Journal of Alloys and Compounds, 207/208 (1994) 170–173
JALCOM 3038

Neutron scattering studies of Yb-bearing silicate glasses

A.J.G. Ellison, C.-K. Loong and J. Wagner
Argonne National Laboratory, Argonne, IL 60439 (USA)

Abstract

The static and dynamic magnetic response of the Yb^{3+} ions in $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ glass and the isochemical crystalline silicate $Na_3YbSi_3O_9$ has been studied by neutron diffraction, inelastic magnetic scattering, and magnetic susceptibility measurements. The rare earth sites in the glass have an average coordination number of 5.6 ± 0.5 and give a mean rare earth–oxygen bond length of 2.23 Å; average Si–O and O–O coordination numbers and bond distances are comparable to those in vitreous SiO_2. The magnetic excitation spectrum of the $Na_3YbSi_3O_9$ material was analyzed by a crystal field model using a method of descending symmetry. The magnetic susceptibility and the excitation spectrum of the Yb glasses can be described by a distribution of ligand field effects on the Yb^{3+} ions that are similar to the nominal crystal field in crystalline $Na_3YbSi_3O_9$.

1. Introduction

Binary R_2O_3–SiO_2 systems (where R is a rare earth element) show wide, stable two-liquid fields at high SiO_2 concentrations with critical temperatures in excess of 2500 K. This makes it all but impossible to make binary rare earth silicate glasses with more than 1–3 mol% rare earth oxide. Incorporating large, low valence cations such as Na^+ into the systems, however, drastically lowers liquidus temperatures and renders the two-liquid field metastable, eventually lowering the critical temperature to below the solidus. In these ternary glasses, the Si^{4+} ions remain in fourfold coordination with oxygen atoms, but the coordination environments of the rare earth ions may be affected by the presence of sodium. Knowledge of the local environments of rare earth ions and their chemical and dynamic roles in the glass is important in the understanding of the optical properties of the glasses and in the development of new devices using these glasses.

Neutron scattering can be used to probe the structure and dynamics of glasses. Elastic and inelastic scattering of thermal neutrons by atomic nuclei in condensed matter yield information regarding the space–time correlation of the atoms. In the case of rare earth bearing glasses, the magnetic interaction between the neutron magnetic moments and the electrons in the incomplete f-orbitals also provides insights into the local electronic symmetry of the rare earth ions and their interactions with the environment. In this paper, we present the results of neutron diffraction and inelastic scattering studies of a $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ glass and a related crystalline analog $Na_3YbSi_3O_9$.

2. Experimental details

$3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ and $3Na_2O \cdot Lu_2O_3 \cdot 6SiO_2$ glasses were prepared in 100-g batches by combining appropriate amounts of reagent grade Na_2CO_3, Yb_2O_3 (or Lu_2O_3) and SiO_2 in a mill. The mixture was placed in a Pt crucible and fired at 1000 °C for 1 h to drive off CO_2 from the carbonate. The furnace temperature was then increased to 1400 °C and held there for 8–12 h. The crucible was removed from the furnace and stirred several times to ensure sample homogeneity. After this time the furnace temperature was increased to 1500 °C, and after thermal equilibration at this temperature, the sample was removed and quenched by pouring it onto a massive copper block. Polycrystalline $Na_3YbSi_3O_9$ was prepared by direct crystallization of the glass at 1250 °C. Neutron time-of-flight diffraction experiments for the glasses and the crystalline material were carried out using the glass, liquid and amorphous diffractometer (GLAD) and the high-intensity powder diffractometer (HIPD), respectively, at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The diffraction patterns show that while both $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ and $3Na_2O \cdot Lu_2O_3 \cdot 6SiO_2$ are homogenous glasses, the crystallized $Na_3YbSi_3O_9$ contains a minor glassy component. The use of cold-to-epithermal neutrons in conjunction with the large solid angle coverage, position-sensitive detectors on GLAD permits simultaneous measurements of coherent scattering from the sample to be measured over a wide range of momentum transfer $\hbar Q$. Overlapping data sets from different detectors are then combined, normalized to the incident flux, corrected for absorption, multiple

SSDI 0925-8388(93)03038-K

scattering and self-scattering, and are then merged together to obtain the structure factor $S(Q)$. For heavy elements such as rare earths or actinides, severe neutron absorption may occurs at certain neutron energies corresponding to nuclear resonances. Because Q at fixed energy varies as sin θ, where 2θ is the scattering angle, such resonances appear at different places in Q space depending on the angle at which scattering is observed. This makes it simple to identify the resonances and to avoid including them in the merged data set.

Inelastic neutron scattering measurements were performed using the high resolution, medium energy chopper spectrometer (HRMECS) of IPNS. The instrumental resolution has negligible effect on the nuclear and magnetic excitation spectra since the features are significantly broadened by chemical disorder in the glasses. To fully explore the magnetic and phonon excitations up to 150 meV, incident neutron energies of 40 and 200 meV were chosen for the studies. The magnetic contribution to the total scattering in $3Na_2O\cdot Yb_2O_3\cdot 6SiO_2$ and $Na_3YbSi_3O_9$ was identified by an examination of the momentum transfer dependence of the observed intensities and by a comparison with the spectra of the non-magnetic $3Na_2O\cdot Lu_2O_3\cdot 6SiO_2$ glass. The data were corrected for background scattering and the effect of sample self-shielding by subtracting the combined empty container and neutron absorber (*i.e.* cadmium) runs. Measurements of the elastic incoherent scattering from a vanadium standard provided detector calibration and intensity normalization.

3. Results and discussion

3.1. Neutron diffraction

Glasses do not possess long-range order, so it is conventional to express their structure in terms of distribution functions obtained from the Fourier transform of their structure factors $S(Q)$ of which the pair correlation function $G(r)$, the total distribution function $T(r)$ and the radial distribution function $N(r)$ are perhaps best known:

$$G(r)=\frac{1}{2\pi^2\rho_0}\int_0^\infty [S(Q)-1]Q^2\,\frac{\sin Qr}{Qr}\,\mathrm{d}Q \tag{1}$$

$$T(r)=4\pi r\rho_0 G(r) \tag{2}$$

and

$$N(r)=4\pi r^2\rho_0 G(r) \tag{3}$$

$N(r)$ dr has a direct physical interpretation as the number of atoms lying within a range $(r, r+\mathrm{d}r)$ from any given atom. Figure 1 shows $T(r)$ obtained from the diffraction measurement of $3Na_2O\cdot Yb_2O_3\cdot 6SiO_2$ glass. $T(r)$ oscillates about a line with a slope equal to the density of the glass. Peaks in $T(r)$ represent the most probable (average) bond distances for various combinations of elements. The peaks at 1.63, 2.23 and 2.65 Å correspond to the Si–O, Yb–O and O–O nearest-neighbor distances, respectively. The Si–O and O–O distances are comparable to those found in other silicate glasses [1].

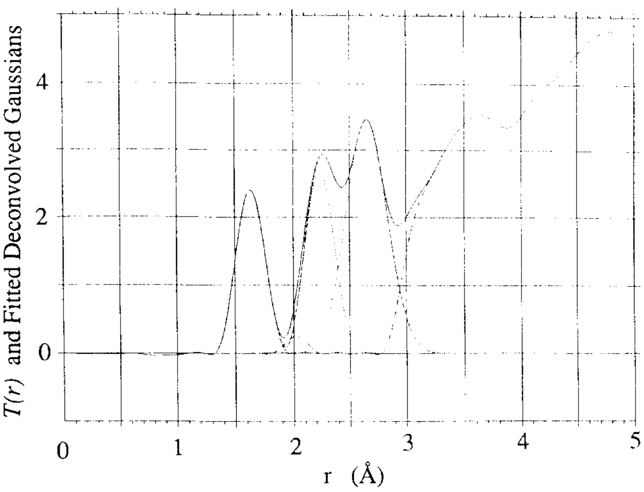

Fig. 1. The total distribution function $T(r)$ of $3Na_2O\cdot Yb_2O_3\cdot 6SiO_2$ glass.

The area under a peak in $N(r)=rT(r)$ is directly proportional to the coordination number of the atoms; from the area of the Si–O peak, for example, we obtain a coordination number for Si of 3.85. This is less than the expected value of 4.0 due to resolution smearing. For the Yb–O peak we obtain a coordination number of 6.1 ± 0.3 for Yb. Below the Yb–O and O–O peaks, however, lies the weak, broad Na–O correlation length peak, but the fitting algorithm used does not converge on a sensible value for either its position or its area. Therefore, it is likely that the coordination number obtained for Yb is an overestimate; we conservatively assign an average coordination number of 5.6 ± 0.5 for Yb. Extended X-ray absorption fine structure (EXAFS) measurements of lanthanide coordination numbers in alkali silicate glasses have typically produced values less than 7 for the coordination number of large lanthanide ions [2,3], so a value of 6 or less might be expected for small rare earth ions like Yb and Lu.

3.2. Magnetic inelastic scattering

Magnetic neutron scattering and optical spectroscopy have been used extensively to measure the splitting of the rare earth energy levels by the electrostatic fields of their surrounding ligands, and to obtain from these data quantitative information regarding the local environments of rare earth ions. Optical experiments provides measurements of 4f electronic transitions over a wide range of energies. The recent advent of siteselective laser spectroscopy has added a new dimension to the studies of rare earth activated luminescence in disordered systems by which the adverse effect of inhomogeneous broadening can be circumvented. However, a detailed comparison of the observed and calculated transition strengths for optical measurements is a challenging task because of the complex intermediate excited states involved in the photon–atom interaction.[4] Optical data are usually analyzed by a goodness-of-fit of the observed energies only. Inelastic neutron magnetic scattering is an ideal tool for probing the low-lying states of the rare earth ions. Magnetic scattering of thermal neutrons arises from an interaction between the neutron magnetic moment and the convection and spin current of the scatterer. Such a weak interaction requires only a first-order perturbation treatment, thereby affording quantitative comparisons of calculated and experimental absolute scattering cross-sections. Here, we present the results of a crystal field analysis of the crystalline $Na_3YbSi_3O_9$ and the vitreous $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ data and compare the observed magnetic susceptibility of the glass with the calculated values estimated by a crystal field model.

According to Kramer's Theorem, the lowest symmetry of a state affected by a ligand electrostatic field for an odd-number electron system is a twofold degeneracy. Thus, the Yb^{3+} Russell–Saunder ground multiplet is at most split into $2\Gamma_6$ and $2\Gamma_7$ doublets. If all the Yb sites in a crystal are equivalent and have a local point symmetry less than a cubic symmetry, one expects a low temperature magnetic excitation spectrum containing a peak at zero energy corresponding to elastic scattering within the ground state doublet and three sharp inelastic lines corresponding to excitations from the ground state to the excited states. If rare earth ions occupy more than one crystallographic site, or if the local symmetry varies from one site to another as in a glass, each set of the Γ_6 and Γ_7 states will have different energies, and the resulting spectrum will be broad. The non-magnetic spectrum of $3Na_2O \cdot Lu_2O_3 \cdot 6SiO_2$ glass was weighted by the average scattering cross-section of its components and subtracted from the total (nuclear and magnetic) excitation spectra of crystalline $Na_3YbSi_3O_9$ and glassy $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$. The obtained spectra, as shown in Fig. 2, represent a measure of the magnetic scattering. Besides a strong and sharp elastic peak dominating the low energy region (±15 meV) in both materials, most of the inelastic scattering of $Na_3YbSi_3O_9$ centers at about 45 meV whereas the spectrum of the Yb glass is flat up to about 70 meV with a long tail extended to over 100 meV. The excitation spectrum of crystalline $Na_3YbSi_3O_9$ can be analyzed in terms of three broad components centered at 13.8, 41.9 and 57.7 meV, as shown in the upper panel of Fig. 2. The large widths of these excitations are probably caused by the effects of multiple Yb sites in the crystal structure and by the effect of chemical disorder from the minor glassy component in the material.

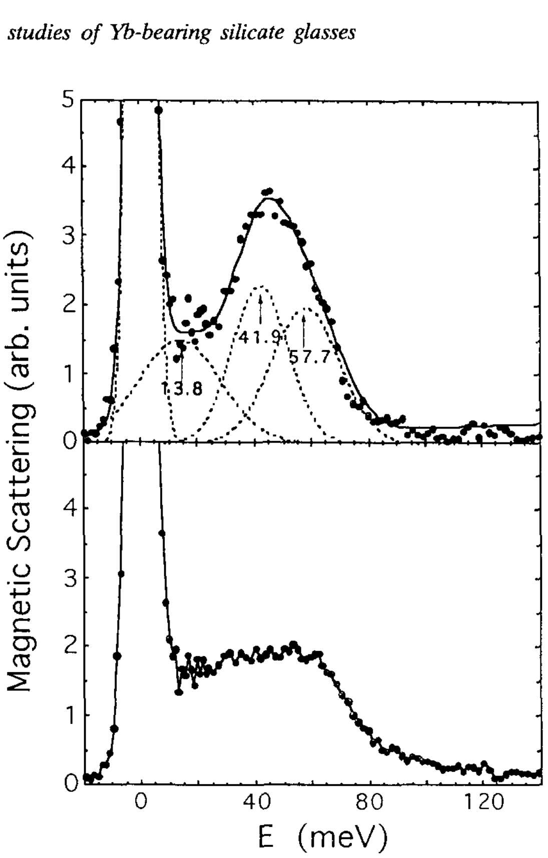

Fig. 2. Upper panel: The magnetic excitation spectrum of $Na_3YbSi_3O_9$ (circles) and a fit to the data (solid line) by a sum of four Gaussian functions centered at 0, 13.8, 41.9, and 57.5 meV denoted by the dotted lines. Lower panel: The magnetic excitation spectrum of the $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ glass (circles). The line is a guide to the eye. $T = 15$ K.

To assess the extent to which the local environments of the rare earth ions may affect the energy scale of the magnetic excitations in the crystalline and vitreous states, we analyzed the spectra using a single-ion crystal field model [5]. We compared the $Na_3YbSi_3O_9$ spectrum with the model first assuming an octahedral coordination with cubic symmetry corresponding to six equidistant O ligands for the Yb ions. After reasonable agreement with the data was achieved, the cubic environment was relaxed to allow for lower symmetries. This approach is supported by the diffraction results which indicates an average 5.6 coordination of the Yb–O atoms and the satisfactory description of a distorted octahedral environment for Yb^{3+} in oxide glasses given previously by Barber and Obermyer [6]. Under the cubic approximation, the Yb ground multiplet splits into two doublets, Γ_6 and Γ_7, and a quartet Γ_8, and transitions between Γ_6 and Γ_7 are forbidden. Therefore, we fitted the $Na_3YbSi_3O_9$ spectrum by assigning the 45 meV band to excitation from the ground state to Γ_8 and obtained the ratio between the fourth and sixth order crystal field parameters. Next, a B_0^2 term was added to fit the 0, 13.8, 41.9 and 57.7 meV peaks as Γ_7, Γ_6, Γ_7 and Γ_6, respectively. The final parameters are $B_0^2=54$, $B_0^4=-57.8$, $B_0^6=86.5$ meV, $B_4^4=-\sqrt{(5/14)}B_0^4$ and $B_4^6=\sqrt{(7/2)}B_0^6$. The calculated energies and intensities for the three transitions agree well the observed spectrum of $Na_3YbSi_3O_9$.

If it is true that the average local environment of Yb^{3+} in the glass is comparable to its average environment in the crystal, then it remains to show that small changes in the crystal field parameters calculated for the crystal can produce a magnetic susceptibility and magnetic scattering spectrum similar to what are obtained for the glass. Figure 3 compares the calculated paramagnetic susceptibility of $Na_3YbSi_3O_9$ crystal obtained using crystal field parameters discussed above with the measured susceptibility of $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ glass. The good agreement between the observed susceptibility of the glass and calculated susceptibility of the crystal lends credence to the proposal that the average ligand field of Yb ions are comparable in the glass and isochemical crystal. Because Yb sites in the glass are not well ordered, we next consider the effect of relaxing the constraints of cubic symmetry for the parameters B_4^4 and B_4^6. Reducing B_4^4 to approximately −5 meV shifts the calculated scattering spectrum to lower energy and slightly improves the agreement between the calculated susceptibility and experiment. Increasing B_4^6 up to 200 meV shifts the calculated spectrum towards higher energies and brings the high temperature part of the high temperature susceptibility into better agreement with the data. In reality, of course, the observed magnetic scattering spectrum is broad enough to accommodate both of these changes. Therefore, the observed scattering is probably best explained as a superposition of not only the ligand field strengths given by these parameters, but those of many other states obtained by small variations in the crystal field parameters away from the nominal values obtained for the crystal.

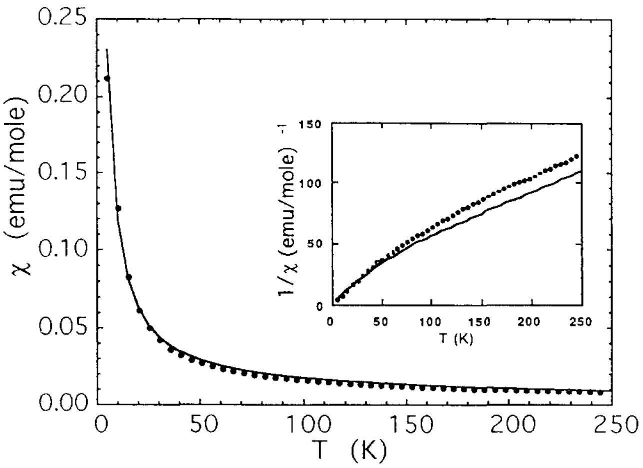

Fig. 3. The measured paramagnetic susceptibility and the inverse susceptibility (inset) of the $3Na_2O \cdot Yb_2O_3 \cdot 6SiO_2$ glass (circles). The solid lines represent the calculated susceptibilities obtained from the crystal field model using the nominal crystal field parameters for crystalline $Na_3YbSi_3O_9$.

4. Conclusion

In conclusion, neutron diffraction and magnetic scattering studies show that Yb and Lu ions in $3Na_2O \cdot R_2O_3 \cdot 6SiO_2$ glasses have average coordination numbers less than 6.0 and mean R–O bond lengths of 2.23 Å. The extent of perturbation of the Yb^{3-} energy levels by the ligand fields in the vitreous state is comparable to that in the crystalline environment.

Acknowledgments

We thank Frans Trouw for his assistance in the HIPD diffraction experiment. Work performed at Argonne National Laboratories is supported by the US DOE, Basic Energy Sciences under Contract No. W-31-109-ENG-38.

References

1 E.H. Henninger, R.C. Buschert and L. Heaton, *J. Phys. Chem. Solids, 28* (1967) 423; E. Lorch, *J. Phys. C, 2* (1969) 229.

2 C.W. Ponader and G.E. Brown Jr., *Geochim. Cosmochim. Acta, 53* (1989) 2893.

3 E.M. Larson, A.J.G. Ellison, F.W. Lytle, A. Navrotsky, R.B. Gregor and J. Wong, *J. Non-Cryst. Solids, 130* (1991) 260.

4 C.-K. Loong and L. Soderholm, *J. Alloys Comp., 207/208* (1994) 153.

5 The Hamiltonian includes the atomic free-ion and crystal field interactions for an f^N configuration, formulated under the scheme of intermediate coupling using spherical tensor techniques. See: H.M. Crosswhite and H. Crosswhite, *J. Opt. Soc. Am., B1* (1984) 246.

6 S.W. Barber and R.T. Obermyer, *Trivalent Ytterbium as a Microprobe in Oxide Glasses*, Owens-Illinois, Toledo.