1H, 23Na and 29Si MAS NMR studies on T site substituted Cl-, Br-, NO2-, (OHH2O)- and H2O sodalites

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Abstract

Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) has been applied to chloride, bromide, nitrite, hydrohydroxy and hydro sodalites using ^{1}H, ^{23}Na and ^{29}Si nuclei. The pure alumosilicate and gallosilicate sodalites exhibit a single symmetric peak in the ^{29}Si spectra. In the gallosilicate sodalites, the replacement of Al by Ga compressed the SiO_4 tetrahedra thereby reducing the TOT angles. Consequently the peak in the ^{29}Si spectra was shifted downfield due to Sideshielding. Partial substitution of Al with Ga led to five Q_4 signals due to $SiO_4(Al_4)$, $SiO_4(GaAl_3)$,$SiO_4(Ga_2Al_2)$,$SiO_4(Ga_3Al)$and $SiO_4(Ga_4)$ environments around the SiO_4 tetrahedron. On average, each replacement of Al by Ga in the $SiO_4(Al)_4$ species led to a downfield shift of 1.3 ppm. In the bromide, iodide and nitrite sodalites (Ga = 30-70%), the intensities of the $SiO_4(Al_4)$ and $SiO_4(Ga_4)$ peaks in the ^{29}Si NMR spectra were significantly higher when compared to the other three environments. Such behaviour clearly demonstrates a nonstatistical distribution of Al and Ga, through the formation of Alenriched and Gaenriched domains within the crystals. It was possible to discriminate between the OH^-, $(OH{\cdot}H_2O)^-$ and H_2O species residing in the sodalite βcages using ^{1}H NMR. In hydro sodalites, the $^{1}H^{1}H$ dipolar coupling of two water protons were considerably reduced by fast dynamic site exchange on the NMR timescale. The ^{23}Na spectra were discussed in terms of Na coordination and NaO interatomic distances with increasing Ga content. The ^{23}Na Multiple Quantum MAS NMR experiments correlated signals in the isotropic (F1) and MAS dimension (F2), as the shifts in the F1 dimension were a linear combination of isotropic chemical shifts and secondorder quadrupolar shifts.

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