Overconstrained $CsCl$-Ga_2S_3 Glasses

E. Bychkov,[1] M. Fourmentin,[1] M. Miloshova,[1] C.J. Benmore,[2] J. Neuefeind[3]

[1]Laboratoire de Phisizo-Chimie de l'Atmosphere (LPCA), Centre National de La Recherche Scientifique (CNRS), Université du Littoral, Dunkerque, France

[2]Intense Pulsed Neutron Source (IPNS) and [3]Chemistry Division, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Sulfide glasses are very promising hosts of rare-earth (RE) ions for a variety of photonic applications. Different binary and multicomponent RE-doped glassy systems (Ge-S, As-S, As-Ge-S, Ge-Ga-S, etc.) are extensively used as fiber optical amplifiers, up-converters, fiber lasers, etc., because of their low phonon density of states and much higher quantum efficiency [1]. Recently, it was found that when alkali metal halide glasses are substituted for gallium sulfide glasses, a device's performance is improved [2, 3]. A detailed knowledge of the structure of these glasses is necessary for understanding such improvement. It is interesting that neither MY nor Ga_2S_3 is a network form, but their combination exhibits stability in crystallization and hydrolysis vitreous alloys [4]. Very little is known about the structure of both quasi-binary $CsCl$-Ga_2X_3 (X = S, Se) and multicomponent chalcohalide glasses of this type. The gallium local environment in the MCl-Ga_2X_3 glasses was suggested to be mixed GaX_3Cl [4] on the basis of a simple analogy with crystalline gallium chalcohalide [5]. This report presents the first findings on the structure of these unusual vitreous materials that have such practical importance.

Methods and Materials

$x$$CsCl$·$(1-x)$$Ga_2S_3$ glasses (where $0.5 \leq x \leq 0.7$) were synthesized in evacuated silica tubes at 1000°C and quenched in water. Completely transparent, slightly yellow pieces were obtained and used for high-energy x-ray diffraction and neutron scattering measurements. A combination of neutrons and x-rays is very useful in this particular case, since their coherent scattering lengths are drastically different for the elements involved, particularly for Cs and Cl. High-energy x-ray data were obtained at BESSRC beamline station 11-ID-C at the APS and analyzed by using the ISOMER-X software package [6]. Further experimental details are published elsewhere [7].

Results

The x-ray structure factors $S_X(Q)$ obtained for selected compositions are shown in Fig. 1. The corresponding total correlation functions $T_X(r)$ after Fourier transform of the data are given in Fig. 2.

The first peak in the $T_X(r)$ at 2.28 Å decreases with increasing x and corresponds to Ga-S and/or Ga-Cl nearest-neighbor correlations, since the atomic sizes of the sulfur and Cl species are very similar. However, the gallium local coordination is nearly octahedral ($N_{Ga-S} \approx N_{Ga-Cl} = 5.7 \pm 0.2$) in both limiting cases because $z_{Cl}/z_S = 1.03$. This situation is completely different in the case of neutrons, since $b_{Cl}/b_S = 3.36$. A typical neutron total correlation $T_N(r)$ function is shown in Fig. 3. The gallium local coordination in the two extremes is either octahedral ($N_{Ga-S} = 5.7 \pm 0.1$) or chainlike ($N_{Ga-Cl} \approx 1.7 \pm 0.1$). Combining the x-ray and neutron data, we can conclude that in the $CsCl$-Ga_2S_3 glassy system, the Ga local environment is pure sulfide and octahedral, in contrast to previous structural models.

Discussion

The above conclusion, based entirely on complementary diffraction results, is very unusual from a number of viewpoints. First, a simple estimate gives an extremely high average coordination number for these glasses, $<n> = 4.9$-5.2, taking into account that $N_{S-Ga} \approx 4$ and that $N_{Cs-Cl} = N_{Cl-Cs} \approx 5$. The average coordination in chalcogenide glassy systems is usually lower by a factor of at least 2 (Table 1).

The high average coordination number is normally unfavorable for glass formation, since the optimally constrained glasses have $<n> \approx 2.4$ [8]. Nevertheless, the compositions in the $CsCl$-Ga_2S_3 system can easily be obtained as bulk glasses and thus represent a puzzle for existing theoretical models.
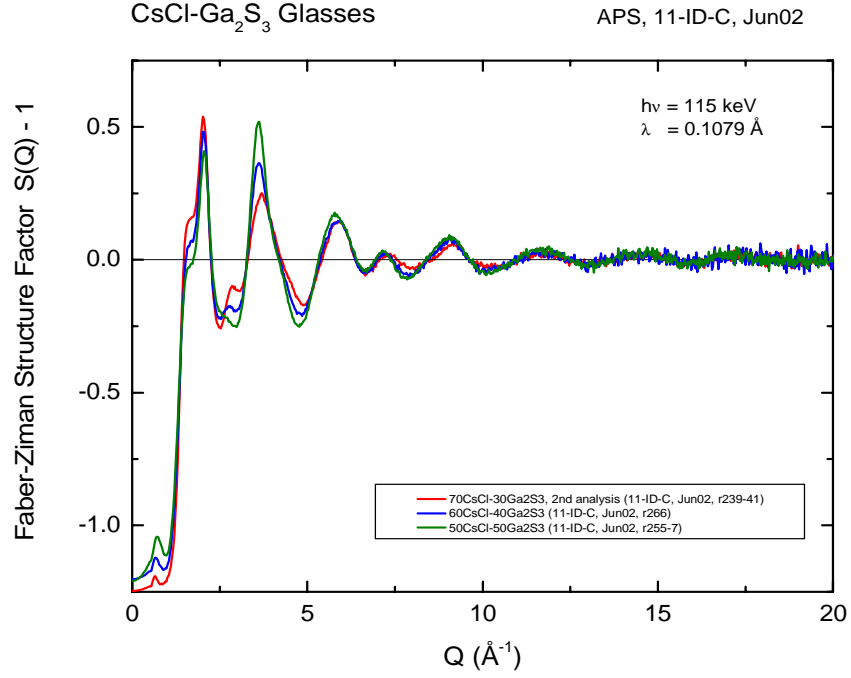
FIG. 1. X-ray Fiber-Ziman structure factor $S_X(Q)$-1 for selected $xCsCl·(1-x)Ga_2S_3$ glasses (where $x = 0.5$, 0.6, 0.7).

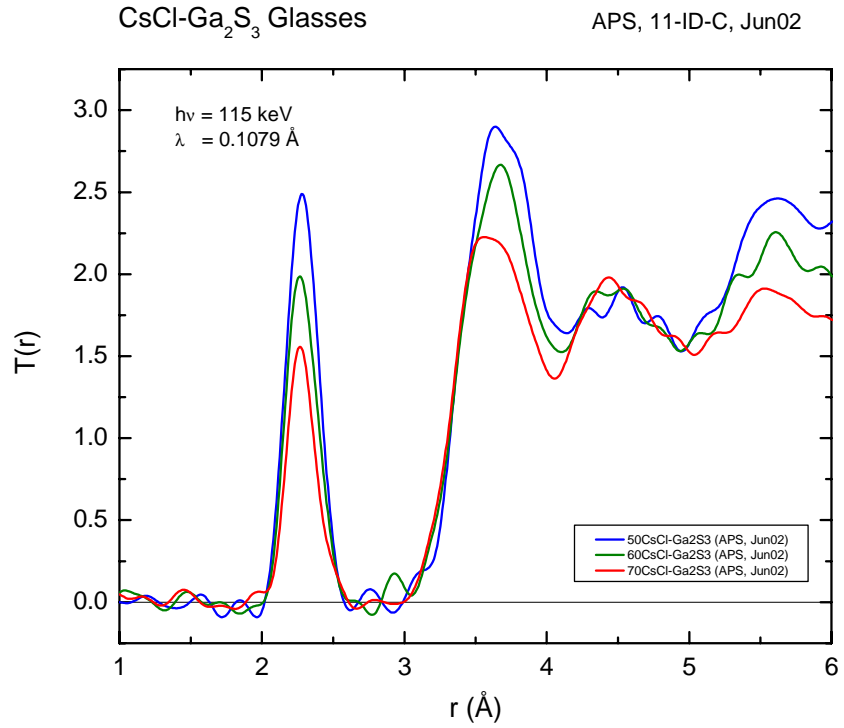FIG. 2. The X-ray total correlation function $T_X(r)$ for selected $xCsCl·(1-x)Ga_2S_3$ glasses (where $x = 0.5$, 0.6, 0.7).
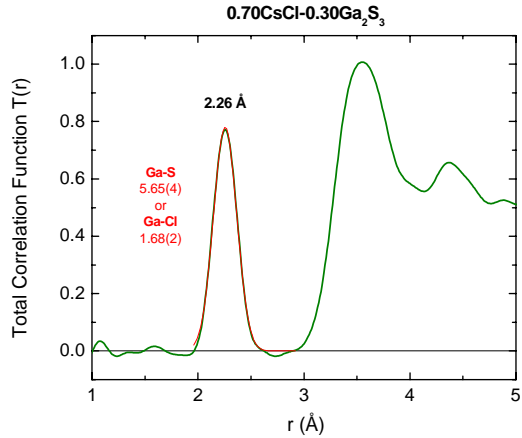
0.70CsCl-0.30Ga$_2$S$_3$

FIG. 3. Neutron total correlation function $T_N(r)$ for a 0.7CsCl·0.3Ga$_2$S$_3$ glass sample.

TABLE 1. Average local coordination in some prototypical chalcogenide glasses.

Glass	<n>
Vitreous Se	2.00
As$_2$S$_3$	2.40
GeSe$_2$	2.67

References

[1] B.G. Aitken and R.S. Quimby, J. Non-Cryst. Solids **213-214**, 281 (1997).

[2] J.R. Hector, J. Wang, D. Brady, M. Kluth, D.W. Hewak, W.S. Brocklesby, and D.N. Payne, J. Non-Cryst. Solids **239**, 176 (1998).

[3] L.S. Griscom, R. Balda, A. Mendioroz, F. Smektala, J. Fernandez, and J.-L. Adam, J. Non-Cryst. Solids **284**, 268 (2001).

[4] Z.U. Borisova, E.A. Bychkov, and Y.S. Tveryanovich, *Interaction of Metals with Chalcogenide Glasses* (St. Petersburg University Press, St. Petersburg, Russia, 1991.

[5] H. Hahn, H. Katscher, and Z. Anorg, Allgemeine Chem. **321** 85 (1963).

[6] J. Urquidi, C.J. Benmore, J. Neuefeind, and B. Tomberli, J. Appl. Crystallogr. **36** 368 (2003).

[7] E. Bychkov, M. Fourmentin, M. Miloshova, F. Hindle, C.J. Benmore, J. Neuefeind, and Y. Tveryanovich, presented at Third European Conference on Neutron Scattering, Montpellier, France, 3-6 September (2003).

[8] J.C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).