Study of the Al coordination in mullites with varying Al:Si ratio by \(^{27}\text{Al}\) NMR spectroscopy and X-ray diffraction

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**ABSTRACT**

Mullite is an aluminosilicate of the composition \(\text{Al}_x(\text{Al}_{1-x}\text{Si}_{2-x})\text{O}_{10-y}\) with \(x\) generally ranging between 0.2 and 0.5. XRD and \(^{29}\text{Si}\) and \(^{27}\text{Al}\) nuclear magnetic resonance (NMR) have been used to investigate the structure of various mullite compositions (\(x = 0.26, 0.36, 0.42,\) and 0.69) as well as sillimanite (\(x = 0\)) and \(\gamma\)-\(\text{Al}_2\text{O}_3\) (\(x = 1\)). \(^{27}\text{Al}\) magic angle spinning (MAS) NMR of the central and satellite transitions have been used to determine the chemical shifts and quadrupole interaction parameters for the various \(\text{Al}_2\text{O}_3\) and \(\gamma\)-\(\text{Al}_2\text{O}_3\) units. The isotropic chemical shifts of the various units are 5.9 ppm for \(\text{Al}_2\text{O}_3\), 69.1 ppm for \(\gamma\)-\(\text{Al}_2\text{O}_3\), 55.0 ppm for \(\text{Al}_2\text{O}_3\), and 45.7 ppm for \(\text{Al}_2\text{O}_3\) where \(\text{Al}_2\text{O}_3\) (T) denotes the aluminum tetrahedra in the double chains, and \(\text{Al}_2\text{O}_3\) (T*) those next to the oxygen \(\text{Oc}^*\). Quantitative numbers of the aluminum occupancy of these sites have been determined for the various powder samples. These results are in good agreement with the average structure model of mullites. NMR and XRD proved the presence of impurities of kyanite in natural sillimanite and of \(\gamma\)-\(\text{Al}_2\text{O}_3\) in the mullites with \(x = 0.42\) and 0.69.

**INTRODUCTION**

Mullite is a member of the aluminum silicates of the composition \(\text{Al}_x(\text{Al}_{1-x}\text{Si}_{2-x})\text{O}_{10-y}\) with \(x\) generally ranging between 0.2 and 0.5. Mullite is an important ceramic material for both traditional and advanced applications. The material is characterized by a very good thermal stability especially under oxidizing conditions. Furthermore, mullite materials have a low thermal expansion coefficient and very low thermal conductivity combined with excellent creep resistance. Mullite has been determined for the various powder samples. These results are in good agreement with the average structure model of mullites. NMR and XRD proved the presence of impurities of kyanite in natural sillimanite and of \(\gamma\)-\(\text{Al}_2\text{O}_3\) in the mullites with \(x = 0.42\) and 0.69.

\(^{27}\text{Al}\) MAS NMR is useful for probing the existence of four-, five- and sixfold-coordinated Al species during the mullite formation and in glasses and gels of the \(\text{Al}_2\text{O}_3\)-\(\text{SiO}_2\) system (Albers 1993; Sanz et al. 1988, 1991; Taylor and Holland 1993; Schneider et al. 1992; Merwin et al. 1991) although it is...