Structural Investigations of Glass Ceramics in the Ga₂S₃-GeS₂-CsCl System

Yannick Ledemi,* Bruno Bureau, Laurent Calvez, Marie Le Floch, Mathieu Rozé, Changgui Lin, and Xiang H. Zhang

Equipe Verres et Céramiques, UMR 6226 Sciences Chimiques de Rennes, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

Mathieu Allix and Guy Matzen

CNRS, UPR3079 CEMHTI, 1D avenue de la Recherche Scientifique, 45071 Orléans cedex2, France, and Université d'Orléans, Avenue du Parc Floral, BP 6749, 45067 Orléans Cedex 2, France

Younes Messaddeq

Laboratorio dos Materiais Fotônicos, Instituto de Química, Universidade Estadual Paulista, 14801-970 Araraquara/SP, Brazil

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Transparent glass ceramics have been prepared in the $Ga_2S_3-GeS_2-CsCl$ pseudoternary system using appropriate heat treatment time and temperature. In situ X-ray diffraction at the heat treatment temperature and ¹³³Cs and ⁷¹Ga solid-state nuclear magnetic resonance have been performed in function of annealing time to understand the crystallization process. Both techniques have evidenced the nucleating agent role played by gallium with the formation of Ga_2S_3 nanocrystals. On the other hand, cesium is incorporated very much later into the crystallites during the ceramization. Moreover, the addition of CsCl, which is readily integrated into the glassy network, permits us to shift the optical band gap toward shorter wavelength. Thus, new glass ceramics transmitting in the whole visible range up to 11.5 μ m have been successfully synthesized from the (Ga₂S₃)₃₅-(GeS₂)₂₅-CsCl₄₀ base glass composition.

1. Introduction

Chalcogenide and chalcohalide glasses have received great interest in the past few years for their unique properties. Their large infrared transparency, high refractive indices, photosensitivity, and low phonon energies if compared to oxide and fluoride glasses make them attractive materials for photonic applications.^{1–6}

Among many sulfide-based glasses, the germanium-galliumsulfide ternary system has been largely studied for its potential as a low phonon energy glass for lasers and optical fiber amplifier applications.^{7,8} Sulfide glasses usually show a lowenergy optical bandgap that induces a strong light absorption in the short-wavelength visible region. It was demonstrated that this drawback can be circumvented by incorporating ionic compounds such as alkali halides into the glassy matrix. Indeed, the addition of electronegative elements into the covalent network tends to localize the lone pair electrons on the sulfur atoms, resulting in a widening of the optical band gap. Tver'yanovich et al. have demonstrated that high quantity of alkali halides can be dissolved in Ga₂S₃-GeS₂ glasses.⁹ Among the different alkali halides incorporated in such glasses, the cesium chloride (CsCl) appears as the best candidate to increase the optical band gap of Ga₂S₃-GeS₂ glasses for two main reasons: the high electronegativity of chlorine, and the large vitreous domain of this pseudoternary system, originating from the radius of cesium which stabilizes the formed complex anion into the glassy network.9 Thereby, we have recently reported the preparation of Ga₂S₃-GeS₂-CsCl glasses transmitting in



Figure 1. (Ga₂S₃)₂₅-(GeS₂)₂₅-CsCl₅₀ glass rod.

the whole visible range up to $11.5 \,\mu\text{m.}^{10}$ A photography of such glass with $(Ga_2S_3)_{25}$ - $(GeS_2)_{25}$ - $CsCl_{50}$ composition is presented Figure 1.

Another feature of great interest has emerged lately from chalcohalide glasses: their ability to crystallize homogeneously and so to prepare designed glass ceramics. Indeed, mixing covalent chalcogenide compounds and ionic alkali halides in a glass matrix permits us to prevent uncontrollable crystal growth within the material. Thus, since a few years, numerous glass ceramics have been reproducibly synthesized from compositions belonging to different systems such as Ge–(Sb/Ga)–S/Se–MX (MX = alkali halide) by appropriate heat treatment.¹¹ Depending on the studied system, such glass ceramics may present interesting properties for both passive and active optical applications.^{12–14} More particularly, recent investigations have shown a large enhancement of rare earth ions (REI) luminescence in Ga₂S₃–GeS₂–CsCl glass ceramics, ^{13,14} thanks to incorporation of the REI into crystallites.

The purpose of our work is to combine the two features described above to obtain new efficient luminescent glass

ceramics in the whole visible range. In other words, we study the feasibility of synthesizing optically active ions (REI for example) doped chalcohalide glass ceramics with transparency in the 400-750 nm spectral range in view of potential applications for low-cost solid-state lighting. To obtain efficient glass ceramics, the REI have to be incorporated in the crystallites. Thus, as a first step, and before adding any REI in the Ga₂S₃-GeS₂-CsCl glassy matrix, it is essential to understand well the crystallization process. Indeed, data are very scarce in the literature. Thus, in this work, a special attention is paid on elucidating the structural modifications occurring during the crystallization of the base glasses. To achieve this goal, Raman spectroscopy, X-ray diffraction (XRD), and solidstate nuclear magnetic resonance (NMR) have been carried out. After describing the influence of the incorporation of CsCl in the Ga₂S₃-GeS₂ glassy network, investigations have been focused on the crystallization process.

2. Experimental Methods

Bulk Ga₂S₃-GeS₂-CsCl glasses were prepared from highpurity polycrystalline germanium (5 N), gallium (5 N), sulfur (5 N), and cesium chloride (3 N). The sulfur used was previously purified by a dynamic distillation, stored in a dry glovebox, and weighed in. The cesium chloride (CsCl) was also stored and weighed in the glovebox because of its high hygroscopicity. The weighed elements (± 0.1 mg) were then loaded into a silica ampule which was sealed under a vacuum of about 10^{-4} mbar. Then the ampule was placed in a rocking tubular furnace and heated up from 20 to 900 °C using a 1 °C/min heating rate to avoid explosion due to the high vapor pressure of sulfide. After a homogenization step of about 8 h, the ampule was quenched in water at room temperature, then annealed for 3 h at a temperature close to its glass transition temperature (T_g) , and finally slowly cooled down to room temperature in order to minimize inner constraints. The obtained glass rod was cut into slices of 2 mm thickness and polished for the different characterization studies. All of the samples were synthesized according to this process.

Slices of the base glass have been heat treated in a ventilated furnace at different temperatures between T_g and crystallization temperature T_x (with an accuracy of ± 2 °C) in order to determine the optimal ceramization temperature. Then, glass ceramics have been treated for different durations. These asprepared glass ceramics have been reproducibly obtained from different glass rods following this process.

Thermal analysis measurements were performed using a differential scanning calorimeter DSC 2910 (TA Instruments) from room temperature to 550 $^{\circ}$ C (to avoid the apparatus deterioration) with a heating rate of 10 $^{\circ}$ C/min.

Raman spectroscopy was carried out using a Renishaw microscope equipped with a He–Ne laser with a wavelength of 633 nm. A low power of about 5 mW was used for the excitation beam, ensuring the absence of sample damaging. The laser beam was focused on the sample surface by a $100 \times$ microscope objective and then recorded from 100 to 600 cm⁻¹ with a resolution of 2 cm⁻¹.

The ¹³³Cs (spin I = 7/2) spectra were recorded at room temperature on a Avance 300 Bruker spectrometer operating at 39 MHz with a 4 mm MAS probe spinning at 14 kHz. The ¹³³Cs quadrupole moment is very low (-3×10^{-31} m²) and the chemical shift range is large (about 400 ppm) due to the size of the electronic cloud. Then, as often, the quadrupolar interaction does not affect significantly the ¹³³Cs spectra and this nucleus behaves as a spin 1/2 nucleus.^{15,16}



Figure 2. Ternary diagram of the Ga_2S_3 -GeS₂-CsCl system with the compositions studied in this work and the vitreous domain by Tver'yanovich.⁹

The ⁷¹Ga (spin I = 3/2) spectra were also recorded at room temperature on an Avance 300 Bruker spectrometer operating at 91.5 MHz with a static probe. Due to the large quadrupolar interaction ($Q = 0.11 \times 10^{-28}$ m²), the ⁷¹Ga static spectra in amorphous compound extend over several hundreds of kilohertz. Full echoes were acquired to improve the signal-to-noise ratio and to avoid any distortion of the baseline. The pulse length, t_{pulse} , was chosen much smaller than $t_{\pi/2}$ ($t_{\pi/2} \approx 4t_{pulse}$) to ensure a linear irradiation regime over the whole frequency range. Note that, because of the strong quadrupolar effect, magic angle spinning techniques did not permit efficient reduction of the broadness of the lines. The reconstructions of the experimental spectra were performed using the Dmfit#20080317 version of the Dmfit software.¹⁷

X-rays diffraction (XRD) measurements have been performed on polished bulk samples at room and high temperatures using a conventional $\theta - \theta$ Bragg–Brentano configuration (Ni-filtered Cu K $\alpha_{1,2} = 1.5418$ Å) on a Bruker-AXS D8 Advance diffractometer fitted with a linear Vantec-1 detector and equipped with an Anton Paar oven chamber (model HTK 1200 N) able to reach temperatures up to 1200 °C.

3. Results

Samples of $(Ga_2S_3)_{25}$ — $(GeS_2)_{75-x}$ — $CsCl_x$ composition, with *x* varying from 0 to 50, have been synthesized in order to study the influence of the insertion of CsCl. The glass compositions prepared are reported in the diagram of the pseudoternary system presented in Figure 2. The vitreous domain established by Tver'yanovich⁹ is also represented. All the glasses prepared for this work are optically homogeneous to the naked eye.

The characteristic temperatures determined by DSC and the cutoff wavelength λ_0 of each glass are reported in Table 1. The cutoff wavelength λ_0 , defined as the shorter wavelength transmitted by the glass, was calculated from the absorption spectra with an absorption coefficient value of $\alpha = 10 \text{ cm}^{-1}$. As expected, a decrease of λ_0 is observed with increasing CsCl concentration in the glass. For the highest CsCl contents, the cutoff wavelength λ_0 reaches values below 400 nm, which corresponds to a total transparency in the visible range, as illustrated in figure 1.

Glass ceramics have been obtained from Ga_2S_3 -GeS₂-CsCl glasses with appropriate heat treatment time and temperature. Among the different $(Ga_2S_3)_{25}$ - $(GeS_2)_{75-x}$ -CsCl_x glasses stud-

TABLE 1: Characteristic Temperatures and Cutoff Wavelength λ_0 of the Ga₂S₃-GeS₂-CsCl Glasses

co	mpositio	on			$T_{\rm r} - T_{\rm r}$	λ_0^a
Ga_2S_3	GeS_2	CsCl	$T_{\rm g}~(\pm 2~^{\circ}{\rm C})$	T_x (±2 °C)	$(\pm 4 \ ^{\circ}C)$	(nm)
25	75	_	432	498	66	461
25	65	10	405	504	99	443
25	50	25	349	—	-	422
25	37.5	37.5	295	—	_	404
25	30	45	283	—	-	382
25	25	50	260	—	_	373

 ${}^{a}\lambda_{0}$ is given for α (absorption coefficient) = 10 cm⁻¹.

- glass	ceramics	-	glass	ceram
- glass	ceranic	-	g' s	r im
glass	cera mice	-	(S	In
glass	CERAMIL	-	glas	Ceium
GC0 ;	GC7 GC12		GC23	GC65

Figure 3. $(Ga_2S_3)_{25}$ - $(GeS_2)_{65}$ - $CsCl_{10}$ base glass and glass ceramics labeled as GCx with x the heat treatment time (in h) applied.



Figure 4. Normalized Raman spectra of the (Ga_2S_3) - $(GeS_2)_{75-x}$ - $CsCl_x$ glasses. The curves are shifted in parallel for clarity.

ied in this work, the x = 10 sample appeared as the best candidate to be homogeneously crystallized with reproducibility. Indeed, the study of the ceramization ability, performed by annealing the different glass compositions, has revealed that crystallization of samples with $x \ge 25$ is heterogeneous and uncontrollable or, in some cases, not even observed.

The usually used criterion for thermal stability against crystallization, $T_x - T_g$, was not determined for glasses with $x \ge 25$ because no exothermic peak appears below 550 °C in their respective thermograms. This strong thermal stability may explain their ceramization inability. On the other hand, an onset crystallization temperature T_x of about ~500 °C has been determined for the x = 0 and 10 samples. While the crystallization of the glass without CsCl at temperature above T_g is very fast and uncontrollable, homogeneous and reproducible glass ceramics have been obtained from the $(Ga_2S_3)_{25}-(GeS_2)_{65}-CsCl_{10}$ glass. This composition has been consequently selected to study the crystallization process in the $Ga_2S_3-GeS_2-CsCl$ glassy system. Several glass ceramics have been prepared by annealing the base glass at $T_g + 20$ °C = 425 °C for different durations, as shown in Figure 3.

Figure 4 presents the normalized Raman spectra of the $(Ga_2S_3)_{25}$ - $(GeS_2)_{75-x}$ -CsCl_x glasses. Note that Ga content is maintained constant in these glasses while CsCl content (*x*)



Figure 5. X-ray diffraction patterns of $(Ga_2S_3)_{25}-(GeS_2)_{65}-CsCl_{10}$ glass every hour from t = 0 to t = 40 h at 425 °C (1 h scans). Insert: X-ray diffraction patterns recorded at room temperature of the same glass annealed 2 and 15 h at 425 °C.

increases. First, in the 210-300 cm⁻¹ region, a band centered at 270 cm⁻¹ is observed for the x = 10 sample. Its intensity decreases with x increasing and totally vanishes for high CsCl content. This band is assigned to the vibration of Ga-Ga homopolar bond in [S₃Ga-GaS₃] ethane-like units.¹⁸ Second, in the 300-360 cm⁻¹ region appear two main peaks centered at 320 and 340 cm⁻¹. For the x = 10 sample, only the band centered at 340 cm⁻¹ is observed. This peak is due to the symmetric stretching $\nu_1(A1)$ modes of the [GeS₄] and [GaS₄] tetrahedra. With addition of CsCl, this broadband splits into a shoulder at 340 cm^{-1} and a peak centered at 320 cm^{-1} that quickly strengthens in intensity. The band at 320 cm^{-1} is attributed to the presence of edge-sharing [Ga2S2S2/2Cl2] units.19 Finally, for the 360-500 cm⁻¹ region, a large shoulder is observed for all of the spectra with no significant evolution in terms of CsCl content. One can note the absence of band at 480 cm⁻¹ usually observed in sulfide glasses and due to stretching modes of S–S bonds in short S_n chains or S_8 rings.

In situ X-ray diffraction has first been carried out on the $(Ga_2S_3)_{25}$ - $(GeS_2)_{65}$ -CsCl₁₀ base glass. Figure 5 presents the in situ XRD patterns collected each hour at 425 °C during 40 h (1 h scans) on bulk samples.

A two-step crystallization mechanism can be clearly identified from these XRD patterns. During the first step, which ends after ~18 h of annealing at 425 °C, the matrix remains mostly amorphous. Indeed, the feature of the corresponding patterns, with large diffusion signature (local maximum at $2\theta = 30^{\circ}$ and 53°), is typical of the amorphous state. Furthermore, the apparition and growth of broad peaks ($2\theta = 29^{\circ}$ and 50°) are typical of the formation of nanocrystals. Two extra diffractograms recorded at room temperature on glass ceramics heat treated ex situ for 2 and 15 h, respectively, as shown in the insert of Figure 5, allow us to clearly identify the nucleation of Ga₂S₃ at this stage.

The second step, starting from about 19 h, corresponds to the sharpening of the Ga_2S_3 broad peaks observed previously plus the appearance of new sharp ones, related to new phases crystallization. This involves a progressive vanishing of the glass



Figure 6. ¹³³Cs MAS NMR spectra of the $(Ga_2S_3)_{25}$ - $(GeS_2)_{75-x}$ -CsCl_x glasses and crystalline CsCl (spinning at 14 kHz). The stars * denote the spinning side bands.

matrix. It is possible to identify GeS_2 as one of the new phase appearing, confirming a strong crystallization of the residual glassy matrix at this point. Despite good resolution data, the complete indexation of the new peaks is unfortunately not straightforward, given the lack of crystallographic data within the literature in this system.

The ¹³³Cs MAS NMR spectra recorded from these glasses using a Hahn echo sequence²⁰ are presented in Figure 6. The reference used for these experiments is crystalline CsCl.

Whatever the initial composition, the shape of the spectra remains unchanged and is typical of an amorphous environment around the $^{133}\mbox{Cs}.$ There is a statistical disorder around the cesium, demonstrating its complete incorporation into the glassy network. The chemical shift measured for the x = 10 sample, which is the lowest CsCl containing sample, is about -150 ppm. This large chemical shift difference compared to CsCl (used as reference) shows that the chemical environment of Cs is far from the chlorine cube, indicating that Cs is also surrounded by sulfide S²⁻ anions in the glassy matrix. Then, the chemical shift increases progressively with increasing the CsCl content in the glass and reaches -50 ppm for the x = 50 glass. Thus, the environment of Cs in the network tends to approach the one encountered in the CsCl cubic structure. Therefore, generally speaking, it can be assumed that the cesium is in a mixed environment constituted of sulfide and chloride anions. With increasing the Cl/S atomic ratio, a progressive substitution of S^{2-} by Cl⁻ anions around the Cs⁺ cations occurs, explaining the increase of chemical shift observed.

The ¹³³Cs MAS NMR spectra recorded from the (Ga₂S₃)₂₅-(GeS₂)₆₅-CsCl₁₀ glass ceramics are presented in Figure 7. No difference is observed between the spectra of the base glass and the glass ceramics heat treated for 12 and 23 h. All of them exhibit a broad line typical of the glassy state as shown by the base glass spectrum. After 65 h of annealing, the broad glassy line intensity has decreased and a sharper line arises from it. This narrower contribution is assigned to a crystalline phase containing cesium. The position of the sharp line, near -150ppm, is far from the one measured in the crystalline CsCl (0 ppm). Therefore, after long heat treatment time of the base glass, the cesium is incorporated into a complex crystalline phase in which Cs⁺ are surrounded by Cl⁻ and S²⁻ anions. Due to the lack of commercial cesium based crystalline compounds containing gallium, germanium, sulfur, or chlorine, the identification of this phase was not possible.

The ⁷¹Ga NMR spectrum recorded in the x = 10 sample on a 300 MHz (7.04 T) spectrometer is presented in Figure 8



Figure 7. ¹³³Cs MAS NMR spectrum of $(Ga_2S_3)_{25}$ - $(GeS_2)_{65}$ -CsCl₁₀ base glass (a) and glass ceramics heat treated 12 h (b), 23 h (c), and 65 h (d). The sharp line encircled on the spectrum (d) is attributed to the crystalline phase. The stars * denote the spinning side bands.



Figure 8. ⁷¹Ga NMR spectrum of $(Ga_2S_3)_{25}$ – $(GeS_2)_{65}$ – $CsCl_{10}$ glass recorded on a 300 MHz (7.04 T) spectrometer (a), and on a 800 MHz (18.8 T) spectrometer (b), both in static mode.

together with the same spectrum acquired thanks to a high-field spectrometer (18.8 T). Both acquisitions have been implemented in the static mode. Indeed, the use of the MAS technique, with a rotor spinning speed which cannot exceed 15 kHz on our apparatus, leads to the superposition of the spinning side bands with the central band, making the spectra unexplainable.

It can be observed in Figure 8 that the line width is in inverse proportion to the field value, which indicates that the line shape originates from the quadrupolar interaction. Moreover, both spectra present the same line shape. Thus, the utilization of a 300 MHz spectrometer does not provoke any spectral distortion, in spite of the strong quadrupolar interaction intensity. The ⁷¹Ga NMR spectra recorded in static mode in the (Ga₂S₃)₂₅-(GeS₂)₆₅-CsCl₁₀ glass ceramics are presented in Figure 9. A sharper line attributed to a crystalline state arises from the broad line attributed to the amorphous phase since the very beginning of the heat treatment. A progressive increase of this sharp line is observed with annealing time to the detriment of the broad glassy contribution. Thereby, after 65 h of heat treatment, the broad line has almost vanished and only the sharp line is visible, showing the environment building (crystalline state) of most of Ga atoms in the matrix.

The 71 Ga NMR spectrum recorded in the same conditions in crystalline Ga₂S₃ (Aldrich, 4 N) is also presented in Figure 9.

4. Discussion

The Raman data collected from the glasses confirm that the structure is built up with [GeS₄] and [GaS₄] tetrahedra which



Figure 9. ⁷¹Ga NMR spectra of the $(Ga_2S_3)_{25}$ – $(GeS_2)_{65}$ – $CsCl_{10}$ base glass (a) and glass ceramics heat treated 12 h (b), 23 h (c), and 65 h (d). The sharp line encircled on the spectrum (b) is attributed to the crystalline phase. ⁷¹Ga NMR spectrum of crystalline Ga₂S₃ is also presented. Spectra recorded in static mode.

are connected through a bridging sulfur to form a threedimensional network. These observations are in good agreement with previous studies carried out on similar system.^{19,21} It is well established that the addition of CsCl into these glasses opens the [GeS₄] and [GaS₄] interconnected tetrahedra chains by forming non bridging complex anion [GaS_{3/2}Cl]⁻ with a Cs⁺ cation as nearest neighbor to compensate for the charge difference.^{21–23} This role played by CsCl is confirmed by the ¹³³Cs NMR spectra which show that Cs⁺ ions, and so Cl⁻, are well integrated into the glassy network with a mixed environment consisting of sulfide and chloride anions.

There are few works in the literature dealing with ⁷¹Ga solidstate NMR in amorphous materials. Besides, some of them concern gallium fluoride glasses^{24,25} and, to our best knowledge, none has been performed on chalcogenide glasses. Indeed the NMR spectra of ⁷¹Ga quadrupolar nucleus in disordered phases are generally very broad, which strongly limits their interpretation. Moreover, whatever the CsCl content (x) in the glass (spectra not shown), their original line shape remains approximately the same. To our knowledge, this type of line shape has never been observed. Generally, quadrupolar nucleus in amorphous material gives rise to well-known line shapes which can be described thanks to the Czjzek quadropolar parameter distribution as described in refs 24–26 for ^{69,71}Ga, in ref 27 for ²³Na, or in refs 28–30 for ²⁷Al. Here, such distribution did not permit any account of the ⁷¹Ga spectra. Note that the Czjzek distribution is based on the central limit theorem and assumes a statistical isotropy around the probe due to the disorder.^{29,31} So they are especially suitable to reconstruct efficient quadrupolar nucleus NMR spectra in glasses in which the chemical bonds are dominated by ionic interaction, typically oxide and halide glasses. On the other hand, in chalcogenide glasses, gallium is 4-fold coordinated and embedded in covalent directional chemical bonds with its first neighbors imposing preferential local symmetry. In that framework, it is not surprising that the Czjzek-type distribution cannot give account of the line shape. Ongoing works are carried out to better understand this original line shape.

There is also little information about the structural modifications following heat treatments in the Ga₂S₃-GeS₂-CsCl system in the literature.¹¹ In this work, the crystallization of the $(Ga_2S_3)_{25}$ -(GeS₂)₆₅-CsCl₁₀ base glass has been studied by X-ray diffraction and solid-state NMR. The two-stage crystallization process observed in the XRD patterns recorded at 425 °C (Figure 5) is in good agreement with the presence of two exothermic peaks on the DSC curves already reported previously.³² Thanks to the fair quality of the patterns, the first step can clearly be attributed to the formation of Ga₂S₃ nanocrystals. The incorporation of Ga into a crystalline phase has also been evidenced by the ⁷¹Ga NMR spectra recorded in function of heat treatment time. Indeed a sharp line arising from the broad glassy contribution (encircled in Figure 9) is observed since the very beginning of the heat treatment. Finally, NMR and X-rays diffraction data are in good agreement and prove that Ga acts as a nucleating agent in this matrix.

On the other hand, regarding the ¹³³Cs NMR spectra recorded on glass ceramics (Figure 7), the cesium ions are incorporated into a crystalline phase only after long heat treatment, meaning during the second stage observed on the XRD data. Some of the XRD peaks which cannot be attributed to either Ga₂S₃ or GeS₂ have to be assigned to crystalline phases containing Cs. Nevertheless, it has not been possible to identify this complex crystalline phase from the existing crystallographic data. The ¹³³Cs NMR result shows a different behavior compared to the one described in glass ceramics belonging to the Sb₂S₃-GeS₂-CsCl system.³³ A similar ¹³³Cs MAS NMR study had been carried out on those glass ceramics and the incorporation of cesium in the crystalline phase was observed since the very beginning of heat treatment. Thus, Cs acts as a nucleating agent in the glass ceramics based on antimony, whereas this role is rather played by Ga in the glass ceramic under study in this paper.

The second objective was to widen the transmittance window in the short wavelength in order to prepare transparent glass ceramics in the 400–750 nm spectral range. Indeed, such composite materials should be afterwards studied for applications in multispectral imaging or as potential hosts for optically active ions. As said previously, glasses belonging to the $(Ga_2S_3)_{25}$ - $(GeS_2)_{75-x}$ -CsCl_x series and having a content higher than x = 25 do not lead to homogeneous and reproducible crystallization because of their high stability.

So, new glassy compositions had to be considered to achieve this objective, with the following requirements: (i) a high CsCl content to ensure a complete transmission in the visible spectral range, and (ii) a good ability to ceramize homogeneously. As observed in the first glass ceramic, the crystallization of Ga₂S₃, which is throwing out from the glass network, leads to a more stable residual glassy matrix as its composition is slowly reaching the center of the vitreous domain. Hence, taking into account this consideration and the role of Ga as nucleating agent, new glass compositions containing a high ratio of CsCl and Ga have been synthesized. Among the different compositions synthesized, the (Ga₂S₃)₃₅-(GeS₂)₂₅-CsCl₄₀ glass appeared to be the best candidate regarding its transparency in the whole visible range and its ability to crystallize homogeneously. Moreover, one can note that this composition presents a relatively low CsCl concentration if compared to the (Ga₂S₃)₂₅- $(GeS_2)_{25}$ -CsCl₅₀ glass (Figure 1), which should minimize its hygroscopic character.10

The characteristic temperatures of this glass, determined by DSC, are $T_g = 319$ °C and $T_x = 446$ °C, giving a thermal stability criterion value of $\Delta T = 127$ °C. Furthermore, while a

Figure 10. $(Ga_2S_3)_{35}$ - $(GeS_2)_{25}$ - $CsCl_{40}$ glass ceramics labeled as GCx with x the second heat treatment duration at 369 °C (in h). All of the samples have been previously heat treated at 339 °C during 15 h (nucleation step).



Figure 11. X-ray diffraction patterns of $(Ga_2S_3)_{35}-(GeS_2)_{25}-CsCl_{40}$ glass ceramics heat treated 15 h at T = 339 °C (nucleation step) and *x* h at T = 369 °C (growth step), labeled as GCx with x = 0, 1, 2, 3, and 4, respectively. Crystalline GaS and Ga₂S₃ X-ray diffraction patterns from the respective PDF cards no. 40-1030 and no. 84-1440 are also presented.

one-step isotherm heat treatment was sufficient to ceramize the $(Ga_2S_3)_{25}-(GeS_2)_{65}-CsCl_{10}$ glass, a two steps process had to be implemented to obtain homogeneous and reproducible $(Ga_2S_3)_{35}-(GeS_2)_{25}-CsCl_{40}$ glass ceramics. Thus, glass ceramics have been successfully prepared by heat treating the base glass at $T_g + 20$ °C = 339 °C during 15 h in a first time (nucleation step) and at $T_g + 50$ °C = 369 °C during 1 to 4 h (crystal growth step). The obtained glass ceramics labeled as GCx with x the duration of the second heat treatment are shown in Figure 10.

Ex situ X-ray diffraction (XRD) has been carried out on the GCx glass ceramics to compare the crystallization process in this composition to the one observed in $(Ga_2S_3)_{25}-(GeS_2)_{65}-CsCl_{10}$ glass ceramics. The collected XRD patterns are presented in Figure 11. The crystalline GaS and Ga₂S₃ XRD patterns obtained from crystallographic database (PDF cards no. 40-1030 and no. 84-1440, respectively) are also depicted.

As for the $(Ga_2S_3)_{25}$ -(GeS₂)₆₅-CsCl₁₀ glass ceramics, the XRD patterns reveal the formation of Ga₂S₃ nanocrystals in the GC2 and GC3 samples ($2\theta = 29^\circ$, 50° , and 58°). However, a slight difference is observed at the very beginning of crystallization for the $(Ga_2S_3)_{35}$ - $(GeS_2)_{25}$ -CsCl₄₀ composition. Indeed, while the GC0 XRD pattern is typical of an amorphous state, a single sharp peak arises at $2\theta = 29^{\circ}$ on the GC1 pattern. It can be assumed from this result that a small amount of GaS nanocrystals is first precipitated in the matrix before the crystallization of the Ga₂S₃ phase. Nevertheless, XRD patterns confirm here that the initiation of crystallization in the Ga₂S₃-GeS₂-CsCl glassy network also takes place around Ga atoms. And even though the Ga₂S₃ phase does not seem to be the first crystallizing phase in the $(Ga_2S_3)_{35}$ - $(GeS_2)_{25}$ -CsCl₄₀ glass, Ga₂S₃ nanocrystals are also precipitated at the beginning of the crystallization process.

5. Conclusions

Transparent and homogeneous Ga_2S_3 – GeS_2 –CsCl glass ceramics have been prepared from a base glass by appropriate annealing. A structural study was carried out in function of heat treatment time using X-ray diffraction and ¹³³Cs and ⁷¹Ga solid-state NMR. Both these techniques give a complementary point of view on the structure and permit to follow the long- and the short-range order in the structure during the heat treatment. Note that NMR and XRD are quantitative tools which could permit to measure the rate of the crystalline phase versus time. To achieve this goal from the ⁷¹Ga NMR spectra, it is essential to reconstruct properly the initial line shape observed in the base glass. Some fundamental works are ongoing on that field.

One of the main results is that CsCl is very well incorporated in the base glass, permitting to obtain totally transparent materials in the visible range by fixing the electrons of the lone pair of sulfur. Moreover, it was demonstrated that Ga plays the role of the nucleating agent in the crystallization process in both $(Ga_2S_3)_{25}-(GeS_2)_{65}$ $-CsCl_{10}$ and $(Ga_2S_3)_{35}-(GeS_2)_{25}-CsCl_{40}$ glass ceramics. The successful preparation of transparent chalcohalide glass ceramics in the whole visible range combined with the nucleation role of Ga demonstrated in the present work are promising results in order to prepare rare earth ions doped glass ceramics. Indeed, the final target of our investigations is to generate a crystalline environment around the REI in order to enhance their luminescence properties and REI are preferentially located near Ga atoms in Ga containing chalcogenide glasses.

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