Structural approach of CsCl-modified Ga₂S₃-La₂S₃ glasses

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Gallium–lanthanum sulfide glasses have specific interesting physical properties, as semiconductor behavior and good transmission at long wavelengths. The addition of CsCl increases the thermal stability region of the glass making it suitable for many applications in optoelectronics. Ga_2S_3-La_2S_3 glasses modified by 10 to 40 % CsCl have been studied by X-ray absorption spectroscopy, at the chlorine K edge and at the gallium K edge at 9 K, in order to get information about the actual structural role of CsCl. The chlorine environment is similar to that in CsCl. The gallium coordination sulfur polyhedra are weakly distorted tetrahedra, identical for all samples. The low temperature measurements shown that the polyhedral corner linkage is also unaltered by the addition of CsCl.

Introduction

Glasses of the system Ga_2S_3-La_2S_3 (GLS) have interesting physical properties, such as the semiconductor behavior and the good transmission at long wavelengths, due to the low vibrational frequency of the gallium-sulfide bond (Hewak et al., 1993). These properties make them suitable for applications in circuits, semiconductor devices, and optical fibers and windows. However, the GLS glasses have relatively small region of thermal stability and then fiber drawing in this system is very limited. An improvement in the physical properties of the system – density, refractive index and glass-transition temperature – as well as the glass forming domain of the system has been experimentally observed in gallium sulfide-based glasses with the addition of metal chlorides, specially cesium chloride (Marmolejo et al., 1999). The increase of the glass-forming region has been associated to a reduction of the connectivity of the glass network. However the exact structural role of CsCl is not yet fully understood.

In GLS glasses the gallium atoms are fourfold coordinated by sulfur atoms and schematic structure of covalent network of GaS_4 tetrahedra can be proposed. By analogy with (Ge,Ga)-based glasses it can be suggested that the addition of CsCl would result in the substitution of a sulfur by a chlorine atom in the coordination tetrahedron of the gallium atoms. The observed enhancement of the glass properties would result from the reduction of the connectivity of the Ga-based network.

In the present work XAS was used to study the eventual modification of the local structure of gallium atoms in Ga_2S_3- La_2S_3 glasses doped by 10 to 40 mol % of CsCl. The purpose of this work was to investigate the existence and the extent of the Ga-Cl bonds and of possible alterations in the polyhedral linkage between the doped glasses and the undoped one.

Experimental

The XAS experiments were performed at the Laboratório Nacional de Luz Síncrotron (LNLS, Campinas, Brazil) (Tolentino et al., 1998). XAS data were collected in $(Ga_2S_3)_{80-x}$–$(La_2S_3)_{20}$-$(CsCl)_x$ glasses, with x= 0, 20 and 40 (respectively called GLS, GLS20 and GLS40 and in model compounds (CsCl and GLS glasses) with a
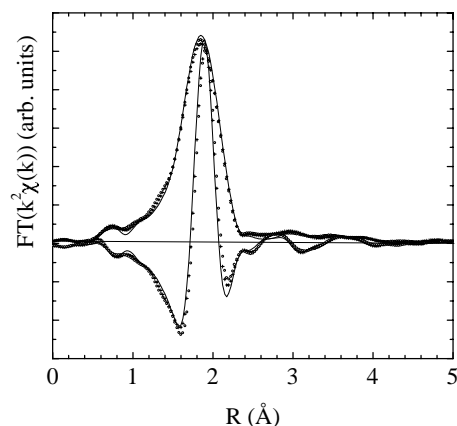

Figure 1 Fourier transform of the k^2-weighted EXAFS signal at the gallium K-edge for GLS (—), GLS20 (O) and GLSC40 (+).

"channel-cut" Si (111) monochromator at the Ga K-edge (10367 eV) and at the Cl K-edge (2822 eV).

At the Cl K-edge the measurements were made in conversion electron yield. The incident beam was monitored by a helium filled ion chamber. Due to the low critical energy of the machine (2.08 keV), higher harmonics contamination from the monochromator is negligible in the conditions of the experiment (Tolentino et al., submitted). Fine powered samples were deposited on conducting adhesive film, the resulting samples thickness being of the order of 10 μm. The XANES spectra were collected in the range 2800 to 2900 eV, with an energy step of 0.3 eV between 2810 to 2840eV and 0.6 eV out of this interval. The total energy resolution was around 0.8 eV.

At the Ga K-edge EXAFS data were collected in transmission mode in GLS, GLSC20 and GLSC40 samples. Homogeneous powdered samples (15 mg/cm²) were obtained by filtration of a dispersion on a cellulose membrane. The XANES spectra were collected in the range 10300 to 10500 eV with an energy step of 0.8 eV. The overall resolution was 3.2 eV. The EXAFS spectra were collected in the energy range from 10290 to 11450 eV with an energy step of 2.0 eV and a counting time of 2s per point. The temperature of the samples was controlled with a closed circuit helium cryostat and the measurements presented here were performed at 9 K. The EXAFS spectra were analyzed using standard procedure of data reduction, using WINXAS code (Ressler, 1997).

The EXAFS signal is obtained after removing of the linear background before the edge and the atomic part of the absorption (5-fold order polynomial fit) The k^2-weighted EXAFS signal $\chi(k)$ is then Fourier transformed over the range 2.0 to 14.0 $Å^{-1}$. The contribution of the selected shell is then back-transformed and fitted in the k-space. Feff6 code was used to performed *ab initio* calculations of theoretical amplitude and phase shifts (Rehr et al., 1991).

Results

The EXAFS signal at the gallium edge is almost limited to the contribution of the coordination shell, as evidenced by the shape of the Fourier transform (figure 1). The signal of this shell was isolated by inverse Fourier transform and fitted using theoretical amplitude
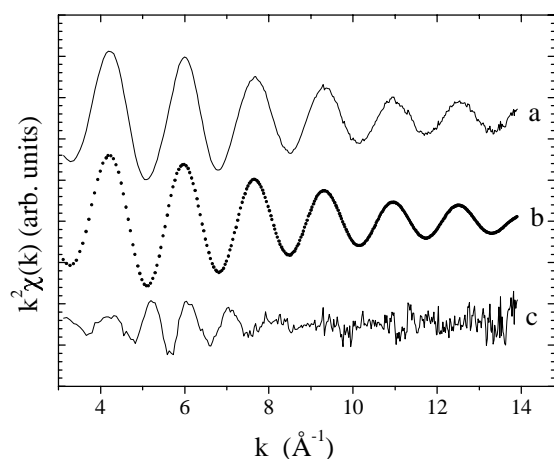
Figure 2 Contributions to the EXAFS signal in GLS glass at 9 K. (a) k^2-weighted EXAFS signal, (b) simulated sulfur coordination shell obtained by fitting and (c) residual signal, corresponding to the next neighboring shells.

Figure 3 XANES spectra at the chlorine K-edge in GLSC20 and CsCl.

and phase shifts obtained *ab initio* calculations using Feff6.0 code (Rehr et al., 1991), with a many body amplitude reduction factor $S_0^2 = 1$. The results of the fitting of the EXAFS signal for the first coordination sphere are identical for all GLSC sample: 4 sulfur atoms at a distance of 2.26 ± 0.01Å (Table I), with a limited structural disorder ($\sigma^2 = 0.004$Å^2).

For all samples an additional contribution of next nearest neighbors is also observed (figure 1, insert). This contribution can be isolated by subtracting the contribution of the first shell from the total experimental EXAFS signal and a weak damped signal with a main frequency corresponding to a next nearest neighbors contribution (figure 2). This contribution is identical for all samples. It has been checked, by simulations using Feff6 code, that this contribution is not due to multiple scattering within the coordination tetrahedron. It can be then associated mainly to next nearest neighbors gallium. It was checked that the total phase term due to the GaGa pair is almost linear in the considered k-range , we deduce a distance Ga-Ga of 3.5 ± 0.1 Å.

At the chlorine K-edge, the XANES spectra of all GLSC samples are identical, within the experimental noise and similar to that of the reference compound CsCl (figure 3).

Discussion

The gallium atoms have a poorly distorted tetrahedral environment of sulfur atoms in GLS glass, in agreement with that found in the previous EXAFS studies (Benazeth et al. 1989 ; Asal et al. 1997). This environment is found the same in GLSC glasses without any increase of the disorder (Table I). The analysis of the coordination shell around the gallium atom does not show any evidence of Ga-Cl bonds. Due to the close back-scattering phase and amplitude of S and Cl, care was taken to evaluate the maximum ratio of substitution compatible with the Ga K-edge EXAFS experiments. If the covalent Ga-S bond is substituted by an also covalent Ga-Cl bond, the resulting Ga-Cl distance can be approximately estimated from the difference in the atomic covalent radii of Cl and S (1.04 and 0.99 Å
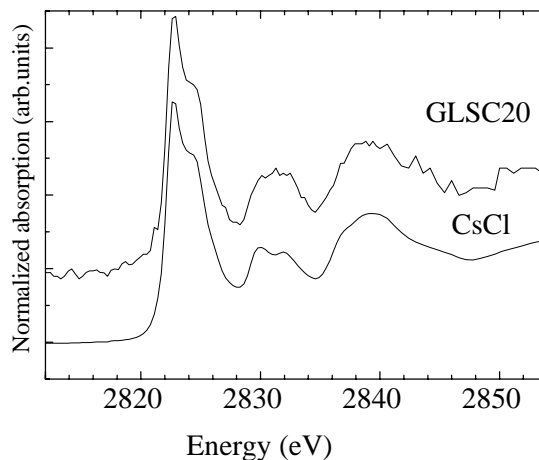
respectively). In that case the Ga-Cl distance would be close to 2.20 Å. The corresponding EXAFS signal corresponding to various S for Cl substitution ratios was simulated using the Feff code. The comparison to the signal in GLSC glasses shows that the ratio of substitution compatible with the Ga K-edge EXAFS experiments does not exceed 1/10. In addition, the XANES spectra at the chlorine edge show the same features as those of CsCl compound (Fig. 3). If a significant part of the chlorine atoms were bonded to gallium atoms, the XANES spectra at the chlorine edge would be significantly altered with respect that of CsCl. All measurement are then in agreement and show that the substitution of Ga-S bond by a Ga-Cl one – if it exists – is quite limited.

A small structural contribution above the first coordination shell is observed in all EXAFS spectra at the gallium edge (figure 1, insert). This contribution was not observed in room temperature measurements and is still quite small at 9K, but can be differentiated from noise and windows effect (Ramos et al, submitted). It is then associated to next nearest neighbors gallium. From the total phase term due to the GaGa pair, we deduce a distance Ga-Ga of 3.5 ± 0.1 Å. This distance can be compared to the Ga-Ga distance in gallium sulfur compounds. The distance Ga-Ga is around 3.16 Å, when the GaS$_4$ tetrahedra are edge-linked and around 3.6 Å when they are linked by corner (Julien-Pouzol, 1982). The second peak is then mainly associated to corner-linked GaS$_4$ tetrahedra. This medium range order contributon is identical in all GLSC glasses.

Table 1. Sulfur coordination shell around gallium in GLSC glasses :
Number of neighbors (N), distance (R), Debye Waller factor (σ^2) and Energy shift (ΔE_0).

	N	R (Å)	σ^2(Å^2)	ΔE_0 (eV)
GLS	4.0 ± 0.2	2.260 ± 0.03	0.0039 ± 0.0004	2.9 ± 0.6
GLSC20	4.1 ± 0.3	2.262 ± 0.03	0.0045 ± 0.0004	3.2 ± 0.6
GLSC40	4.0 ± 0.2	2.257 ± 0.03	0.0042 ± 0.0004	3.2 ± 0.6

Conclusions

EXAFS measurements shown that the introduction of up to 40% CsCl into the glass composition does not alter the Ga-based network in GLSC glasses. In all samples, whatever the introduced CsCl content, the gallium atoms are found with the same little distorted tetrahedral environment, with corner links in between the tetrahedra. The measurements at chlorine K-edge show that chlorine in GLSC glasses is mostly Cs-bonded just as it is in CsCl samples. All measurements are coherent among them, and do not show significant Ga-Cl bonding with the addition of CsCl to GLS glasses. The structural modifications in the glass should be limited in the lanthanum network modifier environment. Complementary measurements at the lanthanum edge (LI and LIII) are planned to assent this point.

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