



## Short range order in Ge-Ga-Se glasses



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### ABSTRACT

Short range order of glassy  $\text{Ge}_{20}\text{Ga}_{10}\text{Se}_{70}$  and  $\text{Ge}_{20}\text{Ga}_5\text{Se}_{75}$  was investigated by neutron diffraction and extended X-ray absorption fine structure spectroscopy (EXAFS) at Ge, Ga and Se K-edges. For each composition large scale structural models were obtained by fitting simultaneously the four experimental datasets in the framework of the reverse Monte Carlo simulation technique. It was found that both Ge and Ga are predominantly fourfold coordinated. The quality of the fits was strongly improved by introducing Ge–Ga bonding. Models giving the best agreement with experimental data show that Ga has a complex effect on the Ge–Se host matrix: i) it enters the covalent network by forming Ga–Ge bonds ii) by decreasing the number of Se atoms around Ge, it contributes to the formation of Se–Se bonds, which may explain the higher solubility of lanthanide ions iii) the average coordination number of Se increases due to the Ga–Se ‘extra’ bonds. The higher average coordination of the network may be responsible for the increase of  $T_g$  upon adding Ga to Ge–Se glasses.

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## 1. Introduction

Chalcogenide glasses possess noteworthy physical properties, such as low phonon energy, optical nonlinearity several orders of magnitude greater than that of silica glass, broad transmittance in the mid infrared range, high ionic conductivity, or large photosensitivity [1–3]. These properties make them prominent candidates for technical applications in telecommunication, optoelectronics, photonics or energy storage [4–6].

Chalcogenide glasses can be described as covalent networks with average connectivity controlled by the coordination number of the participant elements. It has been found that in glasses of the groups 14, 15 and 16 (e.g. Ge-As-Se [7], Ge-As-Te [8], Ge-Sb-Te [9]) all components follow the 8-N rule [10], but group 13 elements, such as gallium or indium can be fourfold coordinated as well. Moreover, according to some recent publications on chalcogenide glasses, the average coordination number of chalcogenide atoms can also deviate from the 8-N rule in the presence of metallic components [11].

Several studies on Ga-Ge-Se glassy system agree that both Ge

and Ga atoms are fourfold coordinated [12,13]. In the chemically ordered network model, Ge-Ga-Se glasses can be pictured to be made up of corner- and edge-shared tetrahedra. The Ga–Se and Ge–Se heteronuclear bonds are prevalent, Se–Se bonds appear only in Se rich compositions while metal–metal (Ge/Ga–Ge/Ga) bonds can be found in Se-deficient glasses only [13–15]. The average coordination number of Se-atoms is controversial. 2-fold coordinated Se atoms are reported on the basis of Raman, extended X-ray absorption fine structure and X-ray photoelectron spectroscopy [15], but Raman and multinuclear solid state nuclear magnetic resonance spectroscopy investigations showed the formation of triply coordinated Se atoms [12], similarly to crystalline  $\text{Ga}_2\text{Se}_3$  [16] and GaSe [17]. To explain the physical properties of these glasses a previous model assumed 3-fold coordinated Se atoms and 6-fold coordinated Ga atoms [18].

Similarly in Ga-Ge-S glasses, it has been found that Ge and Ga are 4-fold coordinated,  $\text{GaS}_{4/2}$  and  $\text{GeS}_{4/2}$  tetrahedral units are cross-linked via bridging sulfur atoms [19,20]. A small number of Ge–Ge and S–S bonds were reported in  $\text{Ge}_{25}(\text{As,Ga})_{10}\text{S}_{65}$  glasses, possessing some chemical disorder [21]. Formation of  $\text{GaS}_{4/2}$  tetrahedra from  $\text{Ga}_2\text{S}_3$  necessarily brings about the formation of metal–metal bonds that can either be Ge–Ge or Ga-Ga [22–24]. We also note here that threefold coordinated S has been suggested

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by a recent Raman scattering study on  $0.8\text{GeS}_2\text{-}0.2\text{Ga}_2\text{S}_3$  [25].

Not only gallium containing chalcogenide glasses deviate from the 8-N rule. The investigation of Ge–In–Se system using X-ray diffraction, neutron diffraction and EXAFS measurements together with reverse Monte Carlo simulation method showed that the coordination number of In is around 3.3–3.5 while that of Se increases with increasing In content and reaches  $\sim 2.5$  for  $\text{Ge}_{17}\text{In}_{15}\text{Se}_{68}$  [11]. In this context, it appeared interesting to explore glass richer in selenium, in particular to investigate the coordination of Se and Ga and the existence of homopolar bonds. Two glasses were selected due to their technological interest for photonics applications:  $\text{Ge}_{20}\text{Ga}_{10}\text{Se}_{70}$  and  $\text{Ge}_{20}\text{Ga}_5\text{Se}_{75}$ . Their structure was investigated by neutron diffraction and EXAFS. Though the neutron scattering lengths of the components are rather close to each other (Ge: 8.185 fm, Ga: 7.288 fm, Se: 7.97 fm) neutron diffraction data are still useful due to their higher accuracy of absolute normalization that permits the determination of (neutron weighted) coordination numbers with a low uncertainty. This is especially useful if the aim is the accurate determination of the coordination number of the main component. Large scale models were generated by fitting the experimental datasets simultaneously by the reverse Monte Carlo simulation technique (RMC) [26,27]. Short range order parameters were obtained by the analysis of particle configurations.

## 2. Experimental

Ge–Ga–Se glasses were prepared by conventional melt quenching method. Ga, Ge and Se with high purity ( $\geq 5$  N) were used. Chemical reagents were put in silica tubes and pumped under vacuum ( $10^{-4}$  mbar) for 20 h. After first sealing, Se was distilled to remove impurities like OH,  $\text{H}_2\text{O}$  and Se–H. After distillation of Se, the ampoule was sealed and put in a rocking furnace for melting at  $850^\circ\text{C}$  during 8 h. The ampoule was quenched into water, followed by annealing at  $T_g\text{-}20^\circ\text{C}$  for 3 h. DSC measurements were performed with 10 mg powdered samples, heated up to  $450^\circ\text{C}$  at heating rate of  $10^\circ\text{C}/\text{min}$ .

The composition of each sample was checked by using scanning electron microscopy with an energy-dispersive X-ray analyzer (SDD X-Max 80  $\text{mm}^2$  Oxford Instruments AZtecEnergy) at 20 kV. The real chemical composition of glass samples ( $\text{Ge}_{21.1}\text{Ga}_{10.3}\text{Se}_{68.6}$  and  $\text{Ge}_{21}\text{Ga}_5\text{Se}_{74}$ ) is in agreement with the nominal composition taking into account the error limit of the EDX method used ( $\pm 1$  at%). Density of glass was determined by using a Mettler Toledo XS64. A 3 mm sample was put in the analytical balance and the density is determined by averaging three measurements.

Neutron diffraction experiments were carried out at the 7C2 diffractometer (LLB, Saclay). The wavelength of the incident radiation was  $0.72\text{ \AA}$ . Powdered samples were filled into vanadium sample holders with 6 mm diameter and 0.1 mm wall thickness. Scattered intensities were corrected for detector efficiency, background scattering, absorption and multiple scattering following standard procedures.

EXAFS spectra were collected at GILDA-BM08 beamline of the ESRF (Grenoble, France) at the Ga, Ge and Se K-edges. The beam was monochromatized by using a fixed-exit double crystal monochromator equipped with Si (311) crystals and operated with flat crystals. Two Pd-coated mirrors working at an incidence angle of  $3.6\text{ mrad}$  were used for harmonics rejection. Data were recorded in transmission mode using ionization chambers filled with Ar gas at different pressures to achieve the optimal efficiency in the working energy ranges (10%, 80% and 90% of absorption for the I0, I1 and IR ionization chambers). Glassy samples were finely ground, mixed with cellulose powder and pressed into pellets. The amount of sample in each pellet was chosen considering the glass composition to give an absorption  $\mu\text{-}1.5$  just above the selected absorption edge.

The extraction of the  $\chi(k)$  EXAFS signals was performed by using the VIPER code [28]. Raw  $\chi(k)$  data (see Fig. 1) were filtered in two steps: first  $k^3\chi(k)$  was forward Fourier-transformed into  $r$ -space using a Kaiser-Bessel window ( $\alpha = 1.5$ ). The  $k$ -range of transformation was  $1.85\text{ \AA}^{-1} - 13.3\text{ \AA}^{-1}$  for the Ga edge and  $1.85\text{ \AA}^{-1} - 16\text{ \AA}^{-1}$  for the Ge and Se edges. The resulting  $r$ -space data were backtransformed using a rectangular window (usually over the  $r$ -space range  $1.1\text{ \AA} - 2.8\text{ \AA}$ ).

Raman scattering spectra were measured at room-temperature by a HR800 (Horiba Jobin-Yvon) type Raman spectrophotometer with 785 nm laser diode as excitation source for 10 s, averaging 10 accumulations. Light intensity of laser beam on the sample was kept at low level to avoid alterations of Raman spectra due to photoinduced structural changes. The position of the  $520\text{ cm}^{-1}$  band of Si was examined at beginning and end of the experiment in order to control any possible band shifts.

## 3. Reverse Monte Carlo simulation

Glass compositions, densities and the datasets fitted by RMC++ code [27] are given in Table 1. Simulation boxes contained 20,000 atoms. Several models were investigated with different combinations of allowed bonds. In order to avoid unphysically short interatomic distances for nearest neighbors, a series of minimum accepted interatomic distances (cut offs), usually  $2.1\text{--}2.2\text{ \AA}$ , were applied in the simulations. Such cut offs were also used to preclude specific bonds, in such case the corresponding cut off has been increased to  $2.9\text{ \AA}$  for the couple of atoms involved in the forbidden pairs.

EXAFS backscattering factors (merging backscattering phases, amplitudes and  $S_0^2$  values) were obtained by the feff8.4 code [29]. For details of fitting EXAFS and diffraction datasets with RMC we refer to the literature [27].

Calculations were carried out according to the following protocol:

1. Initial configurations were obtained by placing atoms at random in the simulation boxes and moving them around to satisfy cut off constraints. In the next step ‘floating atoms’ (with zero neighbors) and unreasonably high total coordination numbers (e.g. 4 or higher for Se) were also eliminated but no target coordination number values were given as constraints.

All simulations were started from the as-obtained configurations. The number of accepted moves was usually around  $1\text{--}2$  times  $10^7$ .

2. Coordination constraint-free runs were carried out to see which types of bonds are needed to get reasonable fits of the experimental data. In these calculations, certain bonds were forbidden by raising the corresponding cut-offs to  $2.9\text{ \AA}$  but the total coordination numbers were not constrained. At first a reference model was obtained by carrying out a simulation in which all bond types were allowed. Then Ga–Ga, Ge–Ge and Ge–Ga bonds were forbidden in various combinations. The obtained models were assessed by their cumulative relative R-factors. The relative R-factor of a model with respect to the reference model is defined by the following equation:

$$R_r = \frac{\sqrt{\sum (S_{\text{mod}} - S_{\text{exp}})^2}}{\sqrt{\sum (S_{\text{mod}}^{\text{ref}} - S_{\text{exp}})^2}}, \quad (1)$$

where  $S_{\text{mod}}$  and  $S_{\text{exp}}$  are the model and experimental curves

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