

**NEWS FROM REFRACTORY LAND – TWO NOVEL PHASES IN THE SYSTEMS
CaO-Al₂O₃-Cr₂O₃ AND CaO-Al₂O₃-MgO**

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The ternary systems CaO-Al₂O₃-MgO and CaO-Al₂O₃-Cr₂O₃ are of fundamental importance for refractories industry. Apart from previous experimental studies, thermodynamic assessments using the Calphad technique have been also employed to get a holistic picture of the relevant phase relationships. However, as pointed out by HALLSTEDT (1995), the computational results have to be treated with care as long as there is still a lack of data on solid-phase relations. This is surprising because one should assume that both systems have been studied in great detail and are well understood. In the course of our own investigations we were able to finally proof the existence of the compounds Ca₃Al₄MgO₁₀ and CaAl₂Cr₂O₇.

Ca₃Al₄MgO₁₀ was first mentioned more than 50 years ago by MAJUMDAR (1964) to be a stable calcium magnesium aluminate. Its existence, however, was later challenged by DÓDONY & BUSECK (2001) based on electron microscopy data. In a sequence of temperature dependent solid-state reactions the formation of the ternary phase Ca₃Al₄MgO₁₀ has been studied. Whereas the compound could not be prepared at 1200 °C, a yield of 85 % of Ca₃Al₄MgO₁₀ was obtained at 1320 °C (melting point: 1330 °C). Single crystals could be retrieved from the sinter pellets. Basic crystallographic data are as follows: orthorhombic symmetry, space group *Pbcm*, *a* = 5.14073(8) Å, *b* = 16.7576(2) Å, *c* = 10.70977(16) Å, *V* = 922.61(2) Å³, *Z* = 4. Using synchrotron radiation it was possible to solve the crystal structure. It contains [(Al,Mg)O₄]-tetrahedra forming a three-dimensional network whose topological characteristics have been determined. Al-Mg distributions on the different T-sites have been investigated. The calcium cations are located in voids of the network.

When a 1:1:1 molar composition of the three components CaO, Al₂O₃ and Cr₂O₃ was reacted at 1500 °C, a previously unknown phase with composition CaAl₂Cr₂O₇ formed. Diffraction experiments at ambient conditions on a crystal with composition CaAl_{2.13}Cr_{1.87}O₇ yielded the following crystallographic data: space group *P3*, *a* = 7.7690(5) Å, *c* = 7.6463(5) Å, *V* = 399.68(6) Å³, *Z* = 3. CaAl₂Cr₂O₇ represents a new structure type. It belongs to the group of double layer structures where individual double layers contain octahedrally and tetrahedrally coordinated cation positions. Linkage between neighboring sheet packages is provided by calcium cations. Thermal expansion has been studied between 29 and 790 °C using in-situ single-crystal diffraction. No indications for a structural phase transition were observed. The thermal expansion tensor has been obtained. A pronounced anisotropy is evident.

DÓDONY, I., BUSECK, P.R. (2001): Phys. Chem. Minerals, 28, 428-434.

HALLSTEDT, B. (1995): J. Am. Ceram. Soc., 78, 193-198.

MAJUMDAR, A.J. (1964): Brit. Ceram. Trans. J., 63, 347-363.