



Temperature-dependent structural evolution and stability of divalent anion bearing alumosilicate cancrinites



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ABSTRACT

A comprehensive study of XO_4^{2-} -cancrinites with $X = Mn, Cr, Se, Mo$ and W was carried out, focusing on the effect of incorporated anions on the framework structure. At room temperature an anisotropic unit cell expansion with increasing anion size was observed. The size of the incorporated anions has no influence on the framework angles or the channel radii. In temperature-dependent (TD) studies four different regimes could be identified: first a quasi-linear expansion of the cancrinites containing water molecules in the ϵ -cages; second, the dehydration process; third the quasi-linear expansion regime of the dehydrated phase to a maximum expanded structure, followed by a phase transformation or decomposition (fourth). The temperature at which the maximum expanded structure is reached, decreases with increasing size of the incorporated anion. Further, it is shown, that thermally stable anions can promote a reconstructive phase transformation to the corresponding cubic nosean-type structure. The absence of an amorphous intermediate state as well as the complete ordering of the template ions indicate a fast transformation mechanism based on the translation of six-ring layers from a hexagonal $ABAB$ to a cubic $ABCABC$ stacking.

1. Introduction

The cancrinite (CAN, $[Na_{6+2y}(XO_4)_y(H_2O)_2][AlSiO_4]_6$ with $0 \leq y \leq 1$) framework is build up by a 3-dimensional network of interconnected TO_4 tetrahedra ($T = Si, Al$). This framework can also be described using a hexagonal $ABAB$ stacking sequence of layers consisting of rings formed by six corner-sharing tetrahedra. This leads to the crystal structure mostly described in space-group $P6_3$ [1]. The structures' characteristic feature is the large 12-membered ring or CAN channel (Fig. 1), running parallel to the crystallographic c axis with a free diameter of $d_{channel} \approx 590$ pm [2–4]. These channels are surrounded by columns of ϵ -cages (Fig. 1), which are built up by six four-membered and five six-membered rings. Channels as well as ϵ -cages contain ions, counterbalancing the six-fold negative framework charge. In the present study sodium cations were used, of which 2 per formula unit are found in the ϵ -cages (together with up to two water molecules) and six in the channels, leading to a two-fold positive charged sodium-filled framework. Therefore, two negative charged templates on the two possible positions or one two-fold negative template anion (statistically distributed across the two possible positions) could be incorporated in the channel.

Several high-temperature studies on natural CANs have been carried

out to determine their temperature-dependent (TD) structural behavior [2,5–8]. All these studies described three regimes: I) the structural evolution of the hydrous phase; II) the dehydration process and III) the expansion of the anhydrous phase. The hydrous phase shows a nearly linear thermal expansion of the unit cell dimensions (a, c, V) [8]. The expansion is strongly anisotropic, the c lattice parameter expansion is more than two times higher than those in a direction [6,8] (axial and volume thermal expansion coefficients (TEC) α : $\alpha_a = 11.6$ (3) $\cdot 10^{-6} K^{-1}$, $\alpha_c = 25.8$ (8) $\cdot 10^{-6} K^{-1}$ and $\alpha_V = 48.8$ (8) $\cdot 10^{-6} K^{-1}$ [8]). Hassan et al. [6] report, that the ratio of the lattice parameters depends on both, the anion and cation size, but the cations influence is stronger. Thermogravimetric analysis [5] for regime-II show a continuous dehydration process of CAN with two signals at 577 K and 956 K. From PXRD data, the dehydration of CAN at 973 K is visible by a discontinuity in the unit-cell expansion, along with an increase of the intensity of the reflections (300), (400) and (101) [5]. The intensity increase of these reflections is caused by the loss of the disordered water molecules located around the threefold axis of the structure and thus the increase of the degree of ordering in the a - b plane [5]. However, in scattering experiments with synchrotron radiation the complete dehydration of the CAN occurs already at 898 K [7]. Other thermogravimetric [9] and single crystal diffraction measurements [10] report

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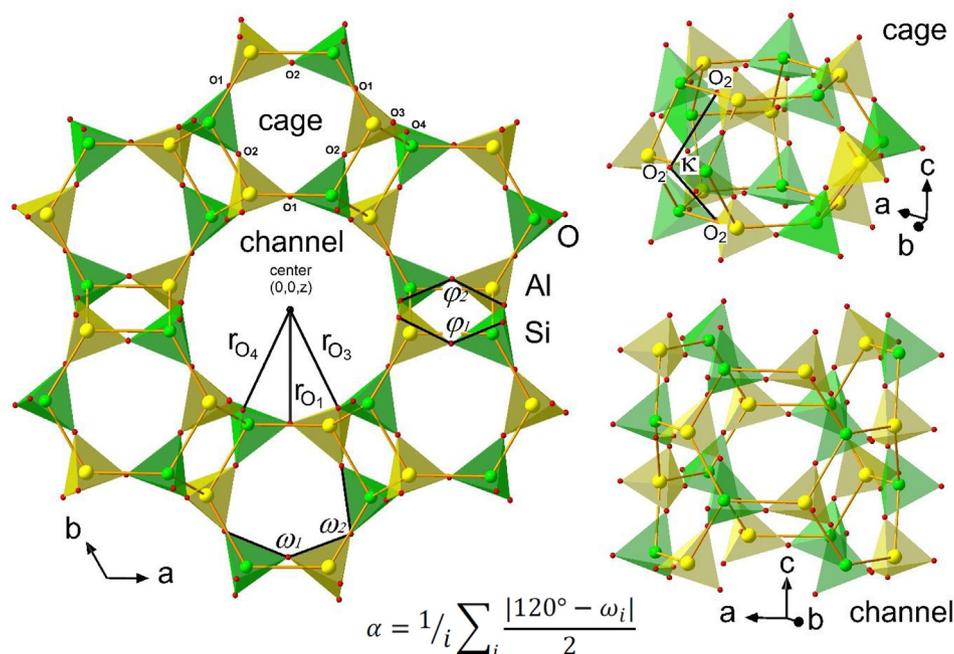


Fig. 1. Building units of a cancrinite together with the characteristic angles and radii.

dehydration temperatures ranging from 570 K to 770 K. Gatta et al. [8] observed on a single crystal a very slow dehydration at 748 K, which took 12 days to be completed.

Regime-III, between the complete water loss to the framework decomposition around 800–900 K [2], corresponds to the thermal expansion behavior of the anhydrous phase. The unit-cell parameters in this expansion interval show a similar average thermal expansion coefficient as the hydrous phase, described with a polynomial function [8]. The structural evolution of CAN in this regime can be characterized by a linear increase of the $\langle \text{Na1-O2} \rangle$ distance ($P6_3$: Na1: 2 b, 1/3, 2/3, $z \approx 0.13$ [7]); in the ϵ -cage pointing framework oxygen atom O2: 6c, $x \approx 0.11$, $y \approx 0.56$, $z \approx 0.73$ [7]; Fig. 1); causing the Na1 to move towards the six-membered ring [5–8]. This movement forces the framework tetrahedra of the six-membered ring to rotate (visible in the increase of the Al-O-Si angle from 143.7 (4)° to 147.7 (5)° [7]), resulting in a more planar six-membered ring. The water loss out of the Na1 coordination leads to an anisotropic elongation of the Na1 displacement along [0001], indicating a strong increase in the thermal and/or positional disorder of Na1. In the first instance the ϵ -cages are affected by the dehydration, the $\text{O}_2\text{-O}_2\text{-O}_2$ angle (κ), correlating with the height of the CAN cages, indicates an initial cage opening and a flattening after complete dehydration [8]. A similar effect could be observed in the four membered rings. The channel diameter is at all not affected by the water loss. As a result, the thermal expansion coefficients decrease during the water release (no further framework expansion during the dehydration) and increase thereafter.

Weller and Kenyon [11] investigated the temperature-dependent (TD) structural evolution of the synthetic CO_3^{2-} cancrinite $[\text{Na}_8(\text{CO}_3)(\text{D}_2\text{O})_n][\text{AlSiO}_4]_6$. This compound releases water in the temperature range from 373 K to 573 K, observable in the contraction of the metric parameters. They also observed [11] an anisotropic expansion of the lattice parameters a and c , where c is more sensitive to the thermal expansion. Around 873 K $[\text{Na}_8(\text{CO}_3)(\text{D}_2\text{O})_n][\text{AlSiO}_4]_6$ decomposes to a nepheline-type structure.

Most reported thermal studies on CANs were performed with natural samples, the exact template ion composition as well as the water content is often very difficult to determine, and the ions influence on dehydration or decomposition temperatures is not yet fully understood. In this study synthetic CANs with two-fold negative anions MnO_4^{2-} ,

CrO_4^{2-} , SeO_4^{2-} , MoO_4^{2-} and WO_4^{2-} are investigated to gather further insights on the influence of the incorporated template-anion on the thermal behavior and stability. The tetrahedral anions with their cubic symmetry and their threefold rotation axis can promote both the CAN and the SOD framework [17] during hydrothermal synthesis. If the incorporated tetrahedral anions are more stable than the framework, with respect to temperature, the CAN structure could possibly convert to a sodalite (SOD) [12–15] or in case of divalent anions a nosean-type structure (NOS) [16,17]. For the CrO_4 -CAN such a transformation to NOS through heating a 1:1 mixture of Na_2CrO_4 and CrO_4 -CAN to 1243 K for 72 h has been reported earlier [18]. This study examines systematically the interactions between tetrahedral anions with varying sizes and the CAN framework, its temperature-dependent behavior and the phase transformations to the NOS-type structure.

2. Experimental

2.1. Synthesis

Samples $[\text{Na}_8(\text{XO}_4)][\text{AlSiO}_4]_6$ ($X = \text{Mn, Cr, Se, Mo, W}$) were synthesized hydrothermally under autogenous pressure in 50 mL Teflon lined steel autoclaves. The mother liquors were prepared by solving NaAlO_2 (Alfar Aesar CAS-No.:1302-42-7), Na_2SiO_3 (Alfar Aesar CAS-No.:6834-92-0), NaOH (Analar NORMAPUR CAS-No.:1310-732) and Na_2XO_4 in 20 mL deionized water. A molar ratio of 1:1:16:3 for $X = \text{Mn}$ (Alfar Aesar CAS-No.: 79048-36-5) and Cr (Alfar Aesar CAS-No.: 10034-82-9) has been taken. For $X = \text{Se}$ (Alfar Aesar CAS-No.: 13410-01-0) a ratio of 1:1:15:2.2 and for $X = \text{Mo}$ (Alfar Aesar CAS-No.: 10102-40-6) and W (Alfar Aesar CAS-No.: 10213-10-2) of 1:1:4:3 was used. The respective mother liquors were heated to 393 K (Mn), 423 K (Se), 473 K (Cr) and 503 K (Mo, W) for 48 h. All samples were washed with deionized water and dried for 24 h at 353 K.

2.2. Characterization

X-ray powder diffraction (PXRD) data at ambient conditions were collected on a Panalytical X'Pert Pro diffractometer (Panalytical B.V., Almelo, Netherlands) using $\text{CuK}\alpha$ radiation in a $\theta/2\theta$ Bragg-Brentano geometry. The instrument was equipped with a divergence slit (0.25°),

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