Short and Medium Range Order in $\text{Se}_{1-x}\text{Te}_x$ Glasses

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Abstract. Complementary XAFS measurements (LURE and NSLS) of $\text{Se}_{1-x}\text{Te}_x$ glasses have been carried out on both the Se and Te K-edges at low and room temperatures. Using a multi-shell best fit analysis procedure, we have reconstructed the Se and Te local environment: (i) *first shell* intrachain nearest neighbors (Se-Se₁, Se-Te₁, Te-Se₁ and Te-Te₁); (ii) *second shell* intrachain (Se-Se₂ and Se-Te₂) and interchain next nearest neighbors (Se $\leftrightarrow$ Se₃ single scattering in the chains Se-Se₁-Se₃ and Se-Te₁-Se₃). For the first and second coordination shells we suggest that the intrachain chemical order increases with Te content. On the other hand, we propose a model of random distribution of Se and Te atoms between the chains.

Many efforts have been devoted to obtain by XAFS method the *intrachain* structural parameters of $\text{Se}_{1-x}\text{Te}_x$ glasses, amorphous thin films and liquids [1-3]. However, relatively little is known about the *medium range* order in the $\text{Se}_{1-x}\text{Te}_x$ glasses. Only the interchain next-nearest-neighbors (Se $\leftrightarrow$ Se₃ single scattering in the chain Se-Se₁-Se₃) have been observed at about 3.64 ~ Å in a-Se and a-Se_{1-x}Te_x glasses [1-3].

In this paper we present the XAFS study of *intrachain* and *interchain* order of $\text{Se}_{1-x}\text{Te}_x$ glasses at low (80 K) and room temperatures. XAFS spectra at the Se K-edge (D21 beamline LURE) and Te K-edge (X11A beamline NSLS) were measured in transmission using a standard setup. The details of the experiment and of the data analysis will be published in the forthcoming paper [4]. The obtained local environment built on exclusive chain model (see Figure 1): (i) intrachain nearest neighbors (Se-Se₁, Se-Te₁, Te-Se₁ and Te-Te₁) and (ii) intrachain (Se-Se₂ and Se-Te₂) and interchain (Se $\leftrightarrow$ Se₃ single scattering in the chains Se-Se₁-Se₃ and Se-Te₁-Se₃) next-nearest neighbors.

From the *first shell* XAFS data we found (see Table 1) that the number of Se-Te₁, Te-Se₁ and Te-Te₁ bonds increases, but the number of Se-Se₁ bonds decreases more rapidly with Te content in the glasses, than would suggest the model of completely random distribution of Se and Te atoms (chemical disorder). Therefore we suggest that the intrachain chemical order increases with Te content in the glasses. Detailed analysis of the distances in relation with the glassy composition shows that in the first coordination shell, the distances increase slightly with Te content up to the composition $\text{Se}_{0.7}\text{Te}_{0.3}$: Se-Se₁ distance elongates from 2.340 Å to 2.347 Å, Se-Te₁ (Te-Se₁) distance elongates from 2.540 Å to 2.545 Å, and Te-Te₁ distance elongates from 2.725 Å to 2.740 Å. Then the distances suddenly increase at the composition $\text{Se}_{0.6}\text{Te}_{0.4}$ up to 2.36 Å (Se-Se₁), 2.55 Å (Se-Te₁, Te-Se₁) and 2.745 Å (Te-Te₁). The obtained Debye-Waller (DW) factors of Se-Se₁, Se-Te₁ (Te-Se₁) and Te-Te₁ pairs show similar behaviour and in the error bar of measurements are independent on the glass compositions. The DW factors of Se-Se₁, Se-Te₁ (Te-Se₁) at low temperature are about 0.0019-0.0022 Å² and increase with the temperature up to 0.0031-0.0038 Å² value as in the trigonal crystalline selenium (t-Se). Therefore, we suggest that thermal disorder gives the main contribution to the DW factors of Se-Se₁, Se-Te₁ (Te-Se₁) pairs as at room temperature as at low temperature (80 K). While, the changes of the DW factor values for the Te-Te₁ bond remain inside the error bar of measurements.

The *interchain* (Se-Se₂, Se-Te₂) and *intrachain* (Se-Se₁-Se₃; Se-Te₁-Se₃) next-nearest neighbors give main XAFS signal (single scattering contributions), respectively, at small and great wave vectors values, due to very different DW factors and give significant contributions to the second peak of FT (2.8-4.1 Å) for the studied glasses. In comparison with the room temperature crystallographic data, our XAFS results (see Figure 2) on t-Se crystal at low and room temperatures show little shorter interchain distances 3.40 and 3.47 Å and the intrachain distances 3.70 and 3.71 Å, respectively. For interchain pair the DW factor increases significantly more rapidly from 0.006 up to 0.028 Å² with temperature than the DW factor for intrachain pair from 0.007 up to 0.013 Å². For the glasses at room temperature the obtained *inter-* and *intrachain* XAFS signals are very small due to the high values of DW factors and only low temperature (80 K) results are presented. The *interchain* distances (Se-Se₂) and DW factors are in the same range as those obtained for the t-Se crystal at room temperature and we suggest that structural disorder is predominant in glasses for Se-Se₂ pair. The distance for this pair increases a little with the Te content in the glasses from 3.40 up to 3.45 Å. The *intrachain* distance (Se-Se₁-Se₃) and DW factors (0.008 up to 0.010 Å²) are a little shorter than the distance and DW factor in the t-Se crystal at room temperature. The intrachain distance increases with variation of Te composition from 3.65 up to 3.70 Å. The intrachain (Se-Te₁-Se₃) contribution has been detected at highest Te content in the glasses and corresponds to the distance Se--Se₃ at 3.97 Å and small DW factor 0.008 Å². The obtained next-nearest neighbor intrachain distances Se--Se₃ are in good agreement with the obtained intrachain

distances Se-Se₁, Se-Te₁ in the first coordination shell of the glasses. Moreover, the analysis of the Te K-edge second shell shows the interchain Te-Se₂ pair at 3.43-3.48 Å and the DW factor about 0.03 Å². From the second shell XAFS data we found that the number of intrachain Se-Te₁-Se₃ bonds increases, but the number of Se-Se₁-Se₃ bonds decreases more rapidly with Te content in the glasses that would suggest the model of completely random distribution of Se and Te atoms inside chains, and is in good agreement with the obtained model of chemical ordering in the first coordination shell. Therefore, as for the first coordination shell, we suggest that the intrachain chemical order increases with Te content in the glasses. On the other hand, the number of interchain Se-Te₂ bonds increases, but the number of Se-Se₂ bonds decreases in agreement with Te content in the glasses, that would suggest the model of completely random distribution of Se and Te atoms between the chains.

Table 1: Structural data obtained from the best-fit analysis of the Se and Te K-edge EXAFS in Se_{1-x}Te_x. N is the number of Se (± 0.1) or Te (± 0.1) atoms located in the first shell at distance R from the Se (± 0.005 Å) or Te (± 0.007 Å); σ^2 is the DW factors (± 0.0005 Å²); ϵ is the fitting error [4].

Compound		Se-Se ₁ and Te-Se ₁			Se-Te ₁ and Te-Te ₁			ϵ ($\times 10^{-4}$)
		N_1	R_1 (Å)	σ^2 (Å ²)	N_2	R_2 (Å)	σ^2 (Å ²)	
t-Se	Se K-edge	2.03	2.370	0.0021				3.6
a-Se		1.94	2.340	0.0020				5.4
a-Sc _{0.9} Te _{0.1}		1.75	2.344	0.0020	0.25	2.539	0.0021	3.6
a-Sc _{0.8} Te _{0.2}		1.44	2.345	0.0019	0.49	2.544	0.0019	2.9
a-Sc _{0.7} Te _{0.3}		1.17	2.347	0.0021	0.77	2.545	0.0020	2.8
a-Sc _{0.6} Te _{0.4}		0.80	2.363	0.0021	1.04	2.557	0.0022	4.6
a-Sc _{0.9} Te _{0.1}	Te K-edge	1.90	2.538	0.0023	0.31	2.724	0.0026	10.0
a-Sc _{0.8} Te _{0.2}		1.72	2.546	0.0022	0.55	2.737	0.0032	4.6
a-Sc _{0.7} Te _{0.3}		1.48	2.548	0.0021	0.65	2.743	0.0036	3.2
a-Sc _{0.6} Te _{0.4}		1.34	2.551	0.0027	0.85	2.745	0.0035	3.6
t-Te					1.94	2.840	0.0019	12.0

Figure 1: The Se_{1-x}Te_x glass structural scheme with obtained in this work intrachain and interchain distances.

Figure 2: Reconstructed RDF's of the second coordination shell of Se_{1-x}Te_x glasses at Se K-edge low temperature (80 K).

References

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