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Synthesis and characterization of chloro-sulphide glass-ceramics containing neodymium(III) ions

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ABSTRACT

In this paper, we describe the preparation of Nd^{3+} doped glass-ceramics in the $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ system. Neodymium has been introduced as metallic powder or incorporated as sulphide. Appropriate heat treatments of the base-glass lead to glass-ceramics with controllable crystal sizes that are transparent in the visible and infrared spectral ranges. X-ray diffraction as well as electron diffraction techniques were used to investigate the crystallization process. Differential scanning calorimetry indicates that neodymium ions are poor nucleating agents in this glass compared to erbium ions. Luminescence measurements were also performed and point out that although the ceramization process increases significantly the luminescence efficiency, the neodymium ions are only partially incorporated in the nanocrystals.

1. Introduction

Sulphide glasses have lower phonon energies than oxide and fluoride glasses. As a result, rare-earth-doped sulphide glasses show radiative emissions with high quantum efficiencies especially in the mid-infrared region. Several studies have been carried out on the spectroscopy of rare-earth doped sulphide glasses [1–6]. Laser action in a neodymium-doped gallium–lanthanum–sulphide glass, in both bulk and fiber form, has been reported [7,8].

Among the many sulphide glasses, the germanium–gallium–sulphide glass system is interesting because of its potential for laser and optical fiber amplifier applications [9]. The incorporation of ionic compounds like caesium halides, especially caesium chloride, increases the glass forming domain of the system [10,11]. Then, by applying adequate heat-treatments to the obtained glasses, it is possible to control crystal growth inside the glass, thus creating a glass-ceramic. The challenge consists in finding the optimal heat-treatment above the glass transition temperature of the host in order to initiate nucleation, and then control the crystal growth to minimize light scattering in the glass-ceramic being fabricated. Thus, glass-ceramics can be defined as composite materials combining the unique forming ability of glass with the mechanical and optical properties of crystals. The effect of ceramization on the optical transmission of a Ge–Ga–Sb–S–CsCl host glass and the luminescence of incorporated Nd^{3+} ions was reported previously [12].

The present investigations aim at pushing forward the preliminary study done with Ge–Ga–Sb–S–CsCl glass, by using an antimony-free base-glass composition. Antimony-free matrices can lead to glass-ceramics with a more homogeneous distribution of crystallites within the matrix and with a blue-shifted band-gap as shown in a previous work [13]. This results in glass-ceramics with less light scattering and a broader spectral domain available for rare-earth spectroscopy. In addition, glasses from the Ge–Ga–S–CsCl system possess a higher degree of connectivity between their building blocks, as compared to their counterparts containing antimony, and thus exhibit higher thermal properties. $70(GeS_2)$–$20(Ga_2S_3)$–$10(CsCl)$ glasses incorporating various amounts of neodymium were synthesized, and then submitted to a proper heat-treatment that induces nucleation and allows to control the crystal growth. Since neodymium ions were employed as probes for the formation of crystals inside the glass, the optical properties of the obtained glass-ceramics were investigated to point out the influence of ceramization on absorption and fluorescence. The visible fluorescence of neodymium ions that will be described in this paper can only be observed in materials with low phonon energies. In a previous work [13], only infrared fluorescence of neodymium ions had been investigated. To make this study complete, glass-ceramics were characterized by thermal analysis and by X-ray diffraction coupled to transmission electron

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microscopy. High-temperature X-ray diffraction investigations have been performed as well.

2. Experimental

The base-glass was synthesized from high purity polycrystalline germanium (5N, Umicore), gallium (5N, Alfa Asear), sulphur (5N, Strem), caesium chloride (3N, Strem) and neodymium (3N, Strem) in its metallic form or neodymium sulphide. Erbium-doped base-glass has also been prepared for comparsion purposes (erbium metallic powder, 3N, Strem).

An appropriate quantity of each material was weighed according to the glass chemical formula and introduced into a silica tube with an inner diameter of 10 mm. A vacuum of about 10^{-5} mbar was achieved in the tube before sealing. The resulting ampoule was introduced into a rocking furnace and heated up to 850 °C with a heating rate of 1 °C/min. Such a slow heating rate is necessary to avoid ampoule explosion due to excessive pressure of sulphur vapors. The ampoule was maintained at 850 °C for 24 h to allow the starting elements to react thoroughly. Then, the glass ampoule was quenched in water at room-temperature and the obtained glass was annealed at 350 °C which is approximately 35 °C below its glass transition temperature T_g to minimize mechanical stress in the glass rod, while avoiding crystallization. The resulting glass rod (diameter = 10 mm, length = 40 mm) was then cut into 2 mm-thick disks for ceramization.

To determine the best experimental conditions for glass-ceramics preparation, thermal analysis was performed with a DSC2010CE differential scanning calorimeter (TA Instruments) in argon atmosphere. Thermal analysis up to 650 °C was carried out in argon atmosphere on MHTC96 calorimeter (Setram). The heating rate was set to 10 °C/min in order to measure the glass transition temperatures (T_g is measured at the inflexion point of the transition) of the samples base-glass. The experimental error is ±2 °C for T_g.

To prepare glass-ceramics, some disks were heated at different temperatures above T_g to determine the best annealing temperature for ceramization. The glass samples were then heated at the chosen temperature for various durations. Each heat-treatment was carried out in the same furnace to ensure reproducibility.

Optical transmission of the glass-ceramics in the visible and near-infrared regions was measured with a Cary 5 double-beam spectrophotometer (Varian) which operates in the 200–3300 nm optical range, whereas a VECTOR 22 (Bruker) FTIR spectrophotometer was used to carry out measurements in the near-infrared.

Visible and near-infrared photoluminescence in the 500–800 nm range was measured at room-temperature with a spectrometer from Photon Technology International.

Transmission electron microscopy was performed for a Philips CM20 fitted out with an Oxford EDS analyzer. The samples to be observed were first grinded in acetone to avoid the dissolution of caesium chloride and a drop of this solution was deposited on a carbon coated copper grid.

Room-temperature X-ray diffraction measurements were carried out on a Bruker AXS D8 diffractometer fitted out with a Vantec 1 linear detector. A copper anode was used, but no monochromator. Steps had a size of 0.016° with a counting time of 10 s each.

High-temperature X-ray diffraction was performed for the same Bruker diffractometer to which an Anton-Paar 1200 °C high-temperature chamber had been added. The Vantec detector was opened up to 8°. The heating slope of 30 °C/min was interrupted by 30-min dwell times every 20 °C from 380 to 600 °C. During dwell times, scans between 20° and 80° were acquired. The samples were 1-mm thick and had 10 mm in diameter.

3. Results

The $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ composition was chosen for its stability against crystallization. The CsCl content did not exceed 10 mol% to prevent an excessive sensitivity against moisture. Introduction of gallium is known to improve rare-earth solubility in glasses [14]. Furthermore, the $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ glass has proven to be suited for neodymium doping with controllable nucleation and growth [13].

A first series of $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ samples with 0.1 wt% neodymium was synthesized to determine the adequate heat-treatment temperature for ceramization. Defining the appropriate temperature consists in making a compromise. If the temperature is too high, nucleation and growth processes are very quick with crystal sizes varying in a large scale, and control is impossible. On the other hand, if the temperature is too low, nucleation is very slow. Finally, the temperature was set experimentally to 400 °C.

Two series of glass samples containing 0.1 wt% of neodymium were then synthesized. To the first series, the neodymium was added as metallic powder, whereas in the second series it was incorporated as neodymium sulphide. All the neodymium-doped samples were heat-treated at 400 °C, which corresponds approximately to the glass transition temperature. At that temperature, ceramization time is equal to 100 h approximately. This long ceramization time allows a good control of the process in terms of particle size and homogeneous distribution in the host.

3.1. DSC measurements

Table 1 gathers the DSC results of the undoped base-glass and samples from the series containing 0.1 wt% of neodymium that did not undergo any heat-treatment. The glass transition of the base-glass is observed at 400 °C. It is to notice that the glass transition stays around 400 °C for the neodymium-doped samples. Furthermore, it makes no difference on the glass transition whether the neodymium is added to the glass starting products as metallic powder or as sulphide.

On the DSC curves of the $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ undoped base-glass and the 0.1 wt% neodymium-doped samples presented in Fig. 1, no crystallization peak appears below 500 °C. Only one strong crystallization peak appears for both samples at 550 °C. For comparison, DSC measurements were performed for a 0.1 wt% erbium-doped $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ glass sample as shown in the same figure. It indicates that the glass transition still occurs at 400 °C, but surprisingly, this curve exhibits two crystallization peaks. There is a small peak at 486 °C that appears first, followed by a strong one at a temperature slighltly inferior to 520 °C. Thus, the erbium-doped glass crystallizes at lower temperatures than the base-glass and the neodymium-doped one, and the crystallization happens in a two-step process.

Fig. 2 shows DSC curves of $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ 0.1 wt% neodymium-doped base-glass and glass-ceramic samples. The glass-ceramic samples were heat-treated respectively 20, 60 and 100 h prior to the DSC measurements. For every sample, the glass transition occurs around 400 °C. However, differences in the

Table 1
Glass transition temperatures of unceramized samples of $(GeS_2)_{70}$–$(Ga_2S_3)_{20}$–$(CsCl)_{10}$ composition with or without Nd^{3+} ions.

Nd^{3+} (wt%)	T_g (°C)
0 (base-glass)	386
0.1 (metallic)	389
0.1 (sulphide)	386