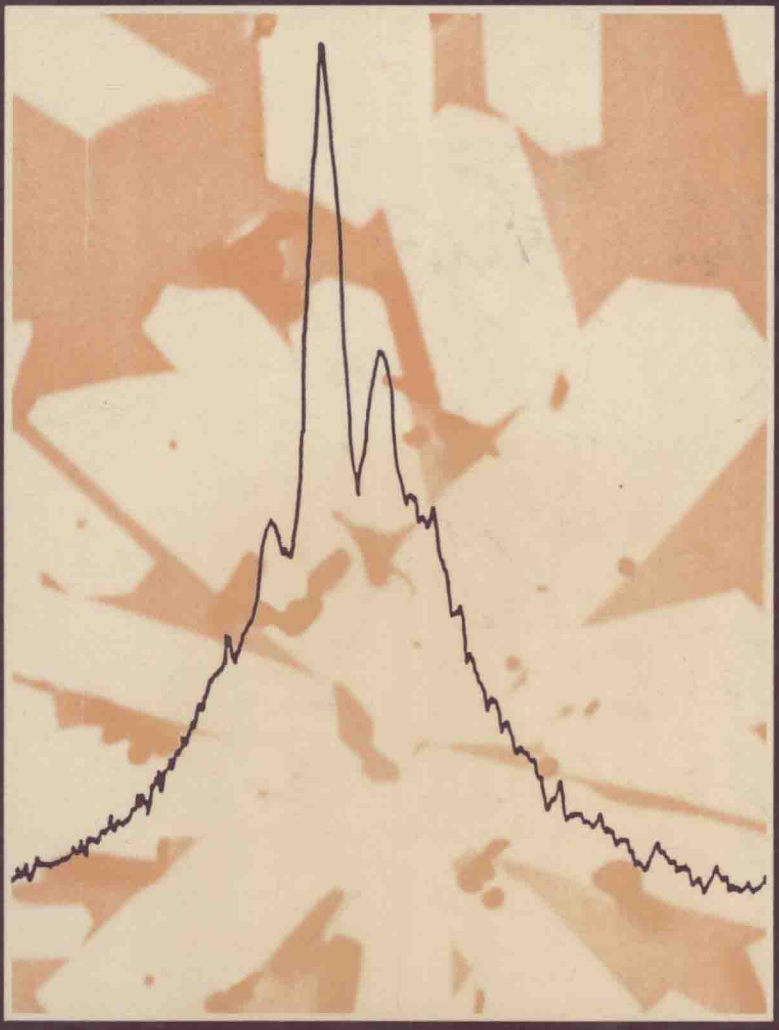

GLASSES AND GLASS-CERAMICS

Edited by M. H. Lewis

Chapman and Hall

Glasses and Glass-Ceramics

Edited by

M. H. Lewis

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Glasses and Glass-Ceramics

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Preface

The emergence of synthetic ceramics as a prominent class of materials with a unique combination of properties has been an important part of the materials-science scene over the past 20 years. These 'high-technology' ceramics have varied applications in areas utilizing their exceptional mechanical, thermal, optical, magnetic or electronic properties. A notable development of the 1970s was that of 'Si-based' ceramics (Si_3N_4, SiC and 'Sialons') as high-temperature engineering solids. More recently the zirconia-based ceramics have evolved as a class of material with significant improvements in fracture-toughness. In the 1980s we are on the threshold of development of ceramic-matrix composites with the promise of overcoming major limitations in engineering design with 'brittle' ceramics and the development of novel properties unattainable with monolithic microstructures. Throughout this period there have been significant but less well-publicized developments in the field of glass-ceramics and glasses. It is the purpose of this publication to review selected topics within this important area of materials science.

A key element in understanding the relation between properties and microstructure is a knowledge of atomic arrangement in ceramic phases. Recent developments in NMR and X-ray absorption spectroscopies have had considerable impact on studies of atomic co-ordination in glasses and crystalline ceramic materials and are reviewed in Chapters 1 and 2.

Glass-ceramics are derived from the parent glasses by controlled crystallization and have properties dictated, in part, by the efficiency of crystal nucleation within the glass volume. Current theoretical and experimental understanding of nucleation kinetics is surveyed in Chapter 3.

Although the majority of glasses and glass-ceramics are 'silicate'-based, novel systems have been explored with alternative anions. Significant property modification accompanies the partial substitution of nitrogen for oxygen in glasses and offers the possibility of unusual oxide/oxynitride phase combinations on crystallization. Chapter 4 is a review of oxynitride glass and glass-ceramic systems. Recent research on halide glasses, reviewed in Chapter 5, is motivated by their exceptional infra-red optical properties with potential for fibre-optical communication systems.

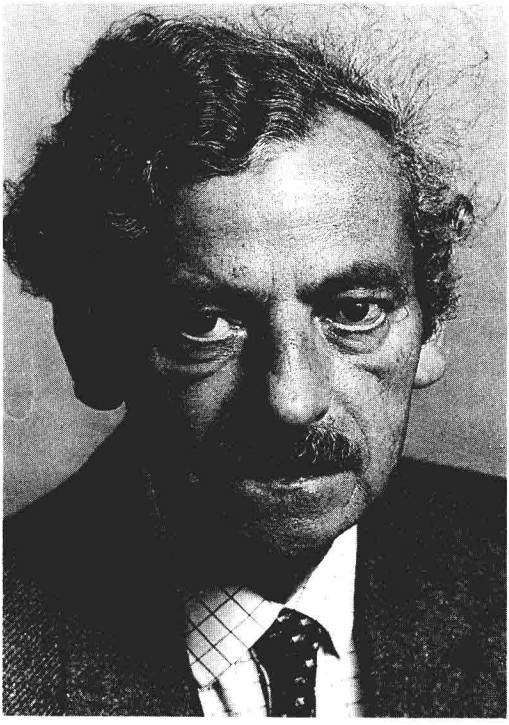
Subsequent chapters review current or potential applications for silicate-

based glasses and glass-ceramics, utilizing properties such as microporosity induced by phase separation, dielectric or piezoelectric properties coupled with ease of fabrication, thermal expansion or chemical durability. The final chapter is a review of progress in fabricating high-strength composites with glass or glass-ceramic matrices utilizing their comparative ease of fabrication and identifying interfacial characteristics which have an influence on the philosophy for subsequent development of structural composites.

These reviews are not exhaustive but identify growth topics in the field and necessarily reflect the work of the respective authors.

This volume is dedicated to the memory of the late Professor P. W. McMillan in recognition of his contribution to the science and technology of glasses and glass-ceramics. Peter McMillan is remembered especially for his research in 'glass-ceramics' and the publication of a text, representing a landmark in this field, which has been reprinted in several languages since its first appearance in 1964 (*Glass Ceramics*, Academic Press, New York and London). It was written during his period as Head of the glass and ceramics group at the Nelson Research Centre of GEC Power Engineering. Peter McMillan subsequently joined the academic research community at a then newly established University of Warwick and, influenced by remarkable foresight on the part of the founding Head of Physics, Professor John Forty, developed a ceramic materials research group which has become prominent internationally and is the basis for the Centre for Advanced Materials Technology. In addition to his prolific publication of original research papers Peter McMillan was editor of a number of journals: the *Journal of Materials Science*, *Glass-Technology*, and the *Journal of Non-Crystalline Solids*. Many of the authors of this review volume are former associates who have continued to research in the field of glasses and glass-ceramics. This publication is both an appropriate memorial and a timely review of developments within this field.

M. H. Lewis
Warwick 1987



Peter W. McMillan 1928–1984

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1

MAS NMR: a new spectroscopic technique for structure determination in glasses and ceramics

R. Dupree and D. Holland

1.1 INTRODUCTION

NMR has long been used to obtain structural information about glasses. Fairly recent reviews of standard wide line NMR have been given by Muller-Warmuth and Eckert (1982), Bray *et al.* (1983) and Bray and Gravina (1985). The information given by these studies has, in the main, been concentrated on quadrupolar nuclei, for example the use of ^{11}B to determine the relative amounts of 3 and 4 fold co-ordinated boron in glasses. Other main themes have been concerned with using dipolar broadened lineshapes to test for the probability of particular local configurations.

Much of the structural information potentially available from NMR experiments is masked in solids by various static anisotropic nuclear interactions which broaden the line and make the small differences in position undetectable. These include the magnetic dipolar interaction, the anisotropic chemical shift interaction and, for nuclei with spin $I > 1/2$, the quadrupolar interaction. The dipolar interaction arises from the magnetic field at one nucleus produced by neighbouring nuclei and varies as the inverse cube of the distance between nuclei. The chemical shift is caused by bonding of the atom to its surroundings so that each crystallographic site will have a particular shift with three components corresponding to the three principal axes. For a site of cubic point group the chemical shift will be isotropic, for sites of lower symmetry the shift will be anisotropic and in microcrystalline and glassy (it is the local symmetry that is important) samples lineshapes such as those shown in Fig. 1.1 will be observed. The three components of the chemical shift are chosen so that $\sigma_{33} \geqslant \sigma_{22} \geqslant \sigma_{11}$ and the asymmetry in the site surroundings is characterized by the asymmetry parameter η where $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma)$. Thus for axial symmetry $\sigma_{22} = \sigma_{11}$ and $\eta = 0$. For lower symmetries $0 \leqslant \eta \leqslant 1$. The isotropic shift σ

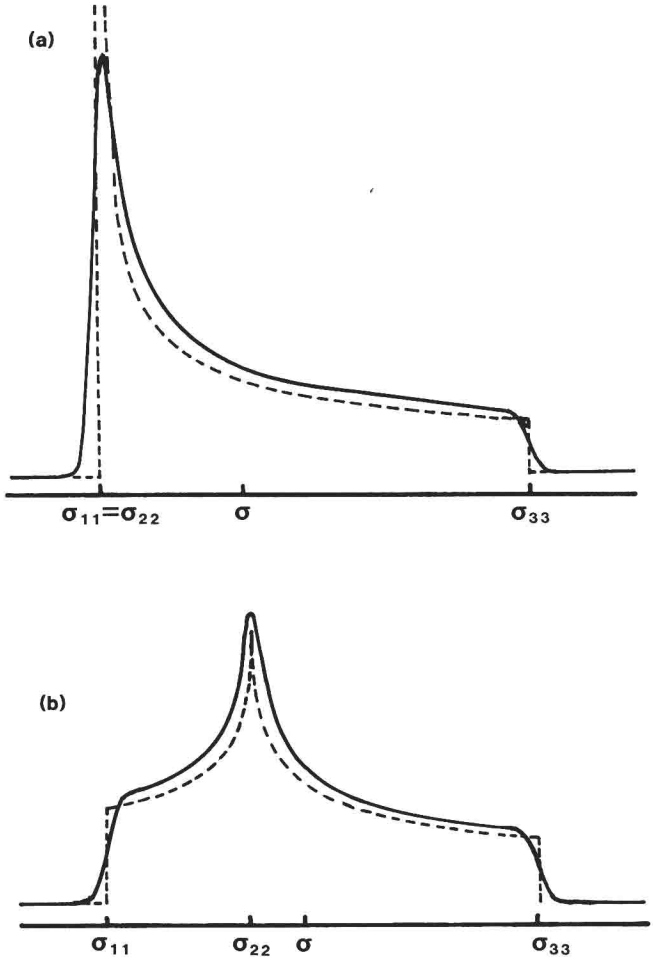

Fig. 1.1 Powder pattern lineshapes for (a) axial site symmetry, (b) lower site symmetry.

is defined as $(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, thus $\sigma, \Delta\sigma = \sigma_{33} - \sigma_{11}$, η are sufficient to describe the chemical shift parameters.

For nuclei with spin $I > 1/2$ the interaction of the nuclear quadrupole moment (eQ) with the electric field gradient ($\partial^2 V/\partial Z^2 = eq$) at the nucleus will alter the nuclear energy levels depending upon the relative orientation of the electric field gradient and the applied magnetic field and to first order in the quadrupolar interaction will give the powder pattern shown in Fig. 1.2(a). If e^2qQ/h is sufficiently large only the central ($\frac{1}{2} \rightarrow -\frac{1}{2}$) transition is

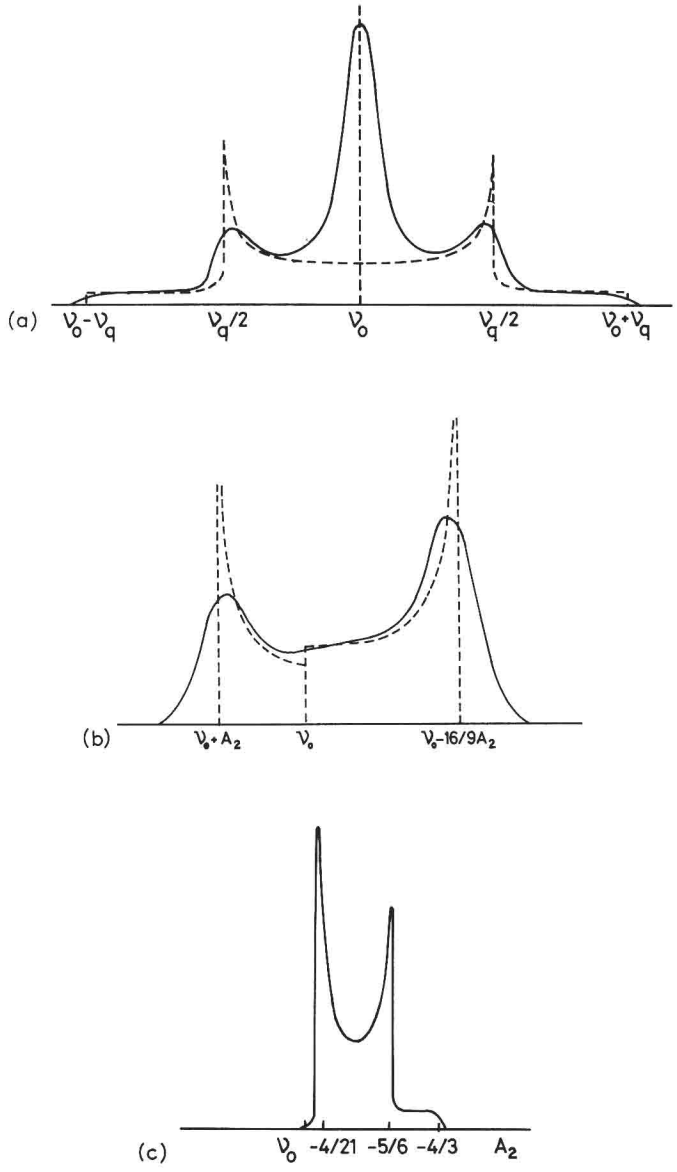

Fig. 1.2 (a) Powder pattern lineshape for $I = 3/2$ nucleus (e.g. ^{23}Na) due to first order quadrupole interaction, i.e. small e^2qQ/h in axially symmetric environment. Dashed line is without dipolar broadening; full line with dipolar broadening. ($\nu_q = \frac{1}{2}e^2qQ/h$.) (b) The central $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition lineshape is observed in an axially symmetric environment for larger e^2qQ/h. ($A_2 = (3/64)\,[(e^2qQ)^2/h]\,(1/\nu_0)$.) (c) The effect of magic angle spinning on this transition. Note that the resonance is displaced from the true chemical shift position.

observable in powders, and it will be broadened and can have a complex shape dependent on the quadrupolar asymmetry parameter; examples are shown in Fig. 1.2(b) and (c).

In a liquid the NMR lines are usually very narrow because all of these broadening mechanisms have, in first order, a $3\cos^2\theta - 1$ angular dependence and this averages to zero under the rapid motion present. Recently various line narrowing techniques, such as magic angle spinning (MAS) where the sample is orientated at 54° 44′ ($\cos\theta = 1/\sqrt{3}$) to the magnetic field and spun rapidly (Andrew, 1981), have been developed such that in favourable crystalline materials a reduction in linewidth of more than two orders of magnitude can be achieved and the underlying structural information present in the spectrum obtained. The improvement is less marked in glasses because of the disorder but the resolution is often sufficient to give much unique structural information.

Figure 1.3 shows, as an example, the static and spinning NMR spectrum of ^{27}Al in a sample of $YAlO_3$ (YAP). Both spectra were acquired for the same

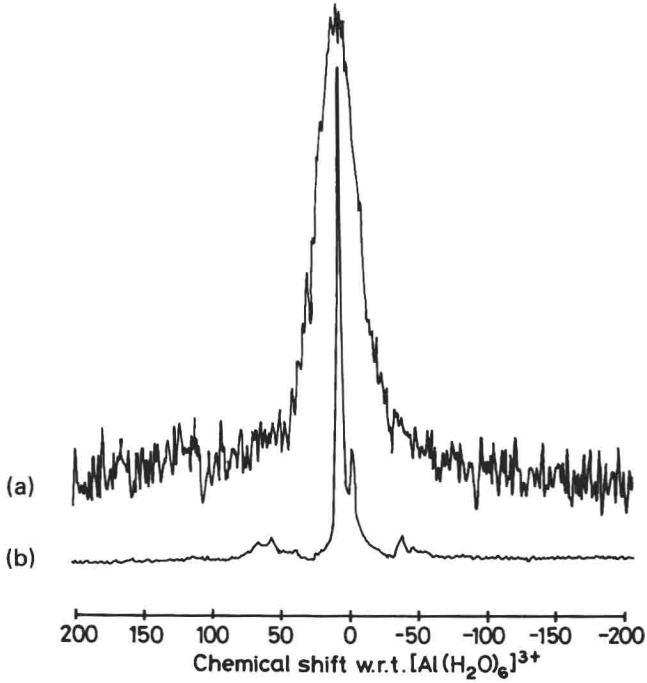

Fig. 1.3 ^{27}Al spectrum of $YAlO_3$: (a) static, (b) MAS. The main peak in (b) corresponds to $[AlO_6]$ in $YAlO_3$ at +9.5 ppm, the small peak at 0.8 ppm and the broad bump centred on ~60 ppm are from $[AlO_6]$ and $[AlO_4]$ units in ~5% $Y_3Al_5O_{12}$ present as second phase. Two small spinning sidebands are also visible at −40 ppm and +60 ppm.

time; not only does the MAS spectrum have a much better signal-to-noise ratio but also it clearly shows the presence of ~5% $Y_3Al_5O_{12}$ (YAG) as a second phase. (The main peak at 9.5 ppm is the octahedral (AlO_6) in YAP, the small peak at 0.8 ppm is the octahedral (AlO_6) in YAG and the broad 'bump' is from tetrahedral (AlO_4) units, shift 72 ppm, in YAG. Also visible are two small, spinning sidebands from the octahedral YAP.)

The value of the chemical shift is very sensitive to the local environment and thus is determined by many variables. Amongst the factors which influence the shift are:

1. The co-ordination number of the atom concerned – the shift range of ^{29}Si is −142 ppm to −221 ppm when six co-ordinated to oxygen compared with ~ −60 ppm to −128 ppm when four co-ordinated;
2. The type of neighbouring atom, e.g. the ^{29}Si shift in quartz where silicon is tetrahedrally co-ordinated to four oxygens is −107.1 ppm compared with −48.5 ppm when tetrahedrally co-ordinated to four nitrogens in β-Si_3N_4. The replacement of one nitrogen by oxygen in Si_2N_2O gives a shift of −63 ppm;

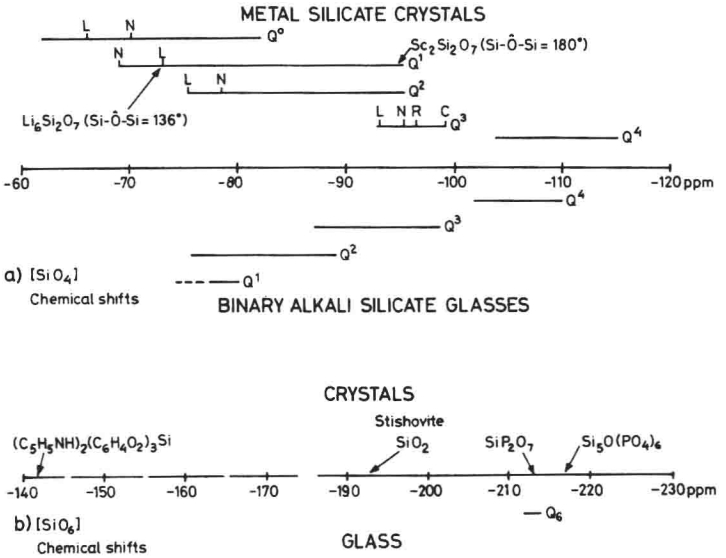

Fig. 1.4 Chemical shift ranges for ^{29}Si in crystalline and glassy oxide environments. (L = Li, N = Na, R = Rb, C = Cs.)

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