Chapter 6

CONCLUSIONS

In this work, two different types of vitreous systems have been considered. The first was a boro-silicate network to which simulated (i.e. non-radioactive) nuclear waste was added. The second was a phosphate host glass bearing a series of lanthanide rare-earth oxides. A summary of the findings and conclusions on each of these two vitreous systems is presented in this chapter.

6.1 Nuclear-Waste Glasses

In order to study the effect of included waste on the host network, glasses with high concentrations (upto 25 wt%) of simulated nuclear waste were studied together with the basic boro-silicate host glass. The method of the RDF was used for this study. X-ray diffraction patterns recorded on the nuclear-waste glasses were used to identify those systems that were vitreous and that were considered 'acceptable' from leaching studies. The vitreous glasses were examined by neutron diffraction together with the basic glass. These studies revealed that the basic units of the host glass (SiO$_4$ tetrahedra and BO$_3$ triangles) remain intact after the addition of waste cations. This conclusion was drawn from the position and the area of the first maximum in the T(r) which is a sum of the Si-O and B-O correlations of the basic units in the host glass. This feature remains unchanged after the addition of waste.
oxides. The added waste cations occupy interstices of the network thereby modifying it in the medium-order range (2 Å to 10 Å). A detailed study of the other features in the total correlation function is difficult on account of the large number of overlapping component correlations arising from the multicomponent nature of the samples. Some of these may be resolved using high resolution diffraction data collected to high values of $Q_{\text{max}}$. The Reverse Monte Carlo method may also be employed in the separation of some of these component functions. The question of the bonding of the waste to the host network has not been addressed in this work. However, the possibility of a weak ionic link between the oxygen atoms of the network and the waste cations cannot be excluded. Thus, surface leaching by aqueous solvents might occur under suitable conditions. From this study, a model of the microscopic structure of glass was built by constraining the inter-tetrahedral bond angles to the range $135^\circ$ to $170^\circ$ as well as the Si-O-B angular range to $140^\circ$ to $170^\circ$.

Radiation effects due to the radioactivity of the actual waste are likely to damage the structure and have not been considered in this work. Irradiation with high energy gamma-rays and other ionizing particles could be used in understanding the change in the network that would occur after several years of radiation damage caused by the waste cations in the glass. Many applications of these oxides which were considered as waste oxides a decade ago have been proposed [Physics Education (1988)]. The gamma radiation from this waste may be used to irradiate vegetables, grains, other foods and for sterilization of various medical and pharmaceutical products. Gamma rays from this waste have also been used to convert the chemical structure of thin plastic sheets to 'Omniderm' to substitute for human skin. The latter can be used for improved recovery of ruptured or burnt skin. Vitrification of this waste for such applications would thus permit the manufacture of mobile radiation sources for the above mentioned uses. It may be noted that although these glasses have been found to be mechanically and chemically stable, their storage in geological structures that are considered stable may at some future date be prone to damage by unforeseen earthquake and volcanic activity. Should such events occur, the possibility of these long-lived radioactive species
entering the biosphere cannot be ruled out. Even though the probability of occurrence of such calamities is low, it points to the need for more than one method of permanent storage of highly-active long-lived nuclear waste to be considered.

6.2 Rare-earth Phosphate Glasses

Rare-earth phosphate glasses with good mechanical strength, transparency, stability and inertness were prepared. These had the general formula

\[(R_2O_3)_{0.2}(P_2O_5)_{0.8}(Al_2O_3)_{0.05} \quad \text{and} \quad (R_2O_3)_x(P_2O_5)_{1-x}\]

where \(x = 0.2 \) and 0.25 and \( R \) stands for La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Er or Ho. In each sample the symbol \( R \) represents both La and one other rare-earth from this series. The densities of these glasses were found to increase with increase in atomic number. This was attributed to the fact that there is a change in the mass of the sample with very little change in the its specific volume. The vitreous nature of the samples was confirmed with preliminary X-ray diffraction. Compositional analyses of the samples using chemical methods and Neutron Activation Analysis showed that there was a small (4 to 10%) discrepancy in composition between that which was expected from the starting mixtures and found from the analyses.

The XRD measurements using MoK\(_\alpha\) radiation showed the basic unit of this glass to be a PO\(_4\) tetrahedron with \(n_p(O)\) of 4 ± 0.07 and a P-O bond distance of 1.55 ± 0.01 Å. The compositional dependence of the intensity function \(i(Q)\) was monitored from the variation in the peak height of the FSDP for the Sm containing glasses. The decrease in the intensity of this feature with increase in Sm concentration was attributed to this cation's role as a network modifier. The effect known as the 'lanthanide contraction' was observed in the correlation functions through the downward shift in position of the second maximum with increasing atomic number of the rare-earth atom. This shift was caused by the R-O correlation which was one of the constituents of the second maximum in \(T(r)\).
The scattering length dependence of FSDP from $i(Q)$ obtained using ND measurements confirmed the network modifying role of the rare-earth cations. The total correlation function $T(r)$ of each glass yielded an $n_P(0)$ coordination number of $4.01 \pm 0.06$ and an $r(P-O)$ distance of $1.55 \pm 0.01$ Å. The second maximum yielded the $n_O(0)$, $n_R(0)$ coordination numbers in the ranges 3.8 to 4.3 and 7 to 8 respectively. The respective $r(O-O)$, $r(R-O)$ distances were $2.53$ Å and in the range $2.44$ Å to $2.26$ Å. The total correlation functions obtained using both XRD and ND were combined to calculate the $n_R(0)$ and $n_O(0)$ coordination numbers as both these functions had different weights. The numbers so obtained agree well with those obtained from Gaussian fits to the features in $T(r)$ within 15%.

The separation of higher order component correlations such as P-P, R-P etc. was not possible through the combination of X-ray and neutron diffraction data. Also, the particular value of $Q_{max}$ used in these diffraction measurements did not permit the further separation of component correlation functions. Thus the X-ray and neutron diffraction data both support a model of this glass in which the network is predominantly made up of tetrahedral PO$_4$ units with two corners being shared ($Q^2$ units) and an inter-tetrahedral angle in the range 143° to 148°. The rare-earth cations form oxygen polyhedra and occupy 'holes' or spaces in the network. These cations are likely to be partially ionically linked to their oxygen neighbours.

Techniques such as EXAFS, Energy Dispersive X-ray Diffraction or measurements with high values of maximum momentum transfer ($Q \approx 30$ Å$^{-1}$) would all be useful in the separation of R-O and O-O correlations which was not possible in the measurements described here. Anomalous scattering experiments on some of these samples with three different incident wavelengths could be used to extract the correlations R-R, R-X and X-X where R is a rare-earth and X is a non-rare-earth atom. Resonance scattering of X-rays using wavelengths on either sides of the L$_{III}$ absorption edges of rare-earth atoms would have a variation of the atomic scattering factor which could be of much value in separation of partial correlations. Computer modelling techniques such as molecular dynamics and Monte Carlo are needed in the further elucidation of these structures.
IR results showed that the glasses doped with different rare-earths have similar structures in which the basic unit is a PO\textsubscript{4} tetrahedron. These data also indicated that added aluminium plays role of a network modifier in a similar way to that of rare-earth ions and also helps in making this system stable and inert as evidenced by its excellent resistance to atmosphereric moisture.

UV/Visible absorption measurements on these glasses found that all of them are good UV absorbers. Four samples namely, La-P, La-Ce-P, La-Tb-P and La-Eu-P had high UV absorption with almost no absorption in the visible range. The absorption peaks in the spectra when compared with the reported data were found to originate from the transitions from the ground state to the excited states belonging to the 4f\textsuperscript{10} configuration. More detailed analyses of the spectra are required and would help in understanding the immediate structural environment of the rare-earth ion in the matrix and thus the lasing properties of some of these glasses. Those members of the series having no absorption in the visible are potentially very good candidates for use as optical fibres. All members could be used as good UV filters.

The a.c. susceptibility measurements in the range 82 K to 300 K indicated that the glasses are paramagnetic in this range. Their behaviour at temperatures lower than 82 K would be of use in understanding the possible interaction between these rare-earth cations. More detailed measurements of their magnetic properties as a function of temperatures lower than 77 K are needed as also further analyses to explain the non-linear behaviour of susceptibility in the temperature range measured here.

X-ray and neutron diffraction techniques play a vital role in the determination of glass structure and are unique in the type of information they obtain. However, it is important to understand their limitations and consider these during the interpretation of the results. The need for many different techniques in the examination of the structures of disordered materials is thus not only desirable but also necessary. It has been shown in this work that despite five different methods which probe the structure, only some general findings may be
had with regard to long-range structures. Computer modelling techniques such as molecular
dynamics are important in this respect in that they augment experimental findings and
permit the extraction of component correlations. However, in some cases these methods
may not be true representations of bulk structures as they deal with only a relatively small
number of atoms compared to real number densities. Considering the complexity of the
structures of disordered materials and the intrinsic limitations of the various techniques that
are applied in examining these structures, it is appropriate to quote the words of JOHN
GROTE [Exploratio Philosophica, II, 229] -

"Advance in knowledge is essentially distinction, not aggregation. Each new particular of
knowledge is not an addition to, but a newly observed part of, a previously conceived whole."