M. Ahern, P. R. Schwartz, L. A. Shaffer, Applied Spectroscopy, **46**(9), 1327 (1992).
[12] U. Natura, R. Martin, G. Goenna, M. Kahlke, G. Fasold, Proceedings of SPIE, **5754**, 1312-1319 (2005).
[13] Elena Lupan, Journal of Non-Oxide Glasses **1**(3), 183 – 189 (2009).

*Corresponding author: niciuh@yahoo.com