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MAS-NMR Spectra of ^{23}Na in Spinel Block of β- and β''-Alumina Structures

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The MAS-NMR spectra of the unexchangeable sodium in Na$^+$- and K$^+$-β''-gallates were sharp and symmetric, and their chemical shifts were far larger than that of sodium on the conduction planes. The results were consistent with the studies that the sodium ion could occupy the tetrahedral site in the middle of the spinel blocks.

Single crystals and powders of good crystallinity of Na$^+$-β-alumina and its gallium analogue, Na$^+$-β-gallate, are made from the Na_2O-Al_2O_3 and Na_2O-Ga_2O_3 systems, respectively. It is well known, however, that single crystals of Na$^+$-β''-alumina can not be synthesized from the Na_2O-Al_2O_3 binary system without the third component e.g. MgO, ZnO,or Li_2O. These additives are called stabilizers, and Mg^{2+} and Li$^+$ ions have been verified1) to occupy primarily the four fold Al(2) site in the middle of the spinel blocks. Single crystals of Na$^+$-β''-gallate, on the other hand, have been crystallized from the Na_2O-Ga_2O_3 binary system. Considerable amounts of Na$^+$ ions in Na$^+$-β''-gallate are unexchangeable for K$^+$ ions, and the Na$^+$ ions are supposed to be at the four fold site in the spinel blocks. Tsurumi et al.2) have found that the unexchangeable Na$^+$ ions are expelled from the crystal during the ion exchange for NH_4^+ ions, and that the a-parameter of the NH_4^+-β''-gallate is significantly smaller than that of the original K$^+$-β''-gallate. They also have clarified the structural differences between the two forms and have concluded that the Na$^+$ ions must occupy primarily the four fold site.3) However, tetrahedrally coordinated Na$^+$ ions in the spinel type close pack of oxide ions are difficult to approve if we think about the large ionic radius of the sodium ion, 0.099 nm. This study was made in order to obtain direct informations about the coordination around the sodium ion.

Three powder specimens were prepared. A commercial refractory brick of Na$^+$-β-alumina (Asahi Glass Co., Ltd.) was pulverized. Powder of Na$^+$-β''-gallate was made by firing a mixture of reagents of Ga_2O_3 and Na_2CO_3 at 1320 °C for 2 h.2) Part of the powder was converted into K$^+$-type by the ion exchange in molten KNO_3 for ca. 130 h. The chemical compositions of the latter two were reported elsewhere3) (the contents of Na_2O were 5.03 and 0.69 wt% respectively).

The high resolution ^{23}Na spectra were recorded at 71.32 MHz on a JEOL GX-270-GSH 270MU NMR spectrometer (6.33T) with magic angle sample spinning at ca. 3 kHz. Sample was irradiated for 5.5 s with a 5 s delay between pulses. Only the ^{23}Na central lines were evident within a measured range from 220 to -200 ppm.

Figure 1 shows the central parts of the results. The chemical shifts were measured from the position of NaCl crystal. The peak positions excluding for spinning side bands (SSB) were as follows: Na$^+$-β-alumina; 55.1, -11.5, -30.7 ppm, Na$^+$-β''-gallate; 37.8, -26.6, -45 ppm, K$^+$-β''-gallate; 41.1 ppm.

The spectrum of K$^+$-β''-gallate contains no broad strong peaks. The broad strong peaks of Na$^+$-β-alumina and Na$^+$-β''-gallate are evidently caused by sodium on the conduction planes. The NMR studies on these type compounds are concerned with peak position(s) and their shapes to understand structural states of conducting sodium ion.$^{4,5)}$ The sharp strong peak at 37.8 ppm of Na$^+$-β''-gallate is also observed at 41.1 ppm for K$^+$-β''-gallate. These peaks are caused without doubt by the unexchangeable sodium. The peaks are sharp and symmetric. Those are in good contrast with the broad peaks caused by sodium on the conduction planes. These chemical shifts are far larger than those on the conduction planes. This means the sodium nuclei are less screened$^{6)}$ than those of the conduction planes and NaCl. The structural state of the unexchangeable sodium is discrete and it is at a symmetric site in the crystal. Moreover, the Na-O distance might be very short. This study eloquently supports the foregoing$^{3)}$ that the sodium is at the four fold site in the spinel block. The large chemical shift and quadrupole effects are expected to be used for the definite determination of its position. By the way, a small peak at 55.1 ppm of Na$^+$-β-alumina must be caused by sodium of the same kind. That is, a trace amount of sodium has its positions in the spinel block of β-alumina. The same thing might be true for β''-alumina. This may be the first report about sodium in the spinel block of β- and β''-alumina.

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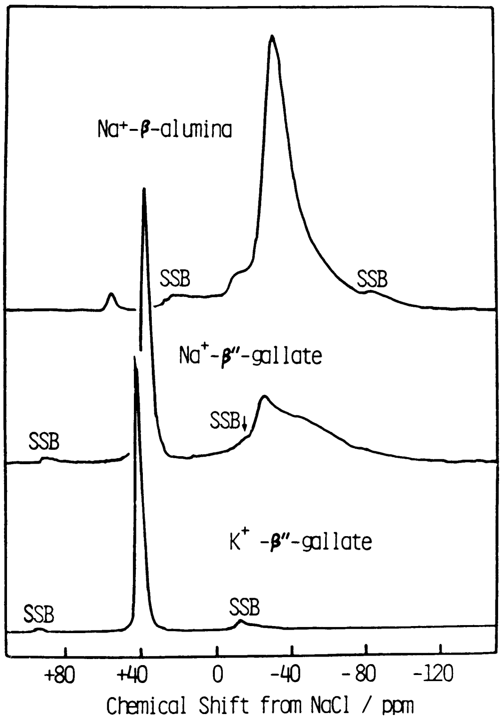

Fig.1. ^{23}Na MAS-NMR spectra.

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