Structural and Dynamic Approaches of Molten Salts by High Temperature Spectroscopies

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The combination of ^{27}Al NMR expriments and Molecular Dynamics simulation confirms the existence of penta-coordinated Aluminium in several molten aluminium oxides. In the case of fluoroaluminate molten salts, NMR and Raman spectroscopies provide complementary approaches leading to a structural description in term of AlF_4^-, AlF_5^{2-} and AlF_6^{3-} species.

Key words: ^{27}Al High Temperature NMR; Oxides; NaF-AlF_3.

1. Introduction

Because of their low viscosity, molten salts do not generally give glassy materials upon cooling, and the investigation of their structure by any spectroscopic methods has to be performed in situ, at relatively high temperature (up to 1020 °C, in the case of fluorides).

In addition, due to their volatility and corrosiveness at high temperature, the different techniques currently used for the structural characterisation of materials, such as Raman, EPR, NMR and XAFS spectroscopies have to be specially adapted.

High temperature Raman spectroscopy has proved to be a powerful technique for the quantitative description of the structure of melts in terms of ionic complex distributions even in systems as difficult as fluorides [1–3].

More recently, high temperature NMR spectroscopy has been successfully applied to molten oxides and fluorides [4–13]. Higher magnetic fields, higher resolution due to real improvement of spectrometer technology now allow to reach previously inaccessible nuclei. Because of the rapid exchange between the different bonding configurations, the NMR spectrum in the melt consists of a single, narrow, lorentzian shaped line, the position of which is quantitatively expressed by the weighted average of the individual contributions. The observation of a single peak is interesting from the dynamical point of view. Indeed, it requires that the different species existing in the melt exchange more rapidly than the frequency separation that their NMR signature would have in a rigid system (several Hz to MHz). The position of the peak is related to the time averaged local structure around the observed nuclei. In many cases, when the number of structural species is higher than two, the relative populations of the different entities in the liquid can be reached more easily by techniques such as Raman spectroscopy, mainly because of the coincidence of the time scales. Yet, the different local information provided by the selective NMR observation of the various nuclei present in the system can help greatly to elucidate the structure. Raman and NMR spectroscopies do not provide the same information but rather complementary data, and it is really essential to combine such different techniques to reach a more accurate view of the structure of melts.

For system that can vitrify, it is now possible to characterise precisely the local structure around the nuclei under interest using high resolution solid state NMR, and thus get a picture of the quenched structure of the liquid. But in general, the viscosities of molten salts are relatively low and only a few systems are known to vitrify [14].

So, the question is: what kind of new information can we really produce with a single NMR line, in a liquid known to consist in a number of different structural species?

2. Experimental

Up to now, NMR measurements at high temperature has been limited by a number of technical problems. For instance, for reactive and corrosive melts, the container must be chosen so as to avoid chemical interaction with the sample. The container must also be airtight to prevent evaporation of the sample or reaction with the sur-

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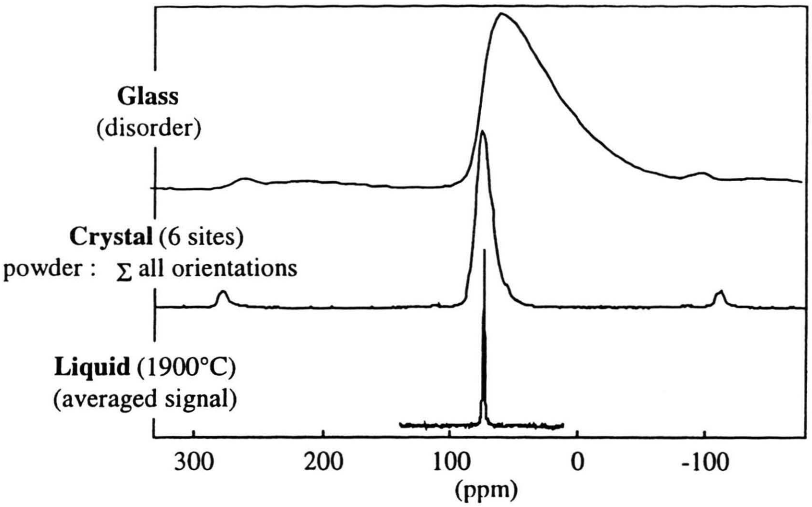

Fig. 1. ^{27}Al spectra of $CaAl_2O_4$ in the melt, the crystal powder and the glass (RT) [8].

rounding atmosphere. Boron nitride of very high purity maintained in an inert gas has proved to be successful [9–12]. The space available for heating devices in high field cryomagnets is very limited: the radiofrequency (RF) coil is close to the sample, and thus close to its temperature.

The heating system developed in Orleans, is based on the direct irradiation of the sample by a CO_2 laser [7–9]. This system ensures the heating of the sample in the NMR probe with a minimal thermal power and without perturbation of the RF coil as it is generally the case when the furnace is included in the probe.

Two kinds of designs can be used depending on the temperature range. From room temperature up to 1500 °C, a container device using a Boron nitride crucible with a screw cap insuring airtightness is irradiated by a CO_2 laser. The rf coil is protected from high temperature by a thermal shield made of porous stabilised zirconia. Electronics and probe are cooled by an air flow at room temperature.

The temperature is measured in a separate experiment and calibrated with the solid-liquid transition of the sample or of some reference sample, clearly identified by NMR. For higher temperature (2000 °C and above), a gas-flow levitation device inserted in the same probe allows to heat the sample without any contact, thus avoiding possible interactions with the crucible. This system has been successfully used in the study of molten oxides [5, 7, 8].

3. Results and Discussion

3.1. Molten Oxides

In Fig. 1 is reported the ^{27}Al Spectrum of molten calcium aluminate $CaAl_2O_4$ at 1900 °C, compared to the high resolution MAS responses obtained for the corresponding glassy and crystalline phases [8]. In the glass, the spectrum is very broad with a typical asymmetric lineshape due to quadrupolar interaction and structural disorder in the glassy network.

The crystalline powder includes all the orientations of the crystallites. Even with high resolution solid state experiments (MAS NMR) one obtains a broad signal with irregularities that can be modelled with several contributions corresponding to the different aluminium sites.

In the liquid, the spectrum consists in a single narrow peak, well resolved, lorentzian, with a linewidth of one hundred Hertz due to rapid exchange between the different environments of aluminium atoms.

For the aluminium in oxides compounds, three coordinations are known. The most usual are tetrahedral and octahedral with isotropic chemical shifts (δ_{iso}) in the ranges from 90 to 60 ppm, and −20 to 20 ppm, respectively, but also a few oxides show pentacoordinated aluminium with a δ_{iso} around 35 ppm. For example, in the crystalline compound $9Al_2O_3{-}2B_2O_3$, four different crystallographic aluminium sites have been described: four-fold, six-fold and two different five-fold coordinated aluminium atoms, the signature of which being well separated by MAS NMR experiment at very high field (17.6 T) and high spinning rate [15].

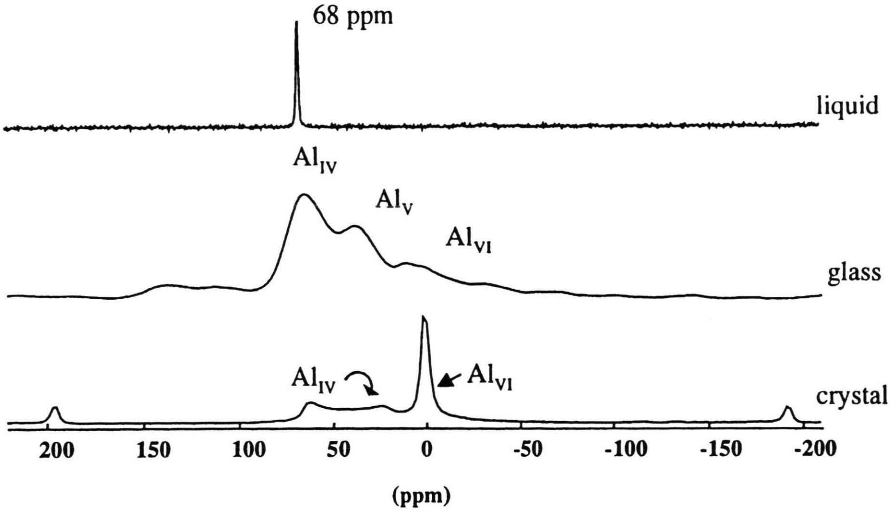

Fig. 2. ^{27}Al spectra of $Y_3Al_5O_{12}$ (YAG) in the melt (2000 °C), the glass and the crystal powder (RT) [7].

In the case of $Y_3Al_5O_{12}$ (Fig. 2), the liquid has been interpreted as a mixture of AlO_4, AlO_5 and AlO_6 species undergoing a rapid exchange [7]. This information could not be based on the unique knowledge of the ^{27}Al NMR isotropic chemical shift (δ_{iso}), but only by the combination with other approaches. Molecular dynamics simulations [5] have described the structure of this melt with the coexistence of the three coordinations $Al_{IV,V}$, and Al_{VI}, where the Al_V is most abundant ($\approx$60%). The ^{27}Al MAS NMR spectrum of the glass at room temperature (Fig. 2), obtained by very rapid quenching, evidences unambiguously the three components that can be assigned from their chemical shift to the Al coordinations 4, 5, and 6.

3.2. Molten Fluoroaluminates

Gilbert and Co-workers have extensively studied the structure of fluoroaluminate molten salts and proposed a quantitative description of the melt in terms of ionic complexes [1–3]. Their model combines results from Raman spectroscopy and thermodynamic data and involves the three fluoroaluminate species AlF_4^-, AlF_5^{2-} and AlF_6^{3-} together with free fluorides. The existence of major amounts of AlF_5^{2-} is still disputed.

We have performed, in collaboration with Robert and Gilbert, ^{27}Al NMR measurements in molten NaF–AlF_3 systems over the same composition range as by the Raman study (from 0.2 to 0.5 for AlF_3) [12].

The ^{27}Al chemical shift increases with the amount of AlF_3, while between 25 and 40 mol%, i.e. between the cryolite and the chiolite composition, the variations of δ are rather small and the average value is around 21 ppm (Figure 3).

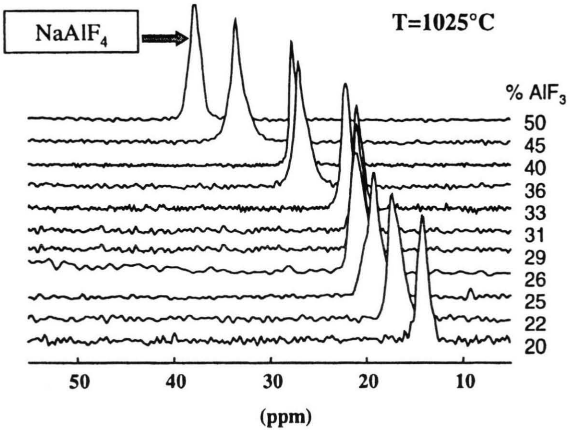

Fig. 3. High temperature ^{27}Al NMR spectra of NaF–AlF_3.

The observed peak position is the average of the chemical shifts of the individual species, weighted by their molar abundance. NMR alone cannot really proove the existence of 2 or 3 different species. We need some additional information that is given typically by Raman data. Figure 4 reports the correspondence between the chemical shifts calculated from the concentrations of each individual species given by Raman [3], and the NMR chemical shifts measured experimentally.

The NMR and Raman data coincide rather well in the whole composition range.

The NMR chemical shift is characteristic of the local environment of the investigated nuclei (coordination, lo-

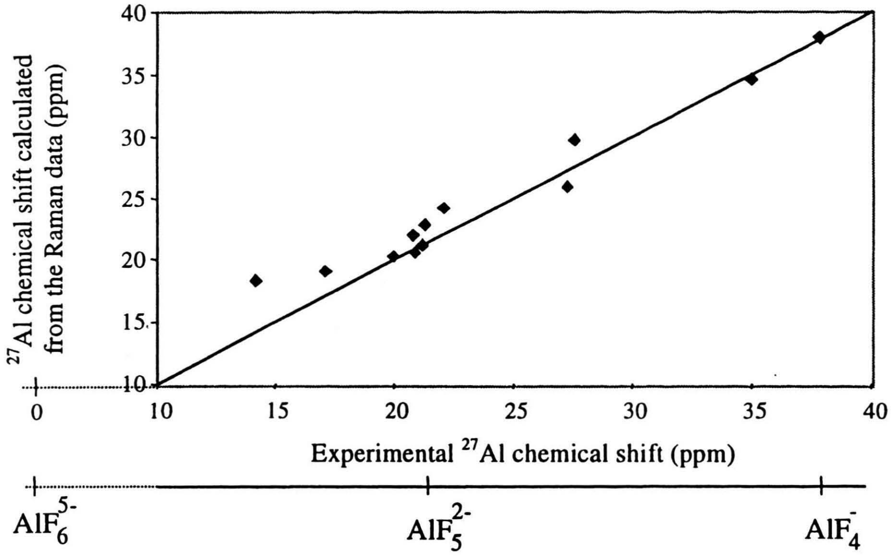

Fig. 4. NaF–AlF_3 melts: comparison between the ^{27}Al NMR chemical shifts measured and calculated from the Raman data [12]. $\delta^{27}Al_{exp.} = \Sigma X(AlF_x)$. $\delta^{27}Al(AlF_x)$ ($X(AlF_x)$ from Raman and $\delta^{27}Al(AlF_x)$ from NMR).

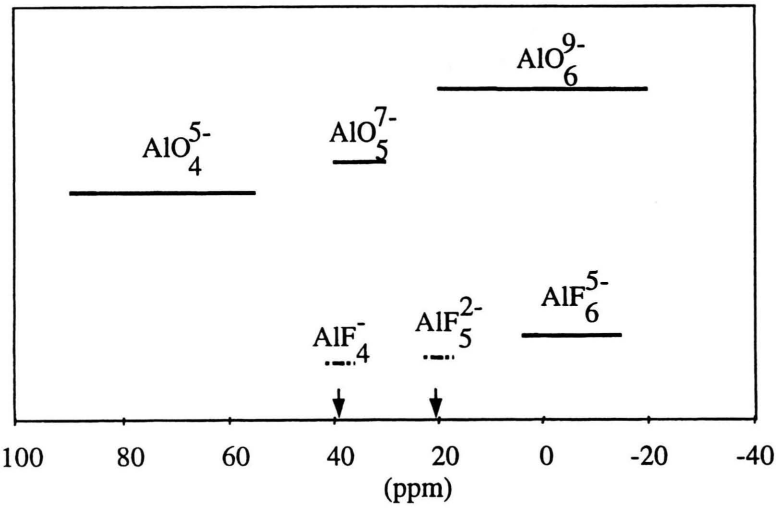

Fig. 5. ^{27}Al NMR chemical shift range in oxides and fluoroaluminates. The experimental values measured for AlF_5^{2-} and AlF_4^- are pointed by the two arrows and correspond respectively to 21 and 38 ppm

cal symmetry...). The chemical shift ranges for the different aluminium coordinations in oxides are well separated: 90 to 55 ppm for AlO_4^{5-}, 30 to 40 ppm for AlO_5^{7-} and 20 to −20 ppm for AlO_6^{9-} [7]. To our knowledge, only a very few NMR studies of fluoroaluminate melts have been reported [16–19]. The combination of ^{23}Na and ^{27}Al MAS NMR and XRD data for the different crystalline phases of the NaF–AF_3 system shows that the chemical shift for octahedral aluminium in these compounds ranges from −15 to +4 ppm.

The chemical shift corresponding to the AlF_4 coordination is deduced from the high temperature NMR spectra of the $NaAlF_4$ melt. Raman studies have shown that only AlF_4^- is present in this liquid [3]. Thus the chemical shift measured at 38 ppm has been assigned to the AlF_4^- species [12].

Kohn et al. [20] studied a jadeite glass doped with cryolite and proposed an ^{27}Al chemical shift of 21 ppm for AlF_5^{2-}, which corresponds to the average value of the δ_6 (AlF_6^{3-}) and the δ_4 (AlF_4^-). We used this to describe the evolution of the high temperature spectra in the cryolitic melts.

Figure 5 shows the ^{27}Al chemical shift ranges for oxides and fluoroaluminates. It is worth noting that in both the oxide and the fluoride systems the range of chemical shifts for the different aluminium coordinations are well separated. Moreover, the averaged values for the aluminium oxides are significantly higher than those of the fluorides. Thus, any oxide-containing impurity in fluoroaluminates will result in an important increase of the measured ^{27}Al chemical shift.

Conclusion

Considering the huge complexity of high temperature liquids, a full description of their structure must obviously involve the combination of several experimental approaches. Each technique has its own particularities (i.e. time scale, interaction ranges ...), and one should seek their complementarity rather than their contradictions in order to produce a fully integrated model.

Acknowledgements

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