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HIGH TEMPERATURE NMR OF OXIDE MELTS

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Synopsis : High temperature ^{23}Na NMR measurements are made on some sodium salts and silicates. The temperature dependence of the ^{23}Na NMR chemical shifts around their melting points have been observed. NaCl, NaBr and $NaNO_3$ show ^{23}Na NMR peak position to positive shift on their solid-liquid transition. The ^{23}Na chemical shifts of solid samples at just below their melting point seem to be related with the structure around sodium nuclei especially, relationships between coordination numbers seeming dominant.

Key words : High Temperature NMR, ^{23}Na, Inorganic Salts, Silicates, Chemical Shifts, Melt Structure

1.Introduction

To understand the microscopic structure and dynamics of molten oxides, it is important to combine various analytic methods such as spectroscopy and diffraction method. Recently, high resolution NMR has been applied to a variety of inorganic solids.[1] It gives an information about the short range order(within the next nearest neighbor) of the nucleus under investigation. So it becomes a powerful tool to investigate the vitreous states of the inorganic materials since they have no long range orders. For example, the structural units present in the silicate glasses(Q_n species; where n represents the number of O-Si bonds connected to the Si nucleus under investigation) have been identified and quantified.[2]

As NMR method gives information about the vitreous states, it have been applied for the studies on molten salts and silicates at high temperature(~2000°C).[3-5] Unfortunately, the NMR peaks corresponding to the structural units present in these materials join as a single peak at elevated temperature, because of exchange reactions between the structural units being within the time scale of the NMR measurements.[3-5] It gives only an averaged structure of the melts. ^{23}Na, ^{27}Al, and ^{29}Si chemical shift values of molten silicates, aluminates and salts have been determined precisely,[4,5] and structural information involving changes of the coordination numbers of the ion have been obtained. In the present study, ^{23}Na chemical shifts are measured on various inorganic melts. The structural changes on their solid-liquid transition are studied. The relationships between crystal structure and ^{23}Na chemical shifts are also discussed.

2.Experimental

NMR measurements were carried out on Bruker MSL-200 spectrometer with wide bore(150mm) magnet operated at 52.938MHz for ^{23}Na nucleus. High temperature NMR line shapes and chemical shifts were observed with a home build high temperature NMR probe[3] which was modified for this experiments. An rf coil was placed at the center of a single heater unit. A Helmholtz rf coil was made of platinum and winded 4 times and placed parallel to the applied magnetic field.

Temperature of the sample was measured by Pt-Pt(Rh) thermocouple placed 1mm below the bottom of the sample. Heater current was supplied by a stabilized DC power source controlled manually. Temperature drift was ±1°C during each experimental run. External chemical shift standard, 3M NaCl solution, was measured at the beginning and the ending of the experiments with the current flow of the electric heater which influences on the position of the NMR peaks(heater current induces about 0.5ppm positive shifts at maximum output(800W)). The typical error for chemical shift is 0.1 ppm.

Samples were contained in crucibles made of alumina for salts or boron nitride for silicates. NaCl, NaBr, Na_2CO_3 and $NaNO_3$ are purchased from commercial sources and used without further purification. Na_2SiO_3 and $Na_2Si_2O_5$ were crystallized from stoichiometric glass. $NaAlSi_3O_8$ was natural mineral(Albite).

3.Results

The temperature dependence of ^{23}Na NMR spectra for NaCl and NaBr around their melting points, 801°C and 747°C, respectively, are shown in figure 1. At melting points, NMR spectra split into 2 peaks corresponding to the liquid and solid states. The liquid states show more positive chemical shift values compared with solid states. These shifts are related to the changes of the coordination environment around sodium ion. Two possibility can be considered which give ^{23}Na NMR peak to positive shifts. First, the decrease of coordination number around Na ion. Second, the increase of Na-X(X=Cl, Br) bond length. Between these two reasons, from the ^{29}Si analogue, the coordination change would have major effect compared with the bond length change. This result is accordance with X-ray and Neutron diffraction results.[8,10] But, for sodium metasilicate(Na_2SiO_3), X-ray diffraction[9] suggests an increase of coordination numbers while the present result suggest a decrease of coordination numbers(^{23}Na positive shift). Chemical shift values for all the compounds measured in this study, NaCl, NaBr, Na_2CO_3, $NaNO_3$, Na_2SiO_3, $Na_2Si_2O_5$ and $NaAlSi_3O_8$ are listed in table.1 together with the room temperature value on which the

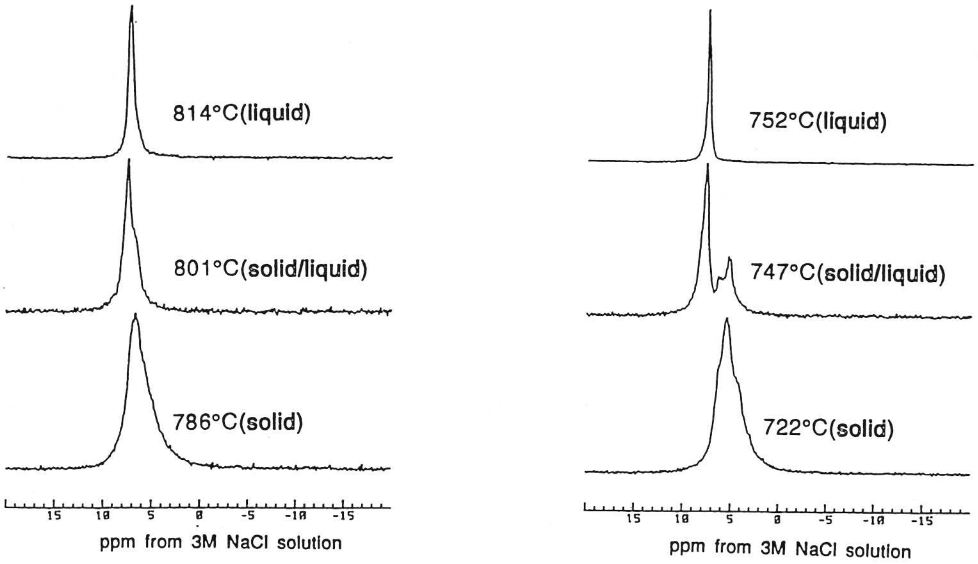

Figure 1. High temperature ^{23}Na NMR spectra for NaCl(left) and NaBr(right) around the melting points.

Table 1. ^{23}Na NMR chemical shifts and local structure around sodium ion. X:X-ray diffraction,[8,9] N:Neutron diffraction.[10]

compound	melting point	coordination numbers (bond length)		^{23}Na chemical shift		
		Crystal	Melt	room temp.	just below melting point	just above melting point
NaCl	801°C	6Cl (2.95Å)	X:4.7(2.80) N:5.8(2.6)	7.9ppm	6.6ppm	7.2ppm
NaBr	747°C	6Br (2.98Å)		6.0	5.4	7.6
$NaNO_3$	308°C	6 O (2.40Å)		-7.3	-13.6	-12.4
Na_2CO_3	852°C				0	0.2
Na_2SiO_3	1088°C	5 O (2.37Å)	X:5.7		9.2	9.7
α-$Na_2Si_2O_5$	874°C	5 O (2.40Å)	X:5.9(2.36)			5.6
$Na_2Si_4O_9$	1110°C		X:4.1			0.9
$NaAlSi_3O_8$ high albite	1118°C	7 O (2.66Å)		-6.8	-10	

second order quadrupole shifts are corrected.[6,7] As shown in table1, ^{23}Na chemical shifts change over wide range for the variety of compounds. They seem to be related with the local structure around Na ion. Roughly to say, the trend of the chemical seems to be related to the coordination numbers of the sodium nuclei. With increasing coordination numbers, chemical shift shows negative shift. But, the coordination numbers do not seem the definite parameter. A further investigation for the variety of compounds is needed to ensure the relation between structure and ^{23}Na chemical shift.

4.Conclusion

^{23}Na chemical shifts were measured for NaCl, NaBr, Na_2CO_3, $NaNO_3$, Na_2SiO_3, $Na_2Si_2O_5$ and $NaAlSi_3O_8$ solid and liquid around their melting points. A positive shift of the ^{23}Na NMR peak position was observed at solid-liquid transition for NaCl, NaBr, $NaNO_3$ and Na_2SiO_3. The decrease of the coordination numbers around Na ion for solid-liquid transition is indicated. On the other hand, ^{23}Na chemical shifts at just below the melting points show wide range of change depending on the local environment around Na nuclei. A rough relation between the coordination numbers and ^{23}Na chemical shifts was observed.

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