Incommensurately modulated structure and phase transitions in $K_4CaSi_6O_{15}$

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As potassium calcium silicates play an important role in several residual materials including ashes from biomass combustion, the oxide system K_2O-CaO-SiO_2 (KCS) has been in the focus of attention for a long time. A better understanding of the chemical and physical properties of these residual materials is demanded to reduce or – even better – prevent serious problems in the combustion chambers such as slagging, corrosion or fouling, which can in the worst-case lead to a complete shutdown of the biomass energy plant.

In case of the K_2O-CaO-SiO_2 system, where experimental data are difficult to be obtained due to volatility of potassium, hygroscopicity or high viscosity of the silicate melts, performing accurate thermodynamic modeling using the semi-empirical CALPHAD technique is very helpful in predicting the behavior of potassium calcium silicates at high temperatures. Therefore, not only the knowledge of all existing binary and ternary phases of this system together with their chemical composition is required, but also information about their thermodynamic properties, such as heat capacity and melting points. For polymorphs, in particular, it is necessary to clarify their structural features and their stability ranges concerning temperature. In a previous series of experiments to decipher the number of existing ternary phases, we proved the presence of $K_4CaSi_6O_{15}$ as a stable compound at ambient conditions and solved its crystal structure [1]. Recently, we further revealed that the compound undergoes two structural phase transitions with increasing temperature (Fig. 1).

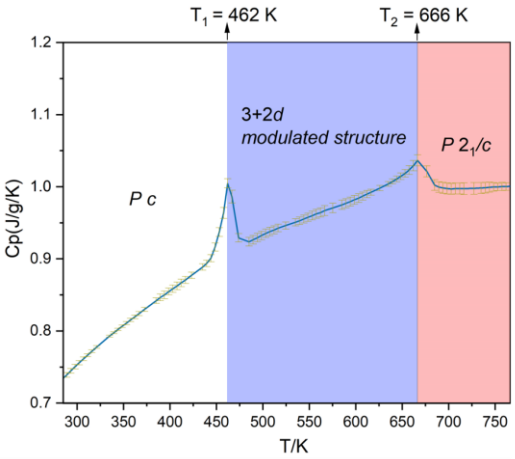

Fig. 1 Heat capacity of $K_4CaSi_6O_{15}$ as a function of temperature

In the present study, monocrystalline $K_4CaSi_6O_{15}$ was prepared from solid-state reactions between stoichiometric mixtures of the corresponding oxides/carbonates. The compound was characterized by single-crystal X-ray diffraction between ambient temperature and 1063 K. Heat capacity measurements indicated that two thermal effects occurred at about T_1=462 K and T_2=666 K. For the high-temperature phase, basic crystallographic data were determined at 773 K: monoclinic symmetry, space group $P\,2_1/c$, a = 6.6494(4) Å, b = 9.2340(5) Å, c = 12.2954(6) Å, β = 93.639(3)°, V = 753.42(7) Å^3, Z = 2. Diffraction data collected between T_1 and T_2 show satellite reflections, which suggest that the phase is 3+2-dimensionally modulated. The satellites can be indexed with two additional vectors: q_1 = (0.057, 0.172, 0.379) and q_2 = (-0.057, 0.172, -0.379).

[1] Hang L., Hildebrandt E., Krammer H., Kahlenberg V., Krüger H., Schottenberger H. $K_4CaSi_6O_{15}$—Solving a 90-year-old riddle. J. Am. Ceram. Soc., 104, 6678-6695 (2021)