Infrared Transmitting Glass Ceramics for Passive and Active Applications

Xianghua Zhang and J.L. Adam
UMR CNRS 6226 Sciences Chimiques de Rennes - Verres & Céramiques
Campus de Beaulieu - Université de Rennes 1
35042 Rennes Cedex - France
E-mail: xzhang@univ-renmes1.fr

Abstract: Glass-ceramics transparent above 10 μm in the infrared, have been synthesized. They are based on germanium and antimony sulphides or selenides associated to alkali halides. They are prepared by heating glass samples at temperatures above the glass transition, as a function of time. Ceramisation can be controlled, so that sub-100 nm crystals are generated in the glass matrix. Then, low light scattering is achieved and the transparency window of the original glass is maintained. When gallium sulphide is added, glass ceramics can be doped with rare-earth ions. Emissions from the $^4F_{3/2}$ and $^4I_{13/2}$ of Nd^{3+} and Er^{3+} ions, respectively, are more intense in glass-ceramics, as compared to their vitreous counterpart. Examination of band profiles and decaytimes show that rare-earth ions are embedded in both crystalline and glassy environments.

1. Introduction

Infrared transmitting materials, especially chalcogenide glasses have been widely studied since decades for different applications such as night vision, infrared laser power delivery, thermal imaging, chemical sensing, laser hosts and optical amplifier[1-3]. All these applications are possible thanks to their wide transmission range from visible to far infrared region. This large optical window is unfortunately associated with the relatively weak chemical bond, leading to brittle materials compared to oxide glasses for example.

One possible way to improve the mechanical performance of glasses is to fabricate composite materials such as glass-ceramics which are currently largely used in various applications such as telescope mirror and cooking tops. The biggest issue for making transparent glass ceramics is the control of the type and the size of crystals inside a glass matrix[4-6]. In order to minimize the optical losses, it is necessary to have small crystals with refractive index close to that of the glass matrix. A good example is the highly transparent oxyfluoride glass-ceramic. This idea is to benefit from the excellent chemical, thermal and mechanical properties of oxide glasses, and also from the low phonon energy crystalline environment for rare earth doping, leading to high quantum efficiency. The crystal size is well controlled under 50 nm thank to the presence of ionic fluoride inside the covalent oxide glass matrix. However, these glass ceramics are transparent from visible to approximately 3 μm due to the presence of a relatively light element, the oxygen.

The crystallisation of chalcogenide glasses have been intensively studied [7-9]. It is however not possible to control the crystal growth inside these glasses and big crystals are generally obtained, leading to completely opaque materials. It is difficult to make reproducible glass ceramics from pure chalcogenide glasses.

Inspired by the success of oxyfluoride glass ceramics, we have tried to make infrared transmitting glasses by introducing ionic halides inside the chalcogenide glasses based on previous works[10-15]. The concept is tested with the GeS_2-Sb_2S_3-CsCl system and transparent glass ceramics have been reproducibly obtained by controlling the crystal size under 100 nm.

The efficiency of these glass ceramics for rare earth

doping is also demonstrated, especially with Er^{3+} and Nd^{3+} ions. In that case, Ga_2S_3 must be added to the ternary compound to improve rare-earth solubility. Emissions from the $^4F_{3/2}$ level of Nd^{3+} and $^4I_{13/2}$ level of Er^{3+} have been measured for the first time in chalcogenide glass-ceramics.

2. Experimental

Precursor glasses for glass ceramic fabrication are fabricated with the commonly used technique for chalcogenide glass synthesis which can be summarized as follows: the starting raw materials are high purity Ge(99.99), Sb(99.99%) or Ga (99.99%), S(99.9%) or Se(99.99%) and CsCl(99.9) or RbI which are introduced into a silica tube (internal diameter about 10 mm). Rare earths are introduced in metallic form. The silica tube was sealed under vacuum (10^{-2} Pa) and put in a rocking furnace to ensure a continuous mixing of the melt. The temperature was increased at a rate of 2 ℃/min to 850 ℃ and kept at this temperature for 10 h. A glass rod is obtained by cooling the silica ampoule in air or in water depending on their resistance to crystallisation. The glassy state of the obtained sample is verified either by visual examination when the sample is transparent in visible range, or by X-ray diffraction combined with optical transmission measurement.

The DSC (Differential Scanning calorimeter, from TA instrument) analysis was performed with 10 mg of sample and a heating rate of 10 ℃/min. The temperature precision is about ±1 ℃.

The measurements in the visible and near infrared region were done with a Cary 5 double-beam spectrometer (Varian, Palo Alto, USA) with transmission reproducibility of ±0.5%. In the mid and far infrared region, they are performed using a Fourier Transform Spectrometer VECTOR22 (Bruker, Ettlingen, Germany) with a transmission precision of ±2%.

For observation under scanning electronic microscope, polished discs were coated with a very thin gold film due to the electrically insulating character of the glass ceramic samples. Some small cracks were created using a cutter. Observation inside these cracks allows eliminating the influence of the gold coating and gives much better images. The microscope was a JSM6301F from JEOL Inc. (Tokyo, Japan).

In order to qualify the glass ceramic samples versus fracture propagation, indentation measurements were performed with a diamond point using a microhardness tester (MXT70 from Matsuzawa inc. Japan).

In order to test the possibility of shaping the glass ceramics by moulding, a precursor glass disc is put between two moulds in silica glasses and hot pressed. The transmission of the obtained glass ceramic is compared with that of the starting glass. The hot pressing process is combined with the process of ceramisation.

Near infrared luminescence of Nd^{3+} was measured at room temperature by using a Horiba Triax-550 monochromator equipped with a thermoelectric cooled DSS-IGA020T InGaAs detector, with a 800-nm semiconductor laser diode as the excitation source. For Er^{3+}, photoluminescence spectra were recorded with excitation at 1.55 μm from a laser diode and detection by a liquid-nitrogen-cooled germanium detector.

3. Results and Discussion

Fig. 1 shows the wide glass-forming region in the ternary system GeS_2-Sb_2S_3-CsCl. It can be seen that more than 20 mol% of purely ionic CsCl can be introduced into the covalent GeS_2-Sb_2S_3 system. Tests of controlled crystallisation have been performed with different precursor glasses and results show that the best composition is $62.5GeS_2$-$12.5Sb_2S_3$-25CsCl which is exactly on the border of the glass forming region. This glass with a glass transition temperature Tg of 260℃

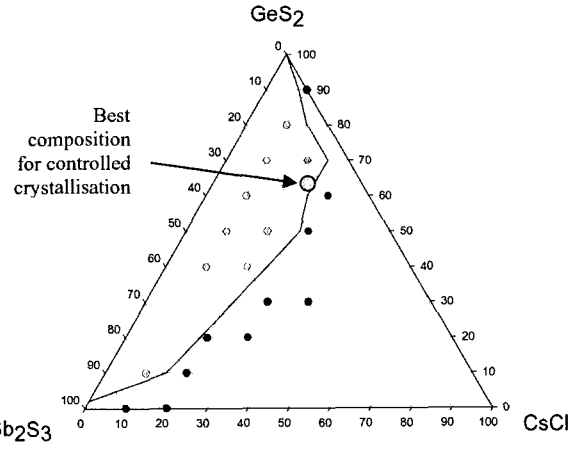


Fig. 1. The glass forming region in the ternary system.

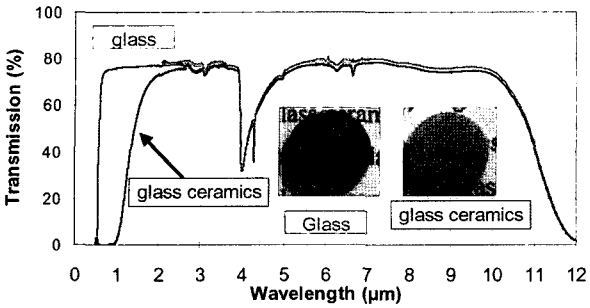


Fig. 2. The transmission of the precursor glass $62.5GeS_2$-$12.5Sb_2S_3$-25CsCl and the glass ceramic with the same composition.

Fig. 3. Observation under scanning electronic microscope of a glass ceramic obtained by annealing the precursor glass $62.5GeS_2$-$12.5Sb_2S_3$-25CsCl at 290°C during 11 h.

can be easily obtained just by cooling the silica ampoule containing the melt in air. Red transparent glass rods with a diameter bigger than 15 mm and a length longer than 100 mm are reproducibly obtained. Other compositions just outside of this glass forming region, $60GeS_2$-$10Sb_2S_3$-30CsCl for example, can not be vitrified even by cooling the silica ampoule in water.

The best thermal process for controlled crystallisation has been experimentally defined by annealing the selected compositions at different temperatures for different durations. A relatively low annealing temperature with long duration is preferred to ensure the reproducibility of the process. The best ceramisation temperature for the $62.5GeS_2$-$12.5Sb_2S_3$-25CsCl glass is 290°C and ceramisation duration can be changed from several hours to more than 300 h by giving highly transparent glass ceramics. An example is given in Fig. 2, showing the transmission of the precursor glass and a glass ceramic obtained by annealing the precursor glass at 290°C for 71 h. It can be seen that the presence of crystals inside the glass matrix induces additional scattering, especially in the short wavelength region. The glass ceramic is as transparent as the precursor glass in the mid infrared region.

According to the turbidity equation proposed by Hendy[16], light scattering induced by crystals inside a glass matrix can be described by using the following equation:

$$\tau = \frac{14}{15\pi}\varphi(1-\varphi)k^8R^7\left(\frac{\Delta n}{n}\right)^2$$

with : φ : volumic ratio, Δn : difference between the glass matrix and crystal refractive index, R : crystal size, k : wavelength vector.

As we can see, the most critical parameter for reducing scattering losses is the crystal size. As the studied materials are intended for mid and far infrared applications, we are in a favourable situation with long wavelengths and consequently small wavelength vector. However, X-ray diffractions show that the crystallised phase is mainly CsCl which has very low refractive index (about 1.5) compared to that of the glass matrix (about 2.2)

Observation of the glass ceramics under scanning electronic microscope shows clearly the presence of crystals inside the glass matrix (Fig. 3) with a size typically smaller than 100 nm. The size and the volume fraction of crystals can be changed by modifying the ceramisation temperature and time. A low ceramisation temperature leads generally to small crystals and the volume fraction tends to increase with increasing time.

The first study on infrared glass ceramics is performed with sulphide glasses because of their transmission in visible region which makes much easier the ceramisation studied. However, sulphide glasses are transparent to the region of 10-11 μm and do not cover completely the second atmospheric window of 8-14 μm. For this reason, selenide glasses have been studied and systematic study of the $GeSe_2$ - Sb_2Se_3- RbI system has allowed to find the good glass composition ($60GeSe_2$-$30Sb_2Se_3$-10RbI) for controlled crystallisation. As shown in Fig. 4, this glass is transparent up to the region of 16 μm and the ceramisation process can be combined

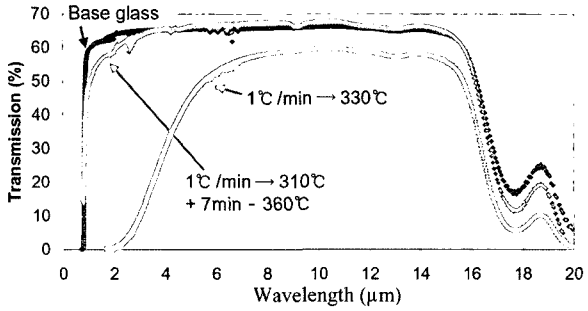
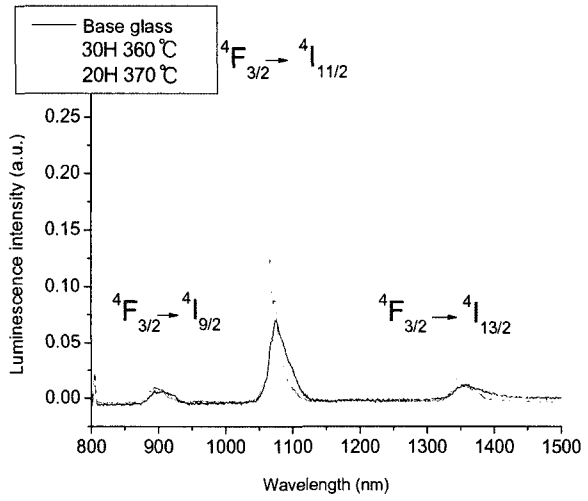
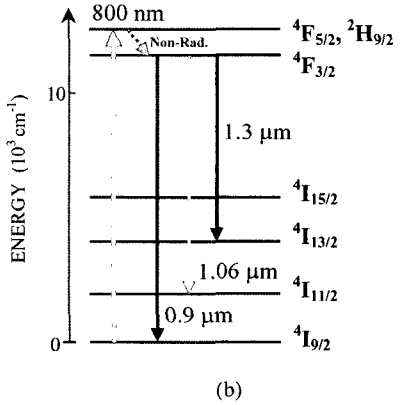


Fig. 4. The transmission of the $60GeSe_2$-$30Sb_2Se_3$-10RbI glass and two moulded glass ceramics.



(a)



(b)

Fig. 5. (a) Emission spectra under 800-nm excitation of GeGaSbS-CsCl glass-ceramics and base glass doped with 0.1 % Nd^{3+} ions. (b) partial energy level diagram of Nd^{3+} ions.

with the moulding process, leading to highly transparent glass ceramic.

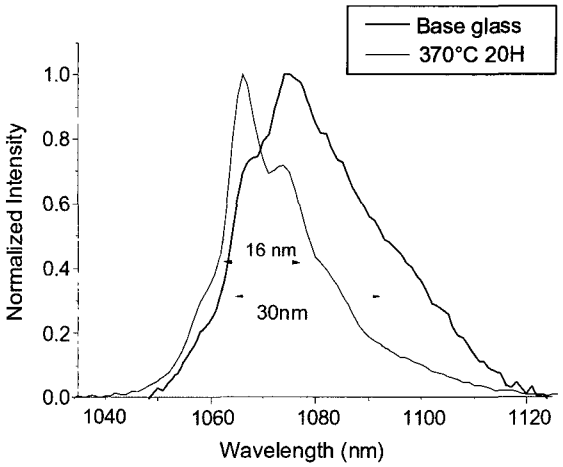


Fig. 6. Normalized spectra of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition in GeGaSbS-CsCl glass-ceramics and base glass doped with 0.1 % Nd^{3+} ions.

Active glass ceramics could be obtained from 70 GeS_2 – 8 Ga_2S_3 – 12 Sb_2S_3 – 10 CsCl glass (GeGaSbS-CsCl) doped with rare-earth ions[17]. Thermal analysis of the glass doped with 0.1 % Nd^{3+} ions ($1.06\ 10^{19}$ ions/cm^3) shows a glass transition at 320 ℃ and two weak crystallization peaks with onset at 410 ℃ and 435 ℃. Best thermal conditions for ceramisation were experimentally determined to be in the 360 ℃ – 370 ℃ range.

Fig. 5 shows the emission spectrum of 0.1 % Nd^{3+} ions in GeGaSbS-CsCl glass and glass ceramics treated at 360 ℃ for 30 h and 370℃ for 20 h. Excitation is at 800 nm. Three emission bands are observed around 900 nm, 1070 nm and 1350 nm corresponding to electronic transitions from the $^4F_{3/2}$ level to $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, respectively. Samples were excited in the same experimental conditions, so that emission intensities can be compared. It can be observed that emission is more intense in glass ceramics, as compared to base glass, by a factor of five for the sample treated at 370 ℃. In addition, the band profiles are modified in glass ceramics.

Fig. 6 shows normalized spectra of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. A broad emission band is observed for the base glass, with maximum intensity at 1074 nm and a full width at half-maximum (FWHM) equal to 30 nm. For comparison, that transition peaks at 1066 nm for the glass-ceramic treated 20 hrs at 370 ℃, and the FWHM is equal to 16 nm. Also, the band is more structured in the glass ceramic, with a secondary peak at 1073 nm.

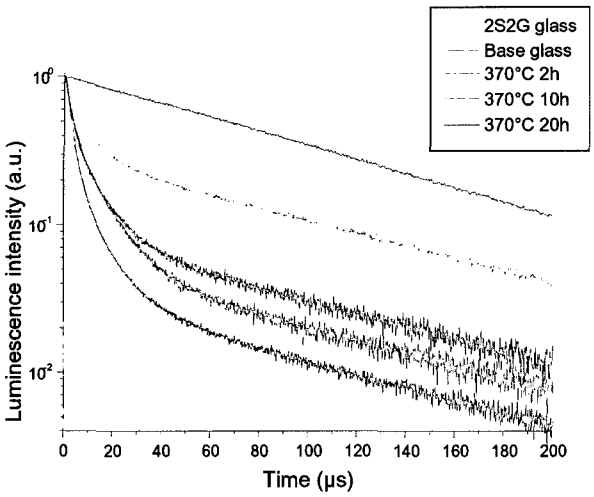


Fig. 7. Decay profiles of the $^4F_{3/2}$ level in GeGaSbS-CsCl glass-ceramics and base glass doped with 0.1 % Nd^{3+} ions. 2S2G is a reference glass based on Ge-Ga-Sb-S.

These results indicate that the local environment around Nd^{3+} ions has changed, at least for a significant part of them, from glassy to crystalline. A detailed study of emission profiles, not presented here, showed that crystalline environment of Nd^{3+} ions starts to appear for time treatment as short as 2 h[18]. After 10 h, the band profile is stable and is similar to that shown for the 20-h treatment pictured in Fig. 6. This suggests that ceramization process is complete after 10 h.

Decay times from the $^4F_{3/2}$ level were recorded by monitoring the 900-nm transition to $^4I_{13/2}$, as shown in Fig. 7. Measurements were performed for the base glass and glass ceramics treated at 370 ℃ for 2, 10, and 20 h. For comparison, data for the standard 2S2G (GeGaSbS) glass[19] doped with 0.1 % Nd^{3+} is also shown. Experimental lifetimes are given in Table 1. For 2S2G, the decay is single-exponential with a lifetime of 97 μs. On the contrary, for GeGaSbS-CsCl base glass and glass ceramics, decays are non-exponential. Actually, they can be divided in two components: a fast component at short times and a slow component at long times. The slow component is exponential and is comparable for all five samples, including 2S2G reference glass, with a decay time between 90 and 105 μs. This suggests that the slow component in GeGaSbS-CsCl glass and glass ceramics is due to Nd^{3+} ions in glassy sites, with a surrounding of sulphur elements, as in 2S2G.

For GeGaSbS-CsCl base glass, the decay curve can be fitted by a double exponential, as shown in Table 1. The lifetime of the fast component at short time is equal to 6.7 μs. The fact that two components are observed for the base glass indicates that two types of Nd^{3+} environment are present. One can suggest that some crystalline particles, whose size is less than 100 nm, are present in the base glass before heat treatment. These nano-size crystals are formed during the cooling stage of glass processing.

Table 1. Lifetimes of the $^4F_{3/2}$ Level in GeGaSbS-CsCl Glass-Ceramics and base glass doped with 0.1 % Nd^{3+} ions. 2S2G is a reference glass based on Ge-Ga-Sb-S. τ_0 : slow component at long times; τ_{sh} : fast component at short times

Sample	τ_0 (μs)	τ_{sh} (μs)
2S2G glass	97	-
Base glass	100	6.7
Glass-ceramics		(e^{-1})
370℃ 2h	97	4.4
370℃ 10h	105	4.5
370℃ 20h	90	3.9

Upon heating, the fast component becomes non exponential. Then, lifetimes in glass-ceramic are defined as the first e-folding time. The general trend is a decrease of the lifetimes with heat treatment due to the increase of crystalline fraction in glass ceramics. The fact that the fast component is non exponential in glass ceramics suggests that energy transfer occurs due to an increase of Nd^{3+} concentration in the crystalline particles. Above T_g, Nd^{3+} ions can migrate and concentrate in crystalline zones.

Glass ceramics were also synthesized with 0.1 % Er^{3+} content (8.43 10^{18} ions/cm^3). Glass transition was found at 305 ℃, but no exothermic peaks, characteristic of crystallization processes, could be observed with standard 10 ℃/min heating rate. However, ceramisation could be achieved with Er-containing glasses in conditions similar to those for Nd-glass, provided that heating times were long-enough.

Fig. 8 shows the infrared emission from the $^4I_{13/2}$ level of Er^{3+} in GeGaSbS-CsCl glass and glass ceramics treated at 370℃ for 1.5 and 3 h. The "hole" in spectra is due to excitation light at 1.55 μm. With comparison to the base glass, glass ceramics exhibit more intense total luminescence. In addition, the relative intensities of secondary components at 1500, 1524, and 1580 nm against the main component at 1540 nm are higher in glass ceramics. As in the case of Nd, this behaviour is

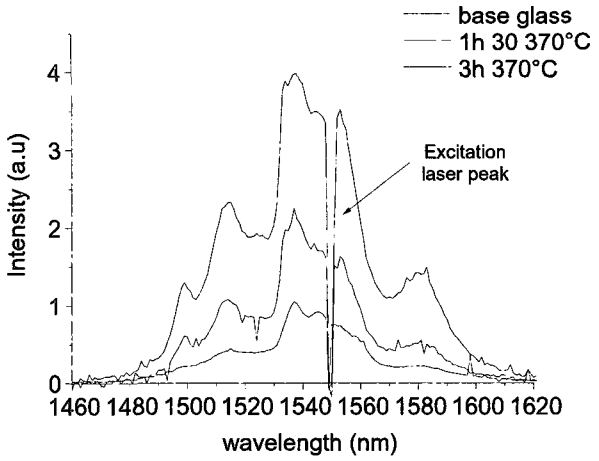


Fig. 8. Emission spectra under 1.55-μm excitation of GeGaSbS-CsCl glass-ceramics and base glass doped with 0.1 % Er^{3+} ions.

explained by the increase of rare-earth crystalline sites in glass ceramics. Also, the existence of secondary components in the base glass is attributed to the presence of some crystalline sites. These components are not observed in 2S2G reference glass[18].

4. Conclusions

In summary, we have demonstrated that infrared glass-ceramics could be synthesized in systems based on germanium and antimony sulphides or selenides, associated to an alkali halide. They are prepared by heating glass samples at temperatures above the glass transition as a function of time. Ceramisation can be controlled, so that only sub-100 nm crystals are generated in the glass matrix. Then, low light scattering is achieved and the transparency window of the original glass is maintained.

When doped with rare-earth ions, GeGaSbS-CsCl glass ceramics show more intense luminescence, as compared to their vitreous counterpart. This was demonstrated for emissions from the $^4F_{3/2}$ and $^4I_{13/2}$ of Nd^{3+} and Er^{3+} ions, respectively. Examination of band profiles and decaytimes show that rare-earth ions are embedded in both crystalline and glassy environments.

5. References

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