

Totally visible transparent chloro – sulphide glasses based on $\text{Ga}_2\text{S}_3 - \text{GeS}_2 - \text{CsCl}$

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In this paper, the influence on optical properties of alkali halides such as CsCl in a covalent glassy matrix has been investigated. Chalcogenide glasses belonging to the (GeS_2) - (Ga_2S_3) -CsCl system with high ratio of CsCl present an entire transparency in the visible range. These glasses maintain good transmission up to $12\mu\text{m}$. Furthermore, the thermo-mechanical properties and the glass hygroscopicity have been investigated as function of the CsCl amount. This new generation of glasses presents a great interest for optical application. They could be used both for passive applications (multi-spectral imaging) and active applications for rare-earth doping due to their good transmission in the visible range, increasing optical pumping possibilities.

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1. Introduction

Chalcogenide glasses are made with chalcogen elements (S, Se and Te) generally mixed with elements like Ge, Ga, Sb, As, etc... They are known for their low phonon energies and high refractive indexes compared with oxide and fluoride glasses, leading to various applications in active optic domain [1-4]. Moreover their wide transparency in the infrared spectral range also gives to them a great interest for passive optic applications [1, 5-6].

Sulphide based glasses are known for their wide range of optical transmission from about 0.45 to $12\mu\text{m}$, with an optical band-gap located in the visible region. These glasses have a yellowish to red colour. The aim of this work was to prepare a multiband transparent glass, with transparency in the visible, $3\text{-}5\mu\text{m}$ and $8\text{-}12\mu\text{m}$ spectral regions. Previous works have shown the role of gallium and alkali-halide addition on the shift of the optical bandgap toward shorter wavelength in $\text{GeSe}_2 - \text{Ga}_2\text{Se}_3$ glasses, without reducing the infrared transmission in the far infrared region [7].

Following this approach, the synthesis of sulphur based glasses with wide transmission in the UV/visible region was investigated. A large number of metal halides MX_n ($n = 1, 2$) and more particularly alkali halides like cesium chloride, can be introduced in large amounts in Ga-Ge-S glasses, increasing their glass forming ability [8-9]. Chalco-halogenide glasses have been largely studied for their attractive properties like high ionic conductivity or high solubility of rare-earth ions [10]. Others systems

like Ge-Sb-S-CsCl or Ga-Ge-Sb-S-CsCl have also been studied for developing infrared transmitting or rare-earth ions doped glass-ceramics [11-12].

In this work we paid a special attention to the $(\text{GeS}_2) - (\text{Ga}_2\text{S}_3) - \text{CsCl}$ pseudo ternary system. The optical and thermal properties of the synthesised glasses were studied according to the CsCl content. As a result, glasses presenting a perfect transparency in the visible range were obtained. Because of the high alkali halide amount in the prepared glasses, the resistance to corrosion by air or water was investigated.

This new generation of glasses presents a great interest for optical application. They could be used both for passive applications (multi-spectral imaging) and active applications for rare-earth doping due to their good transmission in the visible range, increasing optical pumping possibilities.

2. Experimental

2.1 Glass synthesis

The Ga_2S_3 - GeS_2 -CsCl glasses were prepared from high purity polycrystalline germanium (5N), gallium (5N), sulphur (5N) and CsCl (3N). The used sulphur was previously purified by a dynamic distillation and stored in a dry glove box. Then the elements were precisely weighted ($\pm 0.1\text{ mg}$) and introduced into a silica tube under a vacuum of about 10^{-4} mbar. The ampoule was sealed and then introduced in a rocking furnace. The batch

was slowly heated up to 850°C and maintain to this step for 8h in order to permit thorough reaction of the raw materials and to avoid explosion due to the high vapor pressure of sulphur. The ampoule was quenched in water at room temperature. Finally the glass was annealed for 3h near its glass transition temperature (T_g) and slowly cooled down to room temperature in order to minimize mechanical stress in the glass rod. All of the samples were prepared according to this process.

2.2 Samples characterizations

In order to determine the glass transition temperature (T_g) and the crystallisation temperature (T_x), thermal analysis were performed using a differential scanning calorimeter DSC2910 (TA Instruments) from room temperature to 500°C with a heating rate of 10 °C/min. To perform dilatation experiments, glassy cylinders of 4 to 6 mm height were polished and heated at 2°C/min up to the glass transition temperature. The thermal expansion coefficient (α) of the glass samples was measured between 100 and 250°C using a TMA 2940 Calorimeter (TA Instruments).

Transmission spectra in the visible range were recorded with a CARY5 double beam spectrophotometer (Varian) while a BRUKER Vector 22 spectrophotometer operating in the 2 – 25 μm was used for the infrared spectra.

Density, d , was measured using the Archimedes technique which consists in comparing the difference of the glass weight in the air and in a solvent. A Metler Toledo XS64 balance was used with distilled water as solvent.

It is well known that CsCl is a very hygroscopic compound. As a result the resistance to moisture of the prepared samples can be strongly affected. Hence a study of the chemical durability has been performed. The polished samples have been left in distilled water and ambient atmosphere for different durations. Transmission spectra in the IR range were performed in order to observe the evolution of the water or other associated impurities absorption bands according to the immersion time.

3. Results

The compositions of the synthesised glasses are shown in the Ga_2S_3 - GeS_2 -CsCl pseudo ternary phase diagram in the figure 1. This system presents a wider glass forming region compared to Ge – Ga – Se – CsCl system [13]. We have focused our work on the following compositions: $(\text{Ga}_2\text{S}_3)_{25}-(\text{GeS}_2)_{75-x}-(\text{CsCl})_x$, with $x = 0$; 12.5; 25; 37.5 and 50. For a better readability, studied glasses are named GGSCx.

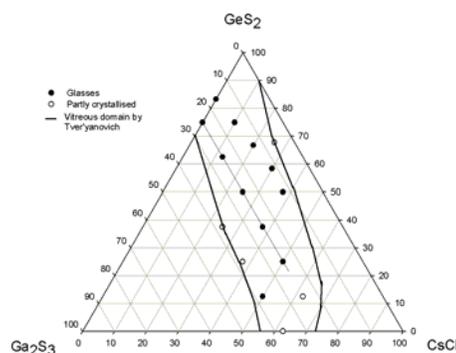


Fig.1. Pseudo – ternary phase diagram of GGSC system with vitreous domain by Tver'yanovitch [9].

All these compositions are optically homogeneous, as it can be seen in figure 2. The GGSC0, GGSC12.5, GGSC25 and GGSC37.5 glasses present a pale to very pale yellowish colour, bleaching with increasing CsCl content. Over 37.5% mol. of CsCl, the glassy samples are entirely transparent in the visible range. Nevertheless, it is noticeable that glasses with high CsCl content (mainly for $x > 25$) present a surface corrosion after several days in the ambient atmosphere. Because of their high sensitivity to atmospheric moisture, glasses with $x > 25$ were stored in a dry glove box.

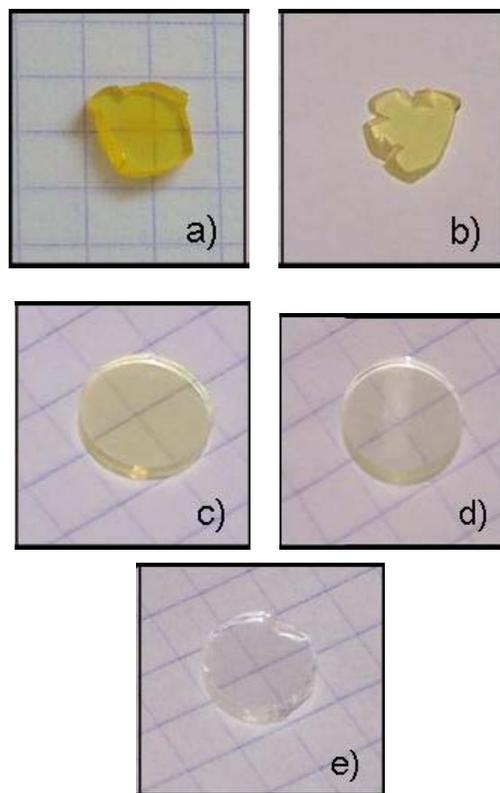


Fig. 2. Photography of GGSCx polished samples ($x = 0$ (a); 12.5 (b); 25 (c); 37.5 (d); 50 (e)).

The transmission spectra of these samples in the short wavelength region are presented in figure 3; the values of their optical bandgap are also indicated. The corresponding cut-off wavelengths, measured for an absorption coefficient $\alpha = 10 \text{ cm}^{-1}$, are given in the table 1. Moreover, the CsCl richest composition (GGSC50) is transparent all over the visible range (400-750 nm) up to $12 \mu\text{m}$ as it can be observed in figures 3 and 4. Its band-gap of about $E_g = 3.33 \text{ eV}$ corresponds to a beginning of transmission λ_0 of 373 nm. To our best knowledge, it is the first report of the synthesis of a chalcogen-halide glass entirely transparent in the whole visible range and in the two IR atmospheric windows.

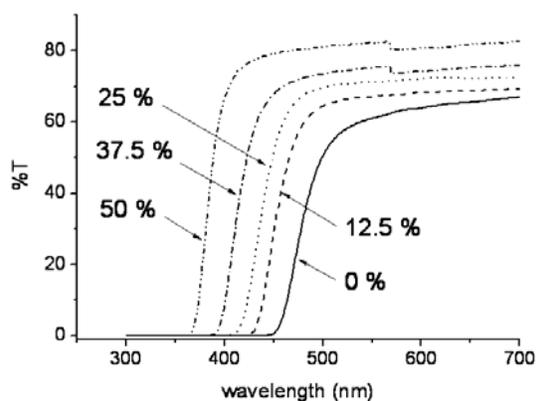


Fig. 3. Transmission spectra in the visible region of GGSC glasses in function of CsCl content (% mol).

Thermo-mechanical properties obtained from DSC, TMA and density measurements are reported in table I. The glass transition temperature decreases with increasing CsCl amount; a difference of 174°C between the T_g of the

GGSC0 and GGSC50 glasses is observed. Furthermore, only the CsCl free glass presents a crystallisation peak with an onset temperature at 494°C , while the others do not present sign of crystallisation below 500°C . As shown in the table 1, the dilatation coefficient and the density increase when the CsCl content increases.

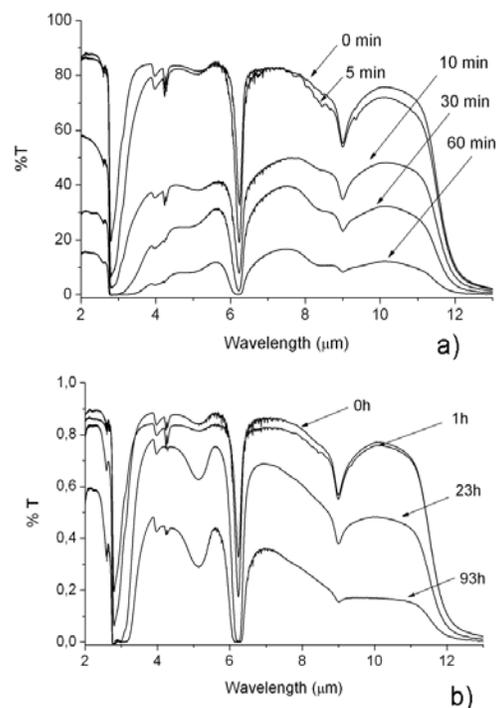


Fig. 4. Transmission spectra of GGSC50 after immersed for different durations in a) distilled water and b) air.

Table 1. Properties of the Ga₂S₃ - GeS₂ - CsCl glasses.

Composition (% mol)			T_g ($^\circ\text{C}$)	T_x ($^\circ\text{C}$)	$\alpha \times 10^{-6}$ (K^{-1})	ρ (g/cm^3)	λ_0 (nm)*
Ga ₂ S ₃	GeS ₂	CsCl					
25	75	0	432	494	8.9	2.784	461
25	62.5	12.5	383	/	14.2	2.990	438
25	50	25	335	/	22.9	3.049	422
25	37.5	37.5	284	/	26.4	3.103	400
25	25	50	258	/	29.6	3.175	373

* : λ_0 is given for α (absorption coefficient) = 10 cm^{-1}

While the GGSC12.5 glass doesn't present any sign of moisture sensitivity, the richer CsCl content glasses present a weak resistance to corrosion. In order to study the chemical durability, the GGSC50 glass – with the highest CsCl content – has been chosen. And the IR transmission spectra of this glass after corrosion by water and air for different times are presented in figure 4. This composition has a very poor durability when immersed in distilled water and even in ambient air. The measured transmission at $10 \mu\text{m}$ falls of about 80 % after 1h in

distilled water or 93h in the ambient air. That's why all the experiments on the CsCl richest compositions were rapidly performed after polishing. It was also observed that the attack occurs on the surface of the sample. Indeed, after a single polishing of the corroded surface, glasses present the same transmission as the initial one. Nevertheless, after long durations of immersion in water, polishing does not permit to reach the initial transmission.

4. Discussion

Incorporation of alkali halide such as CsCl in Ga – Ge – S glasses has been well studied for a structural point of view. Tver'yanovich et al. have defined the structure of glasses in the $(\text{Ga}_2\text{S}_3)\text{-(GeS}_2\text{)-MCl}$ pseudo ternary system [14]. Cesium acts as a network modifier opening the GeS_2 and Ga_2S_3 tetrahedral and pseudo tetrahedral structures of these glasses. Likewise, the incorporation of chlorine leading to the formation of $\text{Cs}^+[\text{GaS}_{3/2}\text{Cl}]^-$ non bridging structural units was demonstrated using Raman spectroscopy. Hence, glasses with wide difference between T_g and T_x are synthesized, giving them a better stability against crystallisation. Furthermore, the decrease of the glass network connectivity by adding CsCl provokes a lowering of the glass transition temperature and an increase in the thermal expansion coefficient. The increase of the thermal expansion coefficient combined with the decrease of mechanical properties will lead to a weaker resistance to thermal shocks.

We can notice that the measured thermal dilatation coefficient for the GGSC0 glass – corresponding to the CsCl free glass – $\alpha = 8.9 \cdot 10^{-6} \text{ K}^{-1}$, is relatively low compared to the values generally observed in chalcogenide glasses. Indeed, most chalcogenide glasses usually have a thermal expansion coefficient of about $15 \cdot 10^{-6} \text{ K}^{-1}$. For example, the value of the commercially glass GASIR[®] is $17 \cdot 10^{-6} \text{ K}^{-1}$ [6], while for pure silica glasses, which is considered as a material with one of the better resistance to thermal shocks, the value reaches $\alpha = 0.55 \cdot 10^{-6} \text{ K}^{-1}$ [15]. It shows that the base glass of this serial, while its stability against crystallisation is very weak ($\Delta T = 62^\circ\text{C}$), will have a good resistance to thermal shocks.

This work was mainly focused on the optical transmittance of these chloro – sulphide glasses. It is well known that the incorporation of CsCl induces a blue-shift of the optical bandgap. As described by Griscom et al., this extended transmission can be advantageous for effective pumping of active ions in the visible for example [10]. The shift of the beginning of transmission can be explained by the addition of electronegative chlorine which provokes a tendency to localize the free electron pairs of the sulphur. This phenomenon induces an increasing band-gap and consequently a shift of the transmission toward shorter wavelength. No modification of the transmission in the mid-infrared was observed, since the multiphonon cut-off is linked to the vibration of Ga-S and Ge-S bonds.

The absorption bands of impurities are due to OH^- (centred at $2.9 \mu\text{m}$), H_2O (at $6.0 \mu\text{m}$) and S-H (at $4.1 \mu\text{m}$) molecular vibrations while the band at $9.0 \mu\text{m}$ is due to the Si-O vibration. These undesired absorptions band can be reduced using different techniques of purification during the synthesis. It was shown that the use of dynamic and static distillation of sulphur considerably decreases the absorption at $4.1 \mu\text{m}$ [16]. Previous works have also demonstrated a considerable elimination of oxygen and water induced absorption bands in chalcogenide glasses by using metallic Mg or Al and distillation of the glass [17]. Therefore, the use of these different techniques of

purification will improve the optical transmittance of the prepared glasses.

However, because of the very weak resistance to moisture induced by the high hygroscopicity of CsCl, resistance to corrosion had to be studied. The richest CsCl content composition was chosen for this study. As previously observed, the GGSC50 glass has a very poor stability against water and ambient moisture. The involved mechanism was not yet completely determined. But we can assume that an ion exchange occurs between Cl^- and OH^- ions on the surface of the bulk. Likewise, the OH^- and H_2O entities will diffuse towards inside the bulk.

Nevertheless glasses prepared with less CsCl (typically 40-45 % mol) can also lead to a perfect transparency in the visible range and consequently an improved resistance against moisture. An optimization of the synthesis process by using different techniques of purification coupled with a judicious choice of the composition will lead to a more resistant and optically homogeneous glass with good transparency in the three atmospheric transparency windows.

5. Conclusions

In this paper, we report for the first time the synthesis of a chalcogenide glass transparent in the entire visible range. The glass transmission was extended toward the short wavelength without modification of the multiphonon cut-off around $12 \mu\text{m}$ by introducing alkali halide compound such as CsCl in the Ge-Ga-S glasses. While stable glasses are obtained by increasing CsCl amount, a decrease of the resistance to corrosion by air or water also occurs. The durability of these glasses will be improved by using lower CsCl content.

Preliminary works have shown the feasibility of doping the highest CsCl content glasses by rare-earth ions like erbium Er^{3+} , Pr^{3+} or Tm^{3+} without reducing the extended transmittance in the visible range. This result can be a certain advantage for pumping even larger energy levels of rare – earth ions. Hence, the improvement of chemical stability and fluorescence of these new glasses are under investigations.

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