# Study of phase transitions in the sodalite system $Ca_8[Al_{12}O_{24}](Mo_{1-x}W_xO_4)_2$

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The aluminate-sodalites $M_8[Al_{12}O_{24}](XO_4)_2$ usually undergo one or more structural phase transitions as a function of temperature, pressure or composition, mostly of ferroic character [1]. $Ca_8[Al_{12}O_{24}](MoO_4)_2$ and $Ca_8[Al_{12}O_{24}](WO_4)_2$, henceforth referred as CAM and CAW, have very similar structures at room temperature with an orthorhombic γ-phase (space group *Aba2* and cell parameters ≈ 26·13·9 $Å^3$), above 645 K a cubic α-phase with space group *I-43m* and cell parameters ≈ 9·9·9 $Å^3$. However, CAM shows two intermediate phases with transitions at 607 K and 618 K [2], while CAW shows only one with a transition at 625 K [3].

The solid solution series $Ca_8[Al_{12}O_{24}](Mo_{1-x}W_xO_4)_2$ has been synthesized by solid-state reaction at 1623 K. The aim of this study is to investigate the influence of anion substitution on the structure, phase diagram, phase transitions, and selected properties of aluminate sodalites.

High-resolution x-ray powder diffraction data of the $Ca_8[Al_{12}O_{24}](Mo_{1-x}W_xO_4)_2$ solid solution series were collected at room temperature employing a Bruker D8 diffractometer (Cu $K\alpha_1$). The Le Bail analysis of these data showed that there are no significant changes in the lattice parameters with composition. DTA experiments in the range 373 K through 873 K showed three thermally induced phase transitions for compositions $0 \leq x \leq 0.25$, while only two phase transitions for $0.3 \leq x \leq 1$ were found.

To study the effects of temperature on the structure of the solid solution, powder diffraction data were collected at different temperatures (λ=0.7099Å, Si (111) monochromator) at the B2 beam line at Hasylab DESY. Two samples with x=0 and x=0.8 were selected as representatives of the two different ranges, where three or two phase transitions ocurre respectively.

For the study of the thermal expansion the OBI Image Plate detector was used [4]. The data were collected in the 2θ range of 2-60°, heating the sample in steps of 50 K from room temperature to 1173 K. Close to the phase transitions (previously determined by DTA analysis) the pseudo-cubic reflections 400, 211 and 411 which could not be resolved by the image plate, were followed in 2 K steps with the high-resolution single counter and analyser setup.

Figs. 1a) and b) show the lattice parameters of $Ca_8[Al_{12}O_{24}](MoO_4)_2$. The first phase transition from γ-orthorhombic to tetragonal-β´ occurs at 608 K. The second phase transition from β´-phase to β-phase occurs at 618 K. The unit-cell metric remains tetragonal through the β-β´transition. In the third phase transition from β to cubic α phase a coexistence region of the two phases was observed. Since no peak broadening indicative of a temperature gradient in the sample was detected we take the coexistence as a sign of a first order phase transition. The pseudo-cubic unit-cell volume Fig.1b) shows a discontinuity at the phase transitions.

Rietveld refinement of the cubic α-phase was performed using the model of CAM [2]. The atomic coordinates were used to calculate the inter- and intra-tetrahedra angles in the structure. Cubic CAM has two types of angles O–T–O, α=120.1° and α´=104.5° [2]. The values of these angles remain almost constant in the temperature range from 668 K to 1168 K. Since the Al–O bond

length remain constant as well (1.74 Å) the AlO4-tetrahedra can be treated as rigid bodies. They do not contribute to the thermal expansion mechanism by changing their shapes. On the other hand, the T–O–T angle γ between the tetrahedra increases from 140° to 144°. The tilt angle φ, which gives the degree of expansion of the sodalite, was calculated as well. From the phase transition temperature to 1173 K the tilt angle decreases continuously from 12° to 10.5°. The thermal expansion of the cubic α-phase of the two samples x=0 and x=0.8 has an average value of $\alpha=8.60(4)\cdot10^{-6}$ $K^{-1}$. We conclude that the decrease of the tilt angle is the principal mechanism responsible for the thermal expansion. Moreover, it seems that the anionic substitution does not have an influence on the thermal expansion of the cubic phase.

The thermal expansion coefficient was used for an extrapolation of the cubic cell parameter $a_o$ into the stability fields of the tetragonal β and β´phases Fig. 1 (dashed line). The phase transition from α-cubic to β-tetragonal of CAM is ferroelastic. The components of the spontaneous strain tensor are $e_{11}=e_{22}= (a_t-a_o)/a_o$ and $e_{33}= (c_t-a_o)/a_o$. The scalar spontaneous strain $\varepsilon_s=(\Sigma e_{ii}^2)^{1/2}$ in the coexistence region of the β and α phases is almost constant $5.5\cdot10^{-3}$. At 620 K there is a jump of the order of $2\cdot10^{-3}$ and in the region of β´ phase it saturates at $7.5\cdot10^{-3}$.

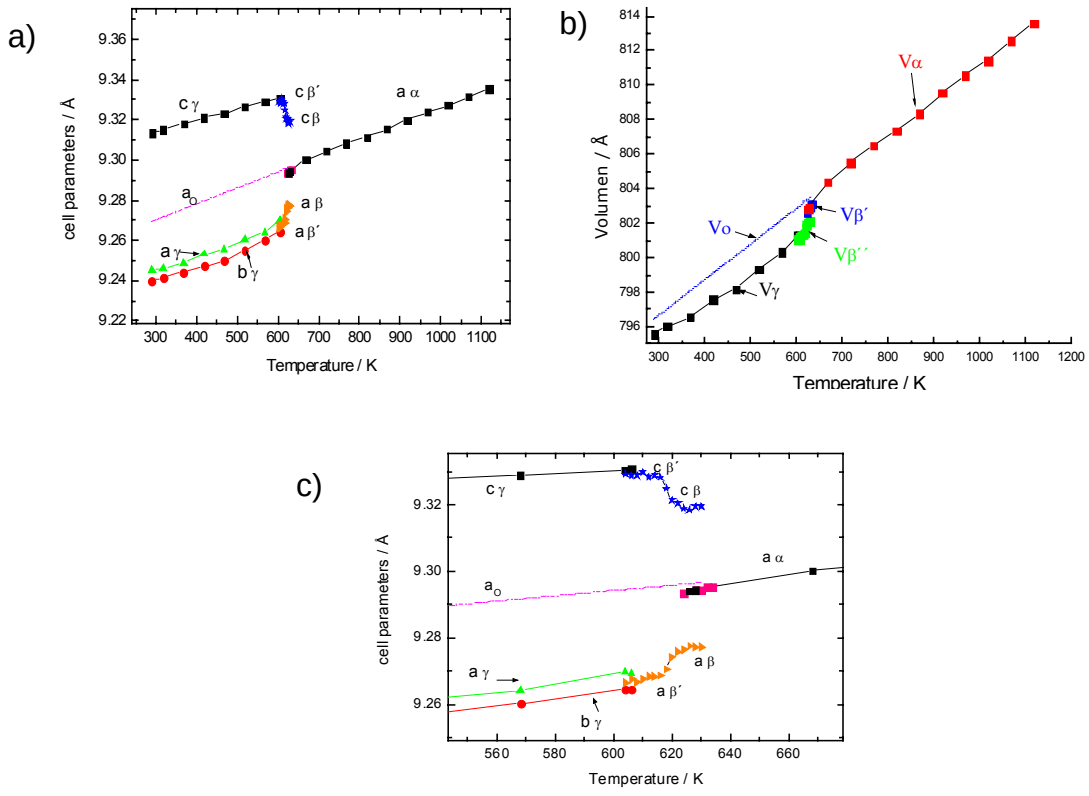


Figure 1 a) CAM lattice parameters as function of temperature, b) Unit-cell volume as a function of temperature. c) Temperature dependence of the lattice parameters across the phase transitions.

## References


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