

Order/disorder in natrolite group zeolites: A ^{29}Si and ^{27}Al MAS NMR study

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ABSTRACT

Disordering of Si and Al in natrolite, scolecite, mesolite, and gonnardite was investigated with ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The results indicate that with the exception of one sample of natrolite (from San Benito County, California), the natrolite, mesolite, and scolecite samples studied all exhibit small degrees (<10% Al occupancy of Si sites) of Si-Al disorder. The spectra for these samples are consistent with Al avoidance. Gonnardite is confirmed to have extensive Si-Al disorder, with only slight preferential Si occupation of the T1 site. Fits of ^{29}Si MAS NMR spectra and mathematical relations based on Al avoidance were used to calculate Si and Al occupancies across the tetrahedral sites in these minerals. Configurational entropies arising from Si-Al disorder in natrolite, mesolite, and scolecite can add an addition 1–2% [up to 11 J/(mol·K)] to the total entropies of these phases at 298.15 K, whereas it may add as much as 7% to that of gonnardite [up to 27.7 J/(mol·K)]. These results also concur with previous observations of a gap in Si-Al disordering between orthorhombic and tetragonal natrolite samples and suggest that the state of disorder in natrolite is a function of temperature. The ^{29}Si MAS NMR spectrum of gonnardite is consistent with a disordered natrolite framework structure, and not an intergrowth of thomsonite and natrolite structural domains.