

Structural variations in the brownmillerite series $\text{Ca}_2(\text{Fe}_{2-x}\text{Al}_x)\text{O}_5$: Single-crystal X-ray diffraction at 25 °C and high-temperature X-ray powder diffraction ($25\text{ °C} \leq T \leq 1000\text{ °C}$)

GÜNTHER J. REDHAMMER,^{1,*} GEROLD TIPPELT,² GEORG ROTH,¹ AND GEORG AMTHAUER²

¹Institute of Crystallography, Rheinisch-Westfälische Technische Hochschule Aachen, Jägerstrasse 17/19, D-52056 Aachen, Germany

²Institute of Mineralogy, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria

³Corresponding address: Neuhofen im Innkreis 224/1, A-4910 Ried im Innkreis, Austria

ABSTRACT

A total of 30 synthetic samples of the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$, $0.00 \leq x \leq 1.34$ solid solution series have been investigated by single crystal X-ray diffraction at 25 °C. Pure $\text{Ca}_2\text{Fe}_2\text{O}_5$ and samples up to $x = 0.56$ have space group $Pnma$, $Z = 4$, whereas samples with $x > 0.56$ show $I2mb$ symmetry, $Z = 4$. The substitution of Fe^{3+} by the smaller Al^{3+} cation decreases unit-cell parameters and average octahedral and tetrahedral bond lengths and induces distinct changes in the O-atom coordination of the interstitial Ca atom. Discontinuities in the structural parameters vs. the $\text{Al}_{\text{tot}}^{3+}$ content and changes in slope of these quantities are associated with the phase transition. The essential difference between the two modifications is the cation-O atom-cation angle within the planes of corner sharing octahedra, which is close to 180° in $I2mb$, but $\approx 184^\circ$ in the $Pnma$ phase, and the existence of two different orientations of the tetrahedral chains in $Pnma$ as opposed to one in $I2mb$. At low overall Al^{3+} concentrations Al^{3+} preferentially enters the tetrahedral site until $\approx 2/3$ of it is filled. Additional Al^{3+} cations, substituted for Fe^{3+} , are equally distributed over octahedral and tetrahedral sites. At high temperature pure $\text{Ca}_2\text{Fe}_2\text{O}_5$ transforms to a body-centered structure at 724(4) °C. Substituting Al^{3+} for Fe^{3+} linearly decreases the transition temperature by 15 °C per 0.1 Al^{3+} down to 623(5) °C for $x = 0.65$.