The transformation mechanism of the sodalite- to the melilite-topology: Thermal expansion and decomposition of bicchulite-type to melilite-type compounds

Dipl.-Min. Lars Peters: Institut für Geowissenschaften, Abt. Mineralogie/Kristallographie,
Christian-Albrechts-Universität zu Kiel, Olshausenstraße, 40, 24098 , Germany
Tel: +49-431-8802692, Fax: +49-431-8804457, E-Mail: lap@min.uni-kiel.de

PD Dr. Karsten Knorr: Institut für Geowissenschaften, Abt. Mineralogie/Kristallographie,
Christian-Albrechts-Universität zu Kiel, Olshausenstraße, 40, 24098 , Germany
Tel: +49-431-8802226, Fax: +49-431-8804457, E-Mail: kk@min.uni-kiel.de

PD Dr. Hannelore Katzke: Institut für Geowissenschaften, Abt. Mineralogie/Kristallographie,
Christian-Albrechts-Universität zu Kiel, Olshausenstraße, 40, 24098 , Germany
Tel: +49-431-8802906, Fax: +49-431-8804457, E-Mail: hanne@min.uni-kiel.de

Dr. Michael Knapp: Materials Science, Darmstadt University of Technology and HASYLAB/DESY,
Hamburg, Notkestraße, 85, 22607 , Germany
Tel: +49-40-89982918, Fax: +49-40-89984475, E-Mail: michael.knapp@desy.de

Prof. Wulf Depmeier: Institut für Geowissenschaften, Abt. Mineralogie/Kristallographie,
Christian-Albrechts-Universität zu Kiel, Olshausenstraße, 40, 24098 , Germany
Tel: +49-431-8802839, Fax: +49-431-8804457, E-Mail: wd@min.uni-kiel.de

Keywords: Sodalite – melilite – thermal expansion – thermal decomposition – reaction mechanism

Schlagworte: Sodalith – Melilith – thermische Ausdehnung – thermische Zersetzung –
Reaktionsmechanismus

MS-ID:
Heft: / ()

lap@min.uni-kiel.de

July 12, 2005

Abstract

The mineral bicchulite, $[\text{Ca}_8(\text{OH})_8][\text{Al}_8\text{Si}_4\text{O}_{24}]\text{-SOD}$, has the sodalite-(SOD-)type structure. At elevated temperatures it decomposes into gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (melilite-type structure), and water (vapour). We report on the thermal expansion of two bicchulite-type compounds, the mineral bicchulite up to $T = 740$ K and $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]\text{-SOD}$ up to $T = 1025$ K. The expansion mechanism is described. *In situ* x-ray powder diffraction experiments were performed to evaluate the thermal decomposition of $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]\text{-SOD}$ into $4 (\text{Ca}_{1.5}\text{Eu}_{0.5})\text{T}^1[\text{T}_2^2\text{O}_7]$ and $4 \text{H}_2\text{O}$, with $\text{T}^i = \text{Al}$ or Si in a ratio of 5:1. A structural mechanism for the transformation from the sodalite to the melilite topology is proposed, based on geometrical considerations.

1 Introduction

Both, the sodalite-(SOD) and the melilite-type structure, have been studied thoroughly for the last 75 years. It is well known that both structures can be found for various compositions and that the p - T -conditions for the formation of compounds crystallizing in the two structure-types often may vary strongly. In this work, the high-temperature behaviour of two compounds of the SOD-type is studied. In section one, a brief introduction to both, the sodalite and the melilite structure-type, is given. In section two, the relevant experimental methods are described. The thermal expansion behaviour of the SOD-type compounds and the corresponding structural expansion mechanism are described in section three. Finally, a mechanism for the transition from the sodalite to the melilite topology is derived from geometrical considerations in section four.

1.1 The sodalite-type structure

The simplest general formula, according to the *IUPAC* recommendation (McCusker, Liebau and Engelhardt, 2001), of sodalite-type compounds is $[\mathbf{M}_8\mathbf{X}_2][\mathbf{T}_{12}\mathbf{O}_{24}]\text{-SOD}$. $\mathbf{M}$ and $\mathbf{X}$ denote cations and anions, respectively, inside the sodalite β -cages and $\mathbf{T}$ the tetrahedrally coordinated cations of the SOD-framework. The structure of the mineral sodalite, $[\text{Na}_8\text{Cl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\text{-SOD}$, was first described by Pauling (1930) and refined by Löns and Schulz (1967). Many symmetries occur in the sodalite family (Depmeier, 1984, 1992). The aristotype of the sodalite topology has space group

$Im\bar{3}m$ with $\mathbf{M}$ at the Wyckoff-position $8c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), $\mathbf{T}$ at $12d$ ($\frac{1}{4}, \frac{1}{2}, 0$), $\mathbf{O}$ at $24h$ ($x, x, \frac{1}{2}$) and $\mathbf{X}$ at $2a$ ($0, 0, 0$). Recent reviews on the structure and properties of sodalite-type compounds were given by Weller (2000) and Depmeier (2005). The mineral bicchulite is of the sodalite-type (Sahl and Chatterjee, 1977; Sahl, 1980), possessing a 'partially collapsed' framework and thus having space group $I\bar{4}3m$. In bicchulite, the $\mathbf{M}$ -position is occupied by Ca^{2+} and the $\mathbf{T}$ -site by Al^{3+} and Si^{4+} in the ratio of 2:1. Instead of two $\mathbf{X}$ -ions, bicchulite contains 8 (OH)-groups per unit cell. In this compound, Ca occupies position $8c$ (x, x, x), Si and Al are at $12d$ ($\frac{1}{4}, \frac{1}{2}, 0$), O at $24g$ (x, x, z) and O(H) at $8c$ (x, x, x). It is still a matter of debate, whether the protons are located at position $8c$ (x, x, x) (Sahl, 1980; Winkler, Milman and Pickard, 2004) or rather at $24g$ (x, x, z) with occupancy 0.333 (Dann, Mead and Weller, 1996). Al/Si- order/disorder has recently been studied by Winkler, Milman and Pickard (2004). A schematic view of the structure is given in Fig. 1.

1.2 The melilite-type structure

In order to facilitate comparison with the SOD-type compounds, the general formula of melilite-type compounds can be written as $\mathbf{M}_2\mathbf{T}^1[\mathbf{T}_2^2\mathbf{X}_7]$. The crystal structure of melilite was first described by Warren (1930). The aristotype has space group $P\bar{4}2_1m$, with $\mathbf{M}$ at $4e$ ($x, x+\frac{1}{2}, z$), $\mathbf{T}^1$ at position $2a$ ($0, 0, 0$), $\mathbf{T}^2$ at $4e$ ($x, x+\frac{1}{2}, z$), and $\mathbf{X}$ at the positions $2c$ ($\frac{1}{2}, 0, z$), $4e$ ($x, x+\frac{1}{2}, z$) and $8f$ (x, y, z) (Malinovskii and Panina, 1996). The unit cell contains 2 formula units. Fig.

2 gives idealized drawings of the structure along the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_3$.

2 Experimental

The SOD-type compounds were synthesized hydrothermally from the corresponding melilite-type compounds at $T=810\text{ K}$ and $p_{\text{H}_2\text{O}}=0.1\text{ GPa}$, as was described by Gupta and Chatterjee (1978). The synthesis of the melilite-type compounds is described elsewhere (Peters, Knorr, Knapp and Depmeier, 2005). The melilite samples were ground and filled into Au-tubes, which were closed by arc welding, after adding about $100\text{ }\mu\text{l}$ of demineralized water. This hydrothermal treatment was repeated until the samples were pure, according to x-ray powder diffraction. The hydrothermal treatment lasted for up to 1000 h. A high-resolution *Bruker – AXS D8*-diffractometer was used for the phase analysis. The diffractometer operates in parallel-beam geometry, having a parabolic multilayer-optics and an asymmetrically cut monochromator as primary optics. $\text{Cu-}K_{\alpha_1}$ -radiation was used. The position-sensitive *Braun* detector was operated at a step width of $\Delta 2\theta = 0.0085^\circ$.

For the measurements on $[\text{Ca}_8(\text{OH})_8][\text{Al}_8\text{Si}_4\text{O}_{24}]\text{-SOD}$, high-temperature diffraction experiments were performed in-house using a home-made U-shaped resistance furnace. The temperature was controlled by a Pt/PtRh10-thermocouple near the sample capillary made of SiO_2 -glass. The thermocouple was calibrated using the NaCl thermal expansion data of Enck and Dommel (1965). Mo- $K\alpha$ radiation was

used for the diffraction experiments with a *MAR2000* image-plate detector. Diffractograms were taken in steps of about $\Delta T = 25\text{ K}$. The maximum temperature was 740 K. The integration of the two-dimensional image-plate diffraction data was performed using the program '*fit2D V 10.132*' (Hammersley/ ESRF, 2001). The high-temperature diffraction experiments on $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]\text{-SOD}$ were performed at the B2 powder diffractometer (*HASYLAB* at *DESY*, Hamburg (Germany)) (Knapp, Baetz, Ehrenberg and Fuess, 2004). Monochromatized synchrotron radiation of wavelength $\lambda = 0.69835(5)\text{ \AA}$ was used for the diffraction experiments. The wavelength was refined via a standard least squares method from the angular position of 6 reflections of NIST SRM640b silicon. The diffracted radiation was recorded using the on-site readable image-plate OBI detector (Knapp, Joco, Baetz, Brecht, Berghaeuser, Ehrenberg, von Seggern and Fuess, 2004). All diffractograms obtained from the experiments at *HASYLAB* were measured against the monitored primary intensity. A *Stoe* capillary heating device was used for *in situ* diffraction experiments with temperature steps of about $\Delta T = 10\text{ K}$ up to 1150 K. The temperature was measured by a Ni/CrNi-thermocouple near the sample capillary made of SiO_2 -glass. The thermocouple was calibrated using the NaCl thermal expansion data of Pathak and Vasavada (1970). A temperature uncertainty of 1 % of the absolute temperature was estimated for all high-temperature experiments reported here.

All diffraction data were evaluated by Rietveld analysis using the program '*Fullprof*' (Rodriguez-Carvajal, 2002).

3 Results and discussion

The bicchulite structure reported by Dann, Mead and Weller (1996) was used as starting model for the Rietveld-refinements. For the Eu-bearing compound, Eu^{3+} and Ca^{2+} were positioned on the **M**-position, assuming statistical distribution. Si^{4+} and Al^{3+} were positioned on the **T**-site of the structure, again assuming statistical distribution, as reported for bicchulite (Sahl, 1980). No indications for deviations from space group $I\bar{4}3m$, nor for deviations from a statistical distribution of Eu and Ca at the **M**-site for the Eu-bearing compound were detected in the powder patterns. The protons were ignored in all Rietveld-refinements, justified by their low scattering power for x-rays.

Lattice parameters, thermal expansion and structural data were obtained from the high-temperature diffraction experiments. Refined atomic positions as a function of temperature are available from the authors on request. Fig. 3 shows the normalized lattice parameters of $[\text{Ca}_8(\text{OH})_8][\text{Al}_8\text{Si}_4\text{O}_{24}]$ -**SOD** and $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD**, respectively, as function of temperature.

The coefficients β_i , γ_i and δ_i , as well as the refined lattice parameter a_0 at $T_0 = 273 \text{ K}$ as given in

$$a_T = a_0[1 + \alpha_T(T - T_0)] \quad (1)$$

with

$$\alpha_T = \beta_i + \gamma_i(T - T_0) + \delta_i(T - T_0)^2 \quad (2)$$

were obtained from the lattice parameters as function of tem-

perature, using a standard least squares method and are given in Table 1.

The thermal expansion coefficient of bicchulite ($11.8(9) \cdot 10^{-6} \cdot \text{K}^{-1}$ at $T_0 = 273 \text{ K}$) exceeds that of the Eu-bearing compound ($3.4(3) \cdot 10^{-6} \cdot \text{K}^{-1}$ at $T_0 = 273 \text{ K}$) by a factor of three. The thermal expansion coefficients of SOD-type compounds reported so far show an immense variation, ranging e.g. from $2.2(5) \cdot 10^{-6} \cdot \text{K}^{-1}$ for $[\text{Na}_{0.3}\text{K}_{2.9}\text{Rb}_{4.8}\text{Cl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]$ -**SOD** to $13.7(6) \cdot 10^{-6} \cdot \text{K}^{-1}$ for $[\text{Li}_{7.97}\text{Na}_{0.03}\text{Cl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]$ -**SOD**, two examples of SOD-type materials with an Al:Si ratio of 1 (Henderson and Taylor, 1978). The authors reported on a correlation between the mean thermal expansion coefficient α and the cubic lattice parameter of aluminosilicate-sodalites with an Al:Si-ratio of 1. It is shown in Fig. 4 that the perceived relationship is valid for bicchulite as well, although it has an Al:Si-ratio of 2, while the behaviour of the Eu-bearing compound (Al:Si = 5) is clearly different. No indication of a structural phase transition could be detected for any of the compounds on heating up to the thermal decomposition. However, in our high-temperature experiments on $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD**, at $T = 1030(10) \text{ K}$ new reflections appeared in the powder pattern which could be identified as belonging to a melilite-type compound. That points at a decomposition of the bicchulite-type compound into the corresponding melilite-type compound and water. The line width of the reflections of the melilite-type compound is considerably larger than the width of the lines of the SOD-type compound. This indicates a significant de-

crease of the crystallite-size during the decomposition. An evaluation of significant anisotropic strain or size effects was beyond experimental resolution. At about $T = 1110(11)$ K the decomposition was complete and only the melilite-type compound persisted. In the present work the decomposition was studied for $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD** only, because the decomposition temperature of bicchulite (at $p_{\text{H}_2\text{O}} = 0.1$ GPa and $a_{\text{H}_2\text{O}} = 1$) was already reported by Gupta and Chatterjee (1978) to be $T_{\text{decomp}} = 916(5)$ K. Due to the limited time scale on which the experiment was performed, it cannot be expected that thermodynamic equilibrium existed during the decomposition process. Thus, the decomposition temperature stated should not be taken at face value. For the Rietveld-refinements of the structures in the two-phase-region, structural models of both phases were included and quantitative phase analyses performed. In the two-phase region, no significant changes in the lattice parameters for both compounds could be observed. A possible explanation for this behaviour might be a temperature-buffering due to the energy consumption caused by the transformation process. Recently an analogous buffering was reported to occur during a pressure induced first order phase transition in spodumene (Arlt and Angel, 2000).

3.1 Structural mechanism of the thermal expansion

The structural mechanisms of the thermal expansion could be derived from the Rietveld-refinements. Bond lengths and

angles of both compounds at room temperature and the corresponding maximum temperatures are given in Tables 2 and 3, respectively. In the following, the expansion mechanisms of both compounds are discussed for each of the coordination polyhedra in terms of bond length- and angular changes considered as relevant.

While the **T**-O-bond length in the framework $[\text{TO}_4]$ -tetrahedra remains constant in both compounds, the **T**-**T**-distance increases considerably. Note that the relative increase in bicchulite exceeds that in the Eu-bearing compound by a factor of 2. The intratetrahedra O-**T**-O angles change towards a stronger distortion of the tetrahedron in bicchulite, while the tetrahedra in the Eu-bearing compound remain virtually 'ideal'. This observation is probably related to the fact, that the Al:Si-ratio of the latter compound is much higher than in bicchulite. It has been observed before (Peters, Knorr, Knapp and Depmeier, 2005) that polyhedra will distort more strongly with temperature, if they are centered by two different cation species. This 'mixing' effect on the **T**-site is therefore expected to be stronger for bicchulite than for the Eu-bearing compound, because of the less homogeneous Al/Si-distribution in the former compound. The intertetrahedra **T**-O-**T** angles expand linearly with temperature in both compounds. This effect becomes noticeable only from the general trends. The main expansion mechanism of the framework is most probably the linear decrease of the tilt angle φ . While in bicchulite its change is $-0.5^\circ/100$ K, it only decreases by about one quarter of this value for $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD**. This observa-

tion correlates well with the thermal expansion data reported above.

In the compounds reported here, the cage-cations **M** and the oxygen atoms of the (OH)-groups form Na_4Cl_4 -like clusters, which have the shape of a deformed *tristetrahedron*. Fig. 5 shows a schematic drawing of the cluster together with a part of the framework. The **M** and the (OH)-groups alternately point at the centers of the six-membered rings of the sodalite β -cages. The **M**-cations are coordinated almost octahedrally by three neighbouring O(H)-oxygens and three of the six oxygens of the cage's six-rings. The **M**–**M**-distance increases with temperature and the relative changes are of the same order of magnitude for both compounds. The **M**–O-distance in the Eu-bearing compound undergoes no significant changes, while in bicchulite the Ca–O-distance increases. This observation lends support to the idea that the $\text{Ca}_4(\text{OH})_4$ -cluster does not follow the expansion of the framework. This reasoning finds support by the observation that in bicchulite the **M**–O(H)-distance decreases with increasing temperature, thus compensating for the reduced bond valence contribution to **M** from the cage O-ions. By way of contrast, the **M**–O(H)-distance increases in the Eu-bearing compound, thereby following the expansion of the framework. A similar effect can be observed for the behaviour of the O(H)-ions. Their distance to the nearest framework oxygens remains constant during the temperature increase in $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD**, again indicating a movement that follows the expansion of the cage, while it increases in bicchulite. Important changes are also

observed for the distances between the (OH)-groups. In bicchulite, the oxygens approach each other significantly, while in the Eu-bearing compound they withdraw. This finds additional support by the increasing distortion of the $[\text{MO}_6]$ -octahedron in bicchulite, while the intra-octahedral angles in this polyhedron stay constant in the Eu bearing compound.

These observations can be summarized by saying that the position and orientation of the $\text{Ca}_4(\text{OH})_4$ -cluster in the sodalite β -cage of bicchulite remains virtually unaffected by the untilting of the sodalite framework, whereas the $[(\text{EuCa}_3)(\text{OH})_4]$ -cluster in $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD** is strongly coupled with the framework, probably as a result of the stronger coulombic interaction. An analogous behaviour was reported for highly charged $[\text{Fe}_4\text{S}]$ -clusters in danalite in comparison to the $[\text{Na}_4\text{Cl}]$ -cluster in the mineral sodalite (Antao, Hassan and Parise, 2003).

Henderson and Taylor (1978) clearly showed a correlation $\alpha(a_0)$ for some SOD-type compounds with an Al:Si-ratio equal to one. This observation seems to hold for bicchulite as well, but is obviously incorrect for the Eu-bearing compound. Dempsey and Taylor (1980) suggested that the differences in the thermal expansion behaviour of sodalites could be explained by the different behaviour of their cage-cation (**M**)–cage-anion (**X**) bonds. In all compounds studied by Henderson and Taylor (1978), the corresponding force-constants of the **M**–**X**-bonds were considered to be broadly similar (Dempsey and Taylor, 1980). The authors concluded that for these compounds the thermal expansion coefficient mainly depends on the degree of

the framework collapse, being larger for larger tilt angles φ . The authors additionally stated that higher force-constants of the **M–X**-bonds act as a restraint for the untilting of the sodalite-framework. This idea was supported by e.g. Hassan and Grundy (1984). In the two compounds reported here, the force-constants of the **M–X**-bonds can be expected to be significantly higher for the compound containing trivalent Eu. Though $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]\text{-SOD}$ shows a larger tilt-angle φ than $[\text{Ca}_8(\text{OH})_8][\text{Al}_8\text{Si}_4\text{O}_{24}]\text{-SOD}$, and thus should be expected to have a higher thermal expansion coefficient (Dempsey and Taylor, 1980), the untilting of the sodalite-framework is resisted by the stronger mean (**M–X**)- and (**M**-framework-oxygen)-bonds, due to the higher coulombic interactions. In conclusion, this work supports the concepts formulated by e.g. Dempsey and Taylor (1980); Hassan and Grundy (1984). No discontinuities in the thermal expansion of the two compounds studied could be observed, because neither the fully expanded state of the framework, nor the special position of $\frac{1}{4}$ for the cage-cations was reached before the thermal decomposition took place (see e.g. Henderson and Taylor, 1978; Dempsey and Taylor, 1980).

4 A possible mechanism for the transformation from the sodalite to the melilite topology

The SOD-type compounds were synthesized by hydrothermal treatment of the melilite-type compounds. During the re-

verse process, thermal decomposition, the melilite-type compound (and water-vapour) are recovered. No extra crystalline phases could be detected by x-ray diffraction methods and no amorphous products left their mark in the background of the diffractograms. We are aware, that the formation of the SOD-type compound from melilite and water cannot be expected to follow the same structural mechanism as the thermal decomposition. In general, the SOD-framework structure with tetrahedral four- and six-membered rings is transformed into a layered structure of tetrahedral five-membered rings. The hypothetical mechanism thus should clarify, how the 3D-framework can be transformed into a layered 2D-structure of four- and six-membered rings. Secondly, a simple mechanism needs to be found which transforms the layer of four- and six-membered rings into a layer entirely consisting of five-membered rings. We assume: *i*) The number of bonds, which need to be broken, should be minimal. *ii*) The crystallographic orientation of the two structures should account for the postulated simplicity of the mechanism. Thus, symmetry elements of the melilite structure should be geometrically related to high-symmetry-directions of the topological symmetry of SOD. This leads to a limited amount of differently oriented domains. *iii*) Once started, the reaction should proceed by self-propagation. The moderate temperature at which the decomposition takes place casts into doubt a complete disruption of the tetrahedral conformation, and subsequent formation of the new structure from small tetrahedral units. Still, it cannot be avoided that several strong bonds need to be broken during the decomposition.

In reconstructive phase transitions, the symmetry-groups of both phases are connected via a common sub- or super-group (Tolédano and Dmitriev, 1996). We are aware of the fact, that such group-subgroup-relationships are phenomenologic approaches to the theory of reconstructive phase transitions.

4.1 The transformation of the framework-structure to a layered structure

A simple way to transform the sodalite-framework of bicchulite into an approximate layer-type compound is to break three bonds per sodalite cage pointing parallel one of the $\langle 110 \rangle$ -directions. This could be caused by the evaporating water during the decomposition process. A schematic drawing of one sodalite cage with the corresponding (broken) bonds is shown in Fig. 6. Taking that process as an initializing step to the transformation, the occurrence of 6 domains of melilite-type crystallites has to be expected.

In order to find a crystallographic setting which allows an easy comparison of both structures, we transform the melilite structure by using

$$P = \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (3)$$

in

$$\mathbf{a}'_i = \mathbf{a}_i \cdot P, \quad (4)$$

with $\mathbf{a}'_i$ being the transformed basic vectors and $\mathbf{a}_i$ the

initial basic vectors. After transformation, the $\langle 001 \rangle$ - and the $\langle 100 \rangle$ -directions of the melilite-type crystallites are parallel to the corresponding $\langle 110 \rangle$ -directions of the SOD-type. The transformed $\langle 010 \rangle$ -direction of the melilite-type compound is parallel to the corresponding $\langle 100 \rangle$ -directions of SOD. In order to obtain the same setting for both structures, the SOD-type compound has to be transformed by e.g.

$$P = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 1 & 0 & 1 \end{pmatrix} \quad (5)$$

with an origin shift of $[\frac{1}{2}, 0, \frac{3}{4}]$. The obtained transformed basic vectors of the SOD-type structure hence are referred to as $\mathbf{a}''_i$.

For a comparison of the two structures in the corresponding directions see Fig. 7. For the sake of simplicity, the transformed lattice parameters a'_i of the melilite type-compound have been used for both compounds, while the fractional coordinates of the T-cations were obtained from the transformed coordinates of the corresponding room temperature structures of the melilite- and the sodalite-type compound, respectively.

The transformed lattice parameters of the melilite-type compound in the two-phase region (measurement at 1045(10) K) are $a'_1 = a'_2 = 10.9800 \text{ \AA}$, $a'_3 = 10.2360 \text{ \AA}$, and the transformed lattice parameters of the SOD are $a''_1 = a''_3 = 12.6022 \text{ \AA}$, $a''_2 = 8.9111 \text{ \AA}$. Taking into account that $a_1 = a_2$ in the tetragonal system and assuming a simple averaging of the a''_1 and a''_2 lattice parameters of the

SOD-type compound, our model predicts a tetragonal lattice parameter of $a_{1,2} = 10.7566 \text{ \AA}$. This value is in excellent agreement (2 % deviation) with the experimentally obtained lattice parameter $a'_{1,2}$ of the melilite type compound. The volume decrease of the solid phases during the decomposition is about 13 %. The dominating direction hereby is the tetragonal a''_3 -direction, which, following our model, decreases in length by about 19 % during the transformation from the sodalite framework structure to the melilite layer structure.

4.2 The formation of the tetrahedral five-membered rings and the relationship between the two topologies

The displacement of the **T**-cations in the corresponding directions is shown in Fig. 8(a-c). It can be seen that one type of **T**-cations does not undergo any changes in its fractional coordinates, namely those **T** on the special positions (0,0,0), the face-, edge- and the body-center(s) of the transformed cell. The remaining **T**-cations are displaced such that an unfolding of the sodalite β -cage hemispheres is obtained, thus leading to an almost 'flat' conformation of $[\text{TO}_4]$ -polyhedra. Additionally, two types of those 'moving' **T**-cations have to be distinguished. The first type moves only in the a''_3 direction, whereas the other type also moves on the face diagonal of the a''_1 - a''_2 -plane. As can be seen in Fig. 8 (c), the anti-parallel movement of the corresponding four **T**-cations per layer leads to the formation of the tetrahedral

five-membered rings from the six- and four-membered rings of the sodalite framework, thus four bonds are broken and four new bonds build up. The anti-parallel movement most probably gives rise to the averaging of the sodalite a''_1 and a''_3 lattice parameter. Consequently, instead of a mirror plane (in SOD) a $\bar{4}$ -axis appears in the melilite type compound in a'_3 . Fig. 9 shows two characteristic **T**-**T** zigzag chains, which are a typical structural feature of both topologies in the projection along the (melilite) [001]-direction. One type of these chains shown is almost congruent in both structures, with **T**-centers only moving in [001]-direction. Going from the sodalite topology to the melilite topology, the second chain has to be mirrored at the corresponding face diagonal. Thus, the main difference between the two topologies besides the framework-layer problem is the chirality of this second zigzag-chain.

5 Conclusions

A simple geometric relationship between the sodalite and the melilite topology is given. It most probably explains, why only melilite-type compounds plus water and no detectable other phases are formed during the decomposition of bicchulite-type compounds. Note, that assuming the transition mechanism as proposed here, the melilite-type compound first formed by the decomposition of the bicchulite-type compound is not essentially ordered with respect to the occupation of the two topologically distinct **T**-sites. We expect that the melilite-type compound formed from the dis-

ordered bicchulite-type compound bears Al-Si-disorder on both tetrahedrally coordinated positions, with a stoichiometry Al:Si equal to the absolute ratio of both species. Therefore, we conclude that the first formed melilite is thermodynamically metastable. It can be expected that an ordering process takes place afterwards, perhaps at higher temperatures, delivering the activation energy which is necessary for the diffusion of Si and Al in the melilite-type structure. Corresponding experiments are in progress.

Acknowledgments: We wish to thank the Deutsche Forschungsgemeinschaft (DFG) for financial support (De 412/27-1, 2), S. Bass and E. Kirchhoff for their help with some of the syntheses and the workshop staff for the construction of the furnace. Additionally, we wish to thank the *HASYLAB / DESY* for providing beam time at the B2 diffractometer (grant II-04-033). Two anonymous reviewers helped to improve the manuscript and are gratefully acknowledged.

References

- Antao, S.M.; Hassan, I.; Parise, J.B.: The structure of danalite at high temperature obtained from synchrotron radiation and rietveld refinements. *Can. Mineral.* **41** (2003) 1413-1422.
- Arlt, T.; Angel, R.J.: Pressure buffering in a diamond anvil cell. *Min. Mag.* **64** (2000) 241-245.
- Dann, S.E.; Mead, P.J.; Weller, M.T.: Löwenstein's rule extended to an aluminium rich framework. The structure of bicchulite, $\text{Ca}_8[\text{Al}_8\text{Si}_4\text{O}_{24}](\text{OH})_8$, by MASNMR and neutron diffraction. *Inorg. Chem.* **35** (1996) 1427-1428.
- Dempsey, M.J.; Taylor, D.: Distance least Squares Modelling of the Cubic Sodalite Structure and of the Thermal expansion of $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{I}_2$. *Phys. Chem. Mineral.* **6** (1980) 197-208.
- Depmeier, W.: Tetragonal tetrahedra distortions in cubic sodalite frameworks. *Acta Cryst.* **B40** (1984) 185-191.
- Depmeier, W.: Remarks on symmetries occurring in the sodalite family. *Z. Kristallogr.* **199** (1992) 75-89.
- Depmeier, W.: The Sodalite Family - A Simple but Versatile Framework Structure. In: *Micro- and Mesoporous Mineral Phases, Reviews in Mineralogy and Geochemistry* **57** (Eds. G. Ferraris, S. Merlino), p. 203-241. Mineralogical Society of America, Geochemical Society 2005.
- Enck, F.D.; Dommel, J.G.: Behaviour of thermal expansion of NaCl at elevated temperatures. *J. Appl. Phys.* **36** (1965) 389-394.
- Gupta, A.K.; Chatterjee, N.D.: Synthesis, composition, thermal stability, and thermodynamic properties of bicchulite, $\text{Ca}_2[\text{Al}_2\text{SiO}_6](\text{OH})_2$. *Am. Mineral.* **63** (1978) 58-65.
- Hammersley, A.P. /ESRF: fit2D, program for the analysis of twodimensional powder diffraction data. (1987-2001)
- Hassan, I; Grundy, H.D.: The Crystal Structures of Sodalite-Group Minerals. *Acta Cryst.* **B40** (1984) 6-13.
- Henderson, C.M.B.; Taylor, D.: The thermal expansion of synthetic aluminosilicate-sodalites $M_8(\text{Al}_6\text{Si}_6\text{O}_{24})X_2$. *Phys. Chem. Mineral.* **2** (1978) 337-347.
- Knapp, M.; Joco, V.; Baehtz, C.; Brecht, H.H.; Berghaeuser, A.; Ehrenberg, H.; von Seggern, H.; Fuess, H.: Position-Sensitive Detector System OBI for High Resolution X-Ray Powder Diffraction using on-site readable Image Plates. *Nucl. Instrum. Meth.* **A521** (2004/2) 565-570.
- Knapp, M.; Baehtz, C.; Ehrenberg, H.; Fuess, H.: The synchrotron powder diffractometer at beamline B2 at HASYLAB / DESY: status and capabilities. *J. Synchrotron Rad.* **11** (2004/1) 328-334.
- Löns, J.; Schulz, H.: Strukturverfeinerung von Sodalith, $\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}\text{Cl}_2$. *Acta Cryst.* **23** (1967) 434-436.
- Malinovskii, Yu.A.; Panina, Z.V.: X-ray study of

- chromium- and boron-doped synthetic $\text{Ca}_2\text{Al}(\text{Al Si})\text{O}_7$ gehlenites. *Kristallografiya* **41** (1996) 240-247.
- McCusker, L.B.; Liebau, F.; Engelhardt, G.: Nomenclature of structural and compositional characteristics of ordered microporous materials with inorganic hosts. *Pure Appl. Chem.* **73** (2001) 381-394
- Pathak, P.D.; Vasavada, N.G.: Thermal expansion of NaCl, KCl and CsBr by X-ray diffraction and the law of corresponding states. *Acta Cryst.* **A26** (1970) 655-658.
- Pauling, L.: The structure of sodalite and helvite. *Z. Kristallogr.* **74** (1930) 213-225.
- Peters, L.; Knorr, K.; Knapp, M.; Depmeier, W.: Thermal expansion of gehlenite, $\text{Ca}_2\text{Al}[\text{AlSiO}_7]$, and the related aluminates $\text{LnCaAl}[\text{Al}_2\text{O}_7]$ with $\text{Ln}=\text{Tb}$, Sm. *Phys. Chem. Mineral.* (2005), in print.
- Rodriguez-Carvajal, J.: Fullprof V.2.20, program for Rietveld, profile matching and integrated intensity refinement, Laboratoire Léon Brillouin, Saclay (2002).
- Sahl, K.; Chatterjee, N.D.: The crystal structure of bicchulite, $\text{Ca}_2[\text{Al}_2\text{SiO}_6](\text{OH})_2$. *Z. Kristallogr.* **146** (1977) 35-41.
- Sahl, K.: Refinement of the crystal structure of bicchulite, $\text{Ca}_2[\text{Al}_2\text{SiO}_6](\text{OH})_2$. *Z. Kristallogr.* **152** (1980) 13-21.
- Tolédano, P.; Dmitriev, V.: *Reconstructive Phase Transitions in Crystals and Quasicrystals*. World Scientific, Singapore 1996.
- Warren, B.E.: The structure of melilite, $(\text{Ca,Na})_2(\text{Mg,Al})_1(\text{Si, Al})_2\text{O}_7$. *Z. Kristallogr.* **74** (1930) 131-138.
- Weller, M.T.: Where zeolites and oxides merge: semi-condensed tetrahedral frameworks. *J. Chem. Soc., Dalton Trans.* (2000) 4227-4240
- Winkler, B.; Milman, V.; Pickard, C.J.: Quantum mechanical study of Al/Si disorder in leucite and bicchulite. *Min. Mag.* **68** (2004) 819-824.

Figure 1: Schematic view of the bicchulite structure . Small spheres represent oxygen, large spheres **M**-ions, light tetrahedra are $[\text{TO}_4]$ -coordination polyhedra, the black tetrahedron represents the $[\text{OH}]_4$ -tetrahedron. The protons are removed.

Table 1: Refined lattice parameter $a_{1,0}$ at $T= 273$ K, and coefficients for the tensor component α_{11} for the compounds $|\text{Ca}_8(\text{OH})_8|[\text{Al}_8\text{Si}_4\text{O}_{24}]$ -**SOD** and $|\text{Ca}_6\text{Eu}_2(\text{OH})_8|[\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD** .

	$ \text{Ca}_8(\text{OH})_8 [\text{Al}_8\text{Si}_4\text{O}_{24}]$ - SOD	$ \text{Ca}_6\text{Eu}_2(\text{OH})_8 [\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ - SOD
i	1	1
$a_{i,0} \cdot \text{\AA}^{-1}$	8.8233(8)	8.8610(2)
$\beta_i \cdot 10^6 \cdot \text{K}$	11.8(9)	3.4(3)
$\gamma_i \cdot 10^9 \cdot \text{K}^2$	7.3(2)	11.5(8)
$\delta_i \cdot 10^{12} \cdot \text{K}^3$	0	-8.4(7)

Figure 2: Schematic view of the melilite structure along (a) the $[001]$ -axis and (b) the $[100]$ -axis. Small spheres represent oxygen, large spheres $\mathbf{M}$ -ions, light grey tetrahedra stand for $\mathbf{T}^1$ -positions and dark tetrahedra forming $[\mathbf{T}_2\mathbf{O}_7]$ -units represent $\mathbf{T}^2$. Note the tetrahedral layers parallel (001).

Figure 3: Temperature dependence of the normalized lattice parameter a/a_0 of $[\text{Ca}_8(\text{OH})_8][\text{Al}_8\text{Si}_4\text{O}_{24}]$ -SOD (squares) and $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -SOD (diamonds). Lines correspond to polynomial fits with the coefficients given in Table 1.

Figure 4: Mean thermal expansion coefficient α as function of the lattice parameter $a_0 = a_{295\text{ K}}$ for several SOD-type compounds. Empty squares represent data by Henderson and Taylor (1978). Filled diamonds represent the corresponding values for $[\text{Ca}_8(\text{OH})_8][\text{Al}_8\text{Si}_4\text{O}_{24}]$ -SOD and $[\text{Ca}_6\text{Eu}_2(\text{OH})_8][\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -SOD. Note that the value for the latter compound does not fit the observed trend indicated by the solid lines. The broken line indicates the discontinuity in the thermal expansion curve proposed by Henderson and Taylor (1978).

Figure 5: Schematic view of a section of the bicchulite structure . Dark spheres represent **M**-ions, light spheres O-ions, tetrahedra are [TO₄]-coordination polyhedra, the dark polyhedron represents the [Na₄Cl₄]-like cluster (*tristetrahedron*) of **M** and OH-ions. The protons are removed.

Figure 6: Schematic view of one sodalite cage along the [001]-axis. Spheres represent **T**-cations, black lines stand for **T–T**-distances. The grey lines represent linkages of [TO₄]-polyhedra which need to be broken during the initial step of the transformation.

Figure 7: Schematic view of the sodalite-type structure(a-c) along the transformed $[100]$ (a), $[010]$ (b), $[001]$ (c) and the melilite-type structure (d-f) along the transformed $[100]$ (d), $[010]$ (e) and $[001]$ -axes (f). Spheres represent T-cations, black lines stand for T-T-distances. The grey lines represent linkages of $[TO_4]$ -polyhedra which have been broken during the initial step of the transformation. The transformed lattice parameters a'_i of the melilite-type compound have been used for both transformed cells in order to simplify the comparison.

Figure 8: Overlaid projections of the transformed sodalite- and melilite type structures along the transformed melilite [100] (a), [010] (b) and [001] (c) directions. Spheres represent T-cations, black and grey lines stand for T-T-distances in the sodalite-type compound and the melilite-type compound respectively. Grey arrows indicate the displacement of the ions during the transformation.

Figure 9: Overlaid projection of the transformed sodalite- and melilite type structures along the transformed melilite [001] direction. Spheres represent **T**-cations, black and grey lines stand for **T**–**T**-distances in the sodalite- and the melilite-type compound, respectively. Grey arrows indicate the displacement of the ions during the transformation. Note the different chirality indicated by 'm' of one of the characteristic zigzag-chains in the projection of the sodalite- and the melilite structure, respectively.

Table 2: Bond lengths (Å) of $|\text{Ca}_8(\text{OH})_8|[\text{Al}_8\text{Si}_4\text{O}_{24}]$ -**SOD** and $|\text{Ca}_6\text{Eu}_2(\text{OH})_8|[\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD** at room temperature and the corresponding maximum temperature (K). Bold numbers indicate changes with respect to increasing temperature which are statistically significant and/or considered relevant and therefore discussed in the text.

	$ \text{Ca}_8(\text{OH})_8 [\text{Al}_8\text{Si}_4\text{O}_{24}]$ - SOD		$ \text{Ca}_6\text{Eu}_2(\text{OH})_8 [\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ - SOD	
$T(\text{K})$	295(3)	692(7)	298(3)	1024(10)
T–T	3.120(2)	3.138(2)	3.133(2)	3.150(2)
T–O	1.71(1)	1.71(1)	1.72(1)	1.72(1)
M–M	3.58(1)	3.61(1)	3.67(1)	3.73(1)
M–O	2.48(1)	2.52(1)	2.44(1)	2.46(1)
M–O(H)	2.32(1)	2.25(1)	2.34(1)	2.39(1)
O–O(H)	3.06(1)	3.16(1)	3.10(1)	3.10(1)
O(H)–O(H)	2.95(1)	2.71(1)	2.86(1)	2.92(1)

Table 3: Tilt angle φ and bond angles ($^\circ$) of $|\text{Ca}_8(\text{OH})_8|[\text{Al}_8\text{Si}_4\text{O}_{24}]$ -**SOD** and $|\text{Ca}_6\text{Eu}_2(\text{OH})_8|[\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ -**SOD** at room temperature and the corresponding maximum temperature (K). Bold numbers indicate changes with respect to increasing temperature which are statistically significant and/or considered relevant and therefore discussed in the text.

	$ \text{Ca}_8(\text{OH})_8 [\text{Al}_8\text{Si}_4\text{O}_{24}]$ - SOD		$ \text{Ca}_6\text{Eu}_2(\text{OH})_8 [\text{Al}_{10}\text{Si}_2\text{O}_{24}]$ - SOD	
$T(\text{K})$	295(3)	692(7)	298(3)	1024(10)
φ	31.1(3)	29.2(3)	32.1(3)	31.1(3)
O–T–O (4×)	109(1)	107(1)	109(1)	109(1)
O–T–O (2×)	111(1)	114(1)	110(1)	110(1)
T–O–T	131(1)	133(1)	130(1)	133(1)
O–M–O	92(1)	89(1)	93(1)	93(1)
O(H)–M–O(H)	78(1)	72(1)	75(1)	76(1)
O–M–O(H)	95(1)	99(1)	95(1)	95(1)