

HIGH-RESOLUTION NMR SPECTROSCOPY OF LOCAL STRUCTURE OF GLASSES

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To understand the mechanisms of nucleation and growth of crystals from melts and the structure of the growth units, it is necessary to know not only the structure of the crystal, but also the structure of the melt. There are only a few methods available to examine melt structure (Raman spectroscopy, IR spectroscopy, EXAFS, X-ray radial distribution analysis, k_α and k_β emission spectroscopy). Few of these are capable of determining the structural environment of low-concentration components.

This paper will discuss the application of the newly-developed methods of high resolution magic-angle sample-spinning nuclear magnetic resonance spectroscopy (MASS NMR) to the determination of the local structure of various components in alumino-silicate glasses. Specific data for phosphorus, which is a well-known nucleating agent, in these glasses will be presented. Glasses (quenched melts), rather than melts, are examined because high-temperature MASS NMR methods are not yet well developed.

NMR spectroscopy determines the characteristic frequency with which *atomic nuclei* flip from one spin energy level to another when the sample is placed in a powerful magnetic field. The method is chemically useful, because the electrons near the atoms shield the nucleus slightly from the applied magnetic field. Thus, because different local structural environments cause different electron distributions, different sites will have different resonance frequencies. These frequencies are reported as the chemical shifts, which are the ppm deviation of the frequency from that of an experimentally useful standard. MASS techniques are needed for solids to eliminate a number of nuclear interactions that can greatly broaden the peaks. Peaks in MASS NMR spectra of crystals are nearly as narrow as those in more traditional solution-state NMR spectra. Interpretation of the spectra for glasses, for which structural disorder causes peak broadening, is based on empirical comparison with spectra for crystals with known structures.

Aluminum-27, silicon-29, and phosphorus-31 MASS NMR spectroscopy of alkaline-earth metasilicate glasses and $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ glasses to

which from 2–10 wt% P_2O_5 has been added gives the following results. 1) For the metasilicate glasses P enters as alkaline earth orthophosphate structural units and causes polymerization of the silicate portion of the melt by removing Ca and O atoms. The phosphorus-31 chemical shift does not change as P_2O_5 content changes, but the silicon-29 chemical shift becomes more shielded, indicating increased polymerization. 2) For the SiO_2 - $CaAl_2O_4$ glasses: A) All Al is in tetrahedral coordination. B) The P does *not* form Ca-orthophosphate units, but instead forms more complex structural units, probably Ca-alumino-phosphate units (P is +5; Al is +3). C) There is a systematic increase in the shielding at P, Al, and Si with increasing P and Si content.

The data for the metasilicate glasses is consistent with the idea that P increases the nucleation rate because it forms orthophosphate clusters on which the silicate phases can nucleate heterogeneously.

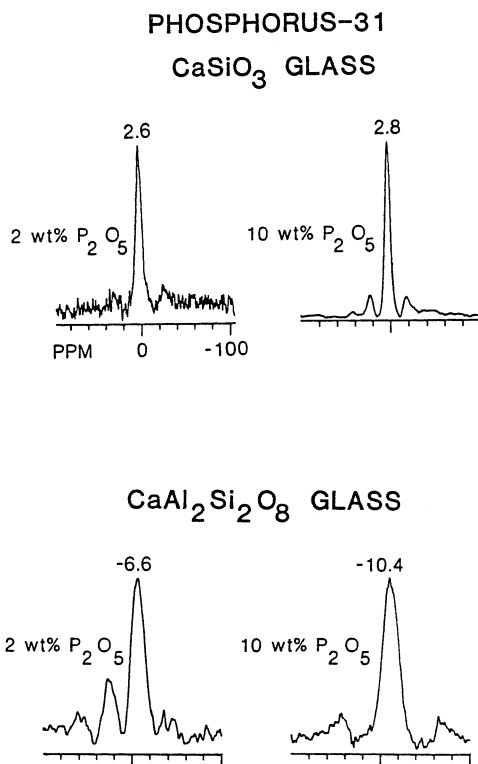


FIG. 1. The figures below show typical MASS NMR spectra of these glasses.

DISCUSSION

Chernov

1. There are electron microscopy and other evidences that the nuclei of a new phase differs from the final stable phase. Do you have any data on that?

2. Lifetime of the clusters—what is done in that directions?

A: 1. We have no data now, but it is probably possible to do some useful experiments, especially at large ΔT .

2. The group with Prof. Alex Pines at Berkeley and Jon Stebbens at Stanford has a high-temperature sample probe and is working on this problem.

Bennema

Can you tell us a basis of general information on the structures of silica melts, what the growth units will be?

From the so called statistical mechanical, tetrahedron model developed by Van der Eerden, what I would expect is that SiO_4^{2+} tetrahedra are important growth units, or in other words, not all very strong Si–O bonds need to be broken before Si and O enter a growing crystal. Whether Si and O enter separately the crystal or as SiO_4 tetrahedra has important implications for the morphology.

What are your ideas about this?

A: There are few data. My prejudice, too, is that SiO_4 tetrahedra or some fragment are the rate controlling growth units, but we cannot rule out individual atoms or larger clusters.

Sunagawa

Is it worthwhile to apply HRTEM to observe the phases you suggested?

A: Attempts to do this have not been successful, but it should be possible to observe clusters if they contain large concentrations of high-atomic number elements.

Sunagawa

This question was made by Sunagawa to Iijima:

1. Is it possible to see a local structure in a glass material by a high resolution electron-microscope?

2. Is it possible to see a local structure which consists of heavy-atoms in a silicate crystal by a high resolution EM?

A (Iijima):

1. For the high resolution electron microscopy, what we see in the micrographs is a projection of a three-dimensional structures. Therefore, it is rather difficult to see small local structures in a glass structure.

2. Yes, it is possible, generally speaking, to differentiate local structures in a crystal by using “electron scattering factor” contrast. But it should be distinguished from the image contrast due to the Bragg diffraction contrast.

Müller-Krumbhaar

It is now possible by some inverse Monte Carlo method, to determine interaction potentials up to fourth-neighbor or up to four-body interactions. The experimental requirements necessary are high-precision data on nearest-neighbor correlations, which I think are accessible by your method.

A: Our data give accurate relative populations of sites for some kinds of crystalline materials (eg. Zeolites). Their results may be accurate enough for the calculations you propose.