

# Crystallization process in $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_20.05\text{Na}_2\text{O})$ ceramic system

I. COROIU<sup>\*</sup>, Gh. BORODI<sup>a</sup>, I. VIDA SIMITI, Al. DARABONT<sup>b</sup>, I. BRATU<sup>a</sup>, E. CULEA, N. JUMATE  
*Technical University, St. Daicoviciu 15, 400084 Cluj-Napoca, Romania*

<sup>a</sup>*National Institute for Research and Development of Isotopic and Molecular Technology, 400084 Cluj-Napoca, Romania*

<sup>b</sup>*Babes-Bolyai University, 00084 Cluj-Napoca, Romania*

Glass-ceramics of  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_20.05\text{Na}_2\text{O})$  composition were prepared by sol-gel method. This method was chosen because offers the advantage of a good chemical homogeneity and a better control of physical and chemical properties in comparison with traditional methods used to obtained glasses and ceramics. X-ray diffraction (XRD), scanning electron microscopy (SEM) and infrared spectroscopy (IR) were used to study the role of gadolinium ions and heat-treatment temperature in the precipitation of the crystalline phases. The X-ray diffraction patterns show that addition of  $\text{Gd}_2\text{O}_3$  exerts an important influence on the crystallization process of the studied samples. The crystalline phase decrease with increasing the  $\text{Gd}_2\text{O}_3$  concentration. SEM and IR data support this assertion. The gadolinium ions play a network modifier role of the glass ceramic structure.

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## 1. Introduction

Sol-gel processes have been intensively developed since they were found to be suitable for preparing materials and designed devices with specific properties [1]. A large variety of advanced ceramic materials including amorphous glasses, polycrystalline and composite ceramics were obtained by sol-gel methods. Silicate systems containing different rare earth oxides, obtained by sol-gel techniques, are important in various fields of technology [2-3] including laser and optical waveguides in telecommunication applications, microelectronics and catalysis.

The purpose of this paper was to study the structure and optical properties of  $0.95\text{SiO}_2-0.05\text{Na}_2\text{O}$  glass-ceramics containing up to 20% molar  $\text{Gd}_2\text{O}_3$  by X-ray diffraction, scanning electron microscopy and IR spectroscopy.

## 2. Experimental

The obtained gadolinium glass ceramics have the following composition  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_20.05\text{Na}_2\text{O})$ , where  $x = 0, 0.01, 0.05, 0.15$  and  $0.20$ . These were prepared starting from tetraethoxysilane (99.9% purity, purchased from Fluka Chemika) as source of silica,  $\text{Na}_2\text{O}_2$  (99.95% purity, purchased from Merck) and respectively,  $\text{Gd}_2\text{O}_3$  (99.99% purity purchased from Aldrich).

The sodium peroxide and gadolinium oxide were converted to the corresponding nitrates,  $\text{NaNO}_3$  and  $\text{Gd}(\text{NO}_3)_3$ . The water solutions of these nitrates were evaporated on a water bath (100 °C). The tetraethoxysilane was mixed with ethanol and water in molar ratio 1:3:1, and then stirred for 1 hour at room temperature. After this hydrolysis, the sodium nitrate and the gadolinium nitrate

were added to give a  $\text{H}_2\text{O}/\text{tetraethoxysilane}$  ratio of 20. Before this operation, the nitrates were again dissolved in water. The obtained solution was stirred about 1 hour with magnetic agitator and then dried at 60 °C.

For thermal treatment the samples were prepared in the following way: the gel was dried at 250 °C and then pressed in the shape of discs with 22mm diameter and approximately 1mm thickness. The samples were heat-treated at 250 °C, 500 °C and 1000 °C in air under normal pressure. The thermal treatment for all temperatures was made for about 48 hours.

The structure and properties of the samples were examined using X-ray diffraction, scanning electron microscopy (SEM) and IR spectroscopy.

The X-ray diffraction measurements were carried out on a DRON 2 type diffractometer applying  $\text{CuK}\alpha$  radiation. The diffraction patterns were compared to standard patterns for phase's identification.

Infrared absorption spectra were measured at room temperature ( $\sim 20$  °C) in the  $400-4000\text{ cm}^{-1}$  range with a resolution of  $4\text{ cm}^{-1}$  using a FT-IR Vector 25 Bruker type IR spectrophotometer and the KBr pellet technique.

Microscopic examination of the samples was made with a Jeol JSM 5600-LV scanning electron microscope.

## 3. Results and discussion

The Figs. 1a and 1b show the X-ray powder diffraction patterns of the studied samples heat-treated at 500 °C and 1000 °C. The samples heat-treated at 500 °C have an amorphous structure, while that heat-treated at 1000 °C a crystalline structure (see Fig. 1a). It has been ascertained that an extensive crystalline phase was developed for  $x=0$  and this crystalline phase decreases for  $x \neq 0$  (see Fig. 1b).

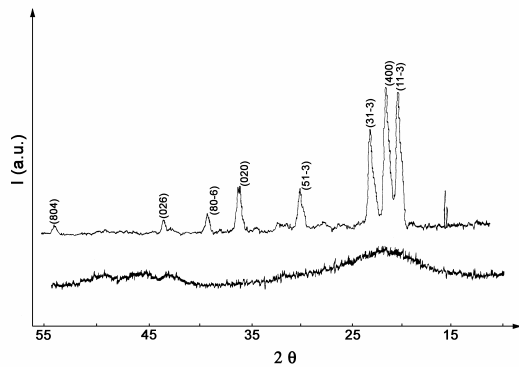


Fig. 1a. X-ray diffraction patterns for the  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_2 0.05\text{Na}_2\text{O})$  samples with  $x=0$  heat-treated at 500 °C and 1000 °C.

For  $x=0$  the crystalline phase is tridymite having monoclinic type lattice with  $a=18.49\text{Å}$ ,  $b=4.99\text{Å}$ ,  $c=25.83\text{Å}$  and  $\beta=177.55^\circ$  lattice parameters. For  $x=0.05$  the crystalline phase diminishes and consists in a mixture of tridymite (crystallised in orthorhombic system with  $a=5.046\text{Å}$ ,  $b=8.236\text{Å}$ ) and cristobalite (crystallised in tetragonal system with  $a=4.971\text{Å}$ ,  $b=6.918\text{Å}$ ). For a higher amount of  $\text{Gd}_2\text{O}_3$  ( $x=0.15$  and  $x=0.20$ ) the crystalline phase further diminishes and consists of the same mixture of cristobalite and tridymite, but the cristobalite becomes the main component.

The increase of the amorphous phase with increasing the amount of gadolinium oxide agrees with the previously reported data [4], showing that the addition of the gadolinium ions generates structural changes of the host glass ceramic matrix. Thus, the gadolinium ions play a network modifier role of the glass ceramic structure.

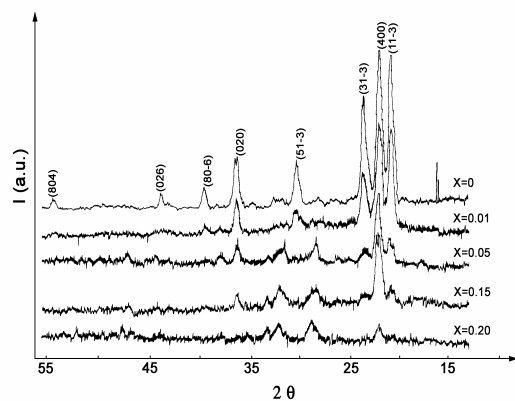


Fig. 1b. X-ray diffraction patterns for the  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_2 0.05\text{Na}_2\text{O})$  samples with  $x=0$ ,  $x=0.01$ ,  $x=0.05$ ,  $x=0.15$  and  $x=0.20$ , heat-treated at 1000 °C.

The IR absorption spectra of the  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_2 0.05\text{Na}_2\text{O})$  samples heat-treated at 250 °C, 500 °C and 1000 °C with  $x=0$ , 0.01, 0.05, 0.15 and 0.20 are displayed in Figs. 2, 3 (a), (b) and (c).

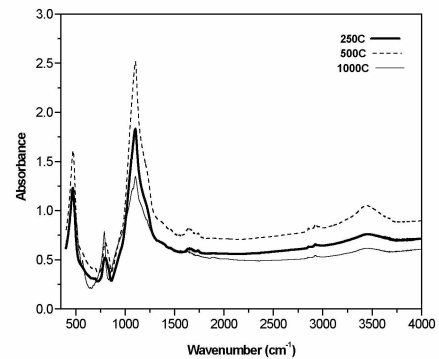
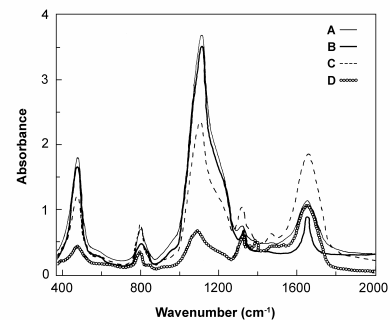
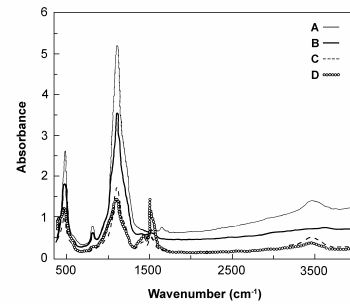


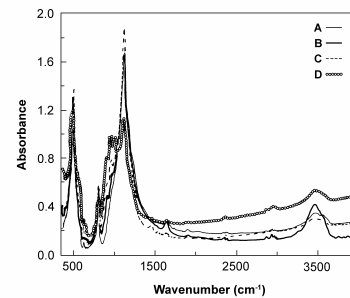
Fig. 2. IR absorption spectra of the  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_2 0.05\text{Na}_2\text{O})$  samples with  $x=0$  heat-treated at 250 °C, 500 °C and 1000 °C.



(a)



(b)



(c)

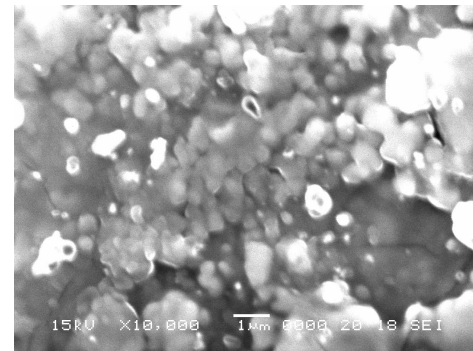
Fig. 3. IR absorption spectra of the  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_2 0.05\text{Na}_2\text{O})$  samples, heat-treated at 250 °C (a), 500 °C (b), 1000 °C (c), with  $x=0.01$  (A),  $x=0.05$  (B),  $x=0.15$  (C) and  $x=0.20$  (D).

The main absorption bands that appear in all spectra are: a sharp absorption band at  $471\text{--}483\ \text{cm}^{-1}$ , a medium absorption band at  $776\text{--}808\ \text{cm}^{-1}$ , a strong absorption band at  $1088\text{--}1117\ \text{cm}^{-1}$ , a small absorption band at  $1380\ \text{cm}^{-1}$ , a small absorption band at  $1626\text{--}1636\ \text{cm}^{-1}$  and a small and broad absorption band at  $3420\text{--}3440\ \text{cm}^{-1}$ . A common analysis shows that the prevalent features present in these spectra are those characteristics of the silicate chains. Thus, the sharp absorption bands at  $471\text{--}480\ \text{cm}^{-1}$  correspond to bending vibrations of Si-O-Si linkages, the medium absorption bands at  $776\text{--}808\ \text{cm}^{-1}$  can be assigned to symmetric stretching vibration of O-Si-O bonds while the strong absorption bands at  $1088\text{--}1117\ \text{cm}^{-1}$  to anti-symmetric stretching vibrations of bridging oxygen's [5]. The absorption band at  $1380\ \text{cm}^{-1}$  visible only at lower heat-treatment temperatures can be ascribed to carbonate groups. The absorption bands at  $1626\text{--}1636\ \text{cm}^{-1}$  and at  $3420\text{--}3440\ \text{cm}^{-1}$  can be attributed to molecular water and stretching vibrations of OH and molecular water, respectively.

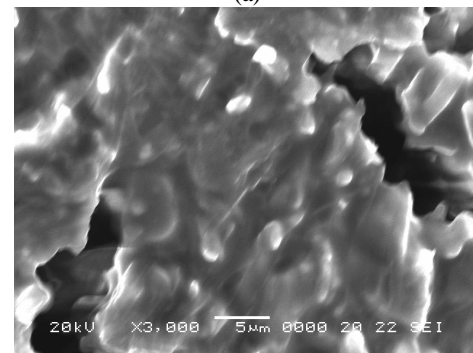
Besides these, some small IR absorption bands like  $548\ \text{cm}^{-1}$ ,  $615\ \text{cm}^{-1}$  and  $645\ \text{cm}^{-1}$  rise for a heat-treatment at  $1000\ ^\circ\text{C}$  and for  $x=0.20$ . It must also emphasize the absorption bands that become visible at  $1000\ ^\circ\text{C}$  for  $x=0.15$  and  $x=0.20$  as:  $895\ \text{cm}^{-1}$ ,  $947\ \text{cm}^{-1}$  and  $995\ \text{cm}^{-1}$  (the latest only for  $x=0.20$ ). In fact, the strong absorption bands at  $1102\ \text{cm}^{-1}$  for  $x=0.20$  is split in four branches. For  $x=0.15$  the latest enumerate absorption bands represent only shoulders. The IR absorption domain between  $600\text{--}620\ \text{cm}^{-1}$  corresponds to ring vibrations of six (or more than six) membered rings composed of  $[\text{SiO}_4]^{4-}$  tetrahedral units, while that about  $650\ \text{cm}^{-1}$  to ring vibrations of four membered rings [6]. Significant deformation of rings leads to the splitting of the ring band and sometimes to shift to lower vibration [7]. The absorption band at  $548\ \text{cm}^{-1}$  should be the result of such deformation corresponding to the bending vibrations of O-Si-O and (Si)O-Si-O(Si) linkages, too. The split of the strong absorption band at  $1102\ \text{cm}^{-1}$  for  $x=0.20$  in four branches ( $895\ \text{cm}^{-1}$ ,  $947\ \text{cm}^{-1}$ ,  $995\ \text{cm}^{-1}$  and  $1102\ \text{cm}^{-1}$ ) should be originate in the mixture of three and six membered rings compounds, distorted, with the allotropic sub-micrometer crystalline phases of the  $\text{SiO}_2$ .

The scanning electron micrographs of the fractured surfaces for samples:  $x=0$ ,  $x=0.01$  and  $x=0.15$  heat-treated at  $1000\ ^\circ\text{C}$ , are presented in Figs. 4 (a), (b) and (c).

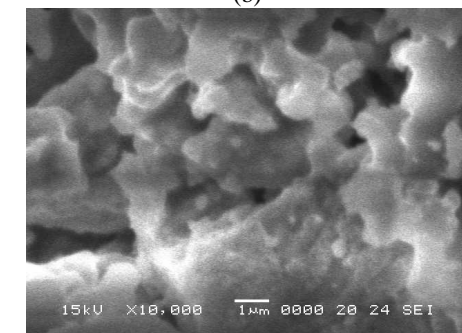
The electron micrograph of the  $x=0$  sample (see Fig. 4a) shows crystalline agglomerates micrometric/submicrometric sized, especially tabular crystallites and grains, surrounded by a little amorphous phase. The addition of gadolinium oxide even in small quantities generates an increase of the amorphous phase. For  $x=0.01$  sample (see Fig. 4b) besides submicrometer grains appear some micrometer polyhedral crystallites with plane facets. The crystalline phase of the  $x=0.15$  sample in smaller quantity (see Fig. 4c) consists of some irregular, rounded, big particles with relative irregular surface.



(a)



(b)



(c)

Fig. 4. SEM micrographs of the  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_2\ 0.05\text{Na}_2\text{O})$  samples, heat-treated at  $1000\ ^\circ\text{C}$ , with  $x=0$  (a),  $x=0.01$  (b),  $x=0.15$  (c)

#### 4. Conclusions

Samples of  $x\text{Gd}_2\text{O}_3(1-x)(0.95\text{SiO}_2\ 0.05\text{Na}_2\text{O})$  composition, where  $x=0, 0.01, 0.05, 0.15$  and  $0.20$  were obtained and studied. X-ray diffraction spectra show that addition of gadolinium oxide diminishes the amount of crystalline phase in the samples. IR data and SEM micrographs support this assertion.

The addition of the gadolinium ions generates structural changes of the host glass ceramic matrix. Thus, the gadolinium ions play a network modifier role of the glass ceramic structure.

**References**

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\* Corresponding author: coroiu@phys.utcluj.ro