Valence state of vanadium in silicate glasses

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The concentration and the redox state of polyvalent elements in glasses is of particular interest owing to its influence on manifold properties of glasses such as colouring or optical transmission, fining, phase separation and crystallization. There are a number of methods available which allow to determine the valence state of vanadium ions. However, each method reflects the redox state in a specific way. Here, the use of X-ray absorption spectroscopy in the near edge region (XANES) will be demonstrated investigating sodium silicate glasses. The results are discussed in comparison with optical spectroscopy.

In this work sodium silicate glasses (NaO_2 - SiO_2: 33-67 and 15-85 mol%) were investigated. The glass melts were prepared under different redox conditions. Premelted sodium silicate glasses were powdered, doped with 0.5% V (as V_2O_5) and remelted in a Pt or Ir crucible in a special high frequency heated furnace at temperatures up to 2000°C. The melts were prepared in air and/or nitrogen atmosphere and subsequently quenched by centrifugal casting. The XANES spectra were registered by measurements at the V K-edge (5465 eV). The experiments were performed at the beamline E4 using Si (111) monochromator crystals. The corresponding X-ray intensities could be determined by ionisation chambers.

The crystalline oxides V_2O_3, VO_2 and V_2O_5 were used as reference compounds for oxidation states (+3, +4, +5) in silicate glasses because the corresponding states are to expect in glassy materials. The normalized XANES spectra are shown in Fig. 1. As it was shown in a previous work by Wong et al. [1] these oxides exhibit various absorption features that can be used to identify valence states and coordination geometries. Besides the main edge which can be assigned to the dipole-allowed electron transition 1s $\rightarrow$ 4p it was found a well-defined pre-edge absorption that is caused by electron transition 1s $\rightarrow$ 3d. The latter transition is a result of overlapping the orbitals of vanadium (3d) and of oxygen (2p). The intensity of this pre-peak strongly depends on the geometry of vanadium-oxygen polyhedron. Thus, the fivefold V-O coordination in a distorted tetragonal pyramid in V_2O_5 yields an intense pre-peak whereas the octahedral V-O groups in V_2O_3 and VO_2 exhibit a reduced intensity in dependence on the regularity of octahedral environments. These two spectroscopic features, i. e. the position of pre-peak or of the main edge and the peak heights, can be used to interpret the spectra of glasses if further effects should be neglected.

The vanadium K-edges of doped sodium silicate glasses (see Fig. 2) reveal a continuous shift of pre-peak and main edge as well as a continuous decrease of the intensity of the peak if reducing conditions are applied. Moreover, it can be seen that the shape and the position of the pre-peak is changed in comparison with crystalline compounds. This should be induced by the formation of more regular V-O polyhedra in glasses as against the distorted structural units in crystalline compounds. The position at the half height of the main edge and the position of the maximum of the pre-peak were used for a first approximation of the averaged oxidation state of vanadium ions because there are different effects that influences the edge position calculated by the first derivative of the absorption spectra. As a reference for the valence state +5 in glasses a sample was used which was melted under strongly oxidising conditions (Glass 1). That gives a change of the averaged valence state of vanadium in Glass 1 of 5.0 to 4.1 of Glass 3 combined with the formation of octahedral V-O units. Previous X-ray absorption experiments on various glasses interpreted the shift of the 1s $\rightarrow$ 3d pre-peak by a mixed valence state V^{4+}/V^{5+} in a similar way [2,3].

The optical absorption spectra measured in the range of 190 to 3200 nm yield information on charge transfer transitions in the ultraviolet range and of d $\rightarrow$ d transitions in the visible and infrared range [4]. Based on extinction coefficients determined by a series of experiments it is possible to calculate the averaged oxidation state assuming the existence of only V^{4+} and V^{5+} species. That gives a value of 4.9 for Glass 1 and 4.3 for Glass 3 that is in agreement with XANES data within the accuracy of both experiments.

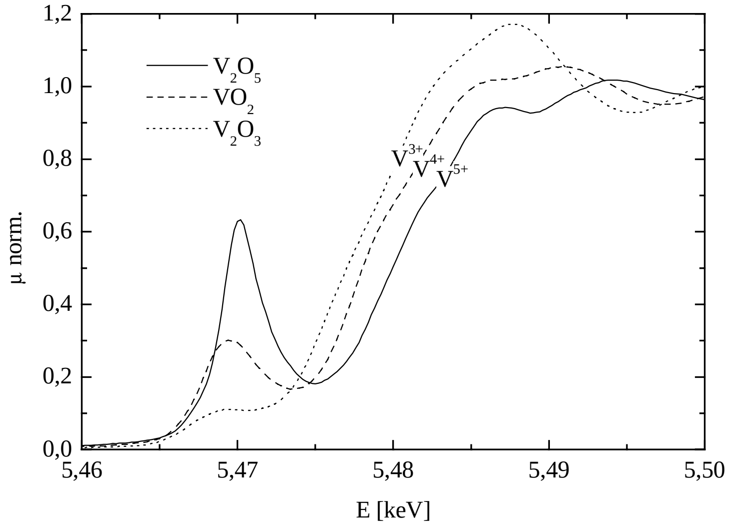

Fig. 1: XANES spectra of crystalline reference compounds at the V K-edge

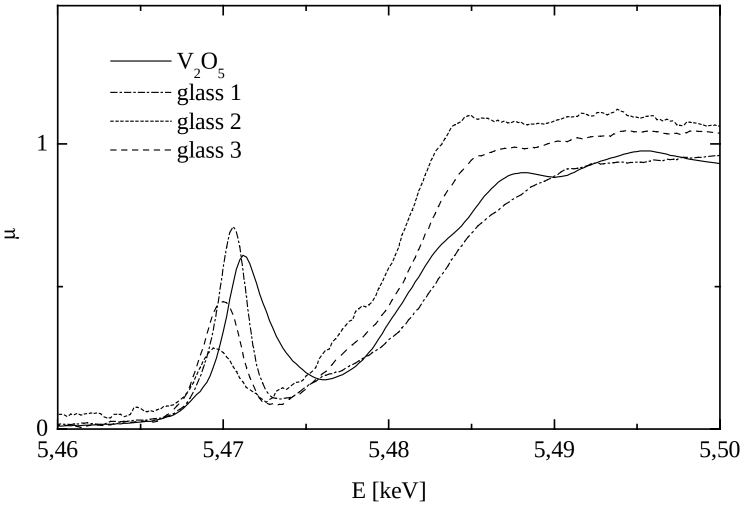

Fig. 2: Normalized absorption spectra of V doped silicate glasses (Glass 1, 2 and 3) in comparison with crystalline V_2O_5

References

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