Journal of Thermal Analysis, Vol. 25 (1982) 109–115

STUDIES OF THE POLYMORPHIC TRANSFORMATIONS OF DICALCIUM SILICATE (Ca_2SiO_4) AND SODIUM TETRAFLUOROBERYLLATE (Na_2BeF_4) BY THERMOSONIMETRY AND DIFFERENTIAL SCANNING CALORIMETRY

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The polymorphic transformations of Ca_2SiO_4 and Na_2BeF_4, have been studied by thermosonimetry, TS. The results for Na_2BeF_4 are compared with results from DSC-investigations. Thermosonimetry is shown to be a good and sensitive method for studying solid state transformations with high activation energies which accompany the α'-Ca_2SiO_4 $\rightleftarrows$ γ-Ca_2SiO_4 and the α'-Na_2BeF_4 $\rightleftarrows$ γ-Na_2BeF_4 transformations.

Dicalcium silicate, Ca_2SiO_4, has several modifications and hence is of special interest wherever it is a constituent, as in Portland cement, in refractory or steelmaking systems. It is well known that the transformation from the so-called α'-form or the β-form to the γ-form, which occurs around 600-700° on cooling, is accompanied by an increase in volume of nearly 10 percent. When this phase change begins, it spreads rapidly through the mass, heat beeing developed; and the great increase in volume which accompanies the change, results in the shattering of the crystals into dust. This process is usually referred to the dusting of the compound.

Since the thermosonimetric method /TS/ is basically a technique for detecting mechanical vibrations induced by volumetric changes in solids [1], we decided to include Ca_2SiO_4 in our studies of polymorphic transformations in solids by thermosonimetry.

In this work we also included an investigation of the compound Na_2BeF_4, sodium tetrafluoro beryllate, which is known to be a weakened model of Ca_2SiO_4 and with similar polymorphic transformations [2-4]. Fig. 1 gives a diagram of the phase transformations in Na_2BeF_4 suggested by Toropov [4].

$$\gamma\text{-}Na_2BeF_4 \xrightarrow[220^{o}C]{493K} \alpha'\text{-}Na_2BeF_4 \underset{320^{o}C}{\overset{593K}{\rightleftharpoons}} \alpha\text{-}Na_2BeF_4$$

Orthorhombic	Orthorhombic	Hexagonal
olivine	β-K_2SO_4	α-K_2SO_4

343 K 70^{o}C ? 380 K 110^{o}C

β-Na_2BeF_4

Fig. 1. Solid-solid phase transformations in Na_2BeF_4 according to Toropov [4].

EXPERIMENTAL

Materials

The two compounds were prepared from analytical grade reagents. Ca_2SiO_4 was prepared by sintering a tablet of $CaCO_3$ and SiO_2, in the molar ratio 2:1, at 1240^{o} for 17 hrs in the TS-furnace. The product was heated up to 1550^{o} and then cooled.

For the preparation of Na_2BeF_4 stoichiometric amounts of sodium fluoride and beryllium fluoride were melted together in a platinum crucible in a purified nitrogen atmosphere.

Methods

a/ Thermosonimetry. The basis of the experimental set-up is given in earlier presentations of the method by Lønvik et al. [5,6]. All experiments were carried out in air. The heating rate during the TS-investigations of Na_2BeF_4 was 5, 10 or 20 deg/min, while the cooling rate during the investigation of Ca_2SiO_4 was 10 deg/min.

b/ Differential scanning calorimetry. The investigations of Na_2BeF_4 were carried out with a differential scanning calorimeter, DSC-2, from Perkin-Elmer. Platinum crucibles were used as containers. The calibration of the calorimeter followed the procedure given by Perkin-Elmer [7] using metallic indium, tin and zinc as standards. The results of the calibration are given in a paper by Holm and Ræder [8]. The heating rates used were 5, 10 and 20 deg/min. Purified nitrogen was passed through the calorimeter during all runs.

RESULTS AND DISCUSSION

The phase diagram for pure dicalcium silicate is given in Fig. 2. According to this diagram, the α'-Ca_2SiO_4 will convert to γ-Ca_2SiO_4 or β-Ca_2SiO_4 on cooling somewhere between 725 and

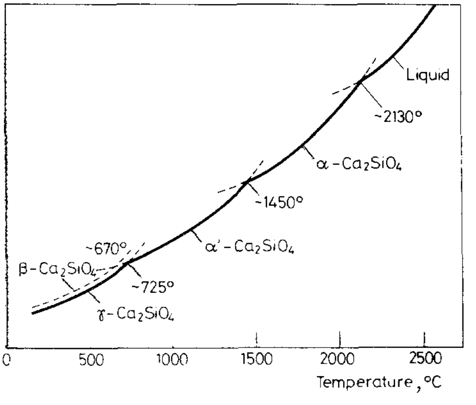

Fig. 2. Schematic illustration of relative stabilities of various modifications of Ca_2SiO_4 [9].

670°. By comparing this phase diagram with the TS-activity diagram for Ca_2SiO_4 in Fig. 3, one finds a region with extremely high TS-activity in this temperature range. There is some activity around 750°, but most of the activity is concentrated in the range 700-600°. This activity is due to the large expansion in volume which accompanies the phase transformations α'-$Ca_2SiO_4 \rightarrow \gamma$-$Ca_2SiO_4$ and β-$Ca_2SiO_4 \rightarrow \gamma$-$Ca_2SiO_4$.

As shown in Fig. 3 the outbursts of activity continue down to about 400°, thus indicating a rather complicated mechanism and a high activation energy for the transformation from the α'-form which has the β-K_2SO_4 structure, to the γ-form with an orthorhombic olivine structure.

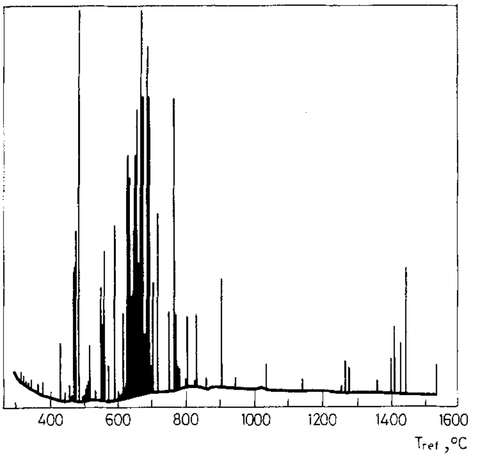

Fig. 3. TS-activity diagram for Ca_2SiO_4 cooling rate; 10 deg/min. Transformations at 1400° and around 700° are shown.

Fig. 4 shows the DSC-diagram /heating curve/ for Na_2BeF_4. The following solid-solid transformations were observed:

$$\beta\text{-}Na_2BeF_4 \xrightarrow{125^\circ} \gamma\text{-}Na_2BeF_4 \xrightarrow{220^\circ} \alpha'\text{-}Na_2BeF_4 \xrightarrow{322^\circ} \alpha\text{-}Na_2BeF_4$$

in good agreement with the data given in Fig. 1.

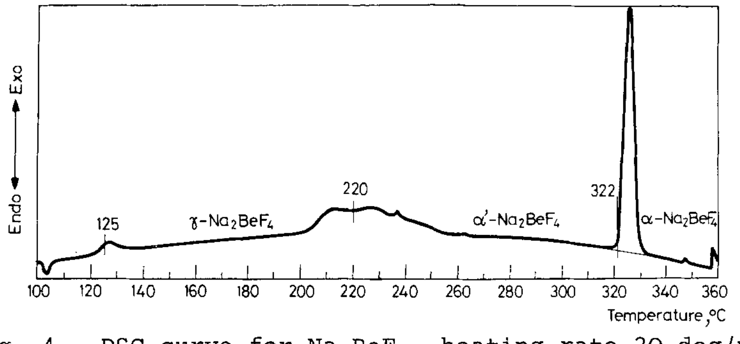

Fig. 4. DSC-curve for Na_2BeF_4, heating rate 20 deg/min.

The DSC cooling curves are given in Fig. 5. From these one sees that the $\alpha' \rightarrow \gamma$ transformation at 220° is only accompanied by a small change in $\underline{C}_p$ on cooling. Most of the energy is released by the transformation, which occurs between 120° and 110°, from the α'-phase directly to the γ-phase or to a mixture of the γ- and the β-phase. On heating β-Na_2BeF_4 transforms to γ-Na_2BeF_4 as can be seen from the peak at 125° in Fig. 4.

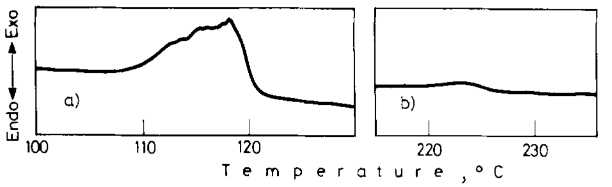

Fig. 5. Parts of a DSC-cooling curve for Na_2BeF_4, cooling rate 5 deg/min. Curve /a/ show transformation from α'-Na_2BeF_4 directly to γ-Na_2BeF_4 at 120° or from α'-Na2BeF_4 through an intermediate phase β-Na_2BeF_4. Curve /b/ shows change in $\underline{C}_p$ at 220°.

The results from the TS-investigations of Na_2BeF_4 are summarized in Figs. 6a, 6b and 7. On heating Na_2BeF_4 we observe a high activity in the region 220-260°, where γ-Na_2BeF_4 transforms to α'-Na_2BeF_4. Fig. 6 shows the TS recording of the first order transformation from α'-Na_2BeF_4 to α-Na_2BeF_4. On cooling Na_2BeF_4 /Fig. 6b/ there is some outburst of activity in a region which

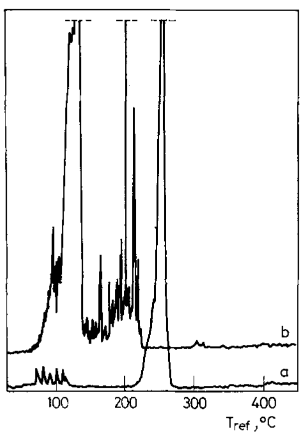

Fig. 6. TS-activity diagram for Na_2BeF_4, /a/ heating curve 10 deg/min, /b/ cooling curve 10 deg/min. Transformations from α'-Na_2BeF_4 to γ-Na_2BeF_4 and β-Na_2BeF_4 to γ-Na_2BeF_4 are shown.

starts at 220° and goes down to about 160°, and again a new region with strong TS-activity from 125° down to about 90°. As can be seen, these results are in good agreement with the DSC-cooling curves presented in Fig. 5.

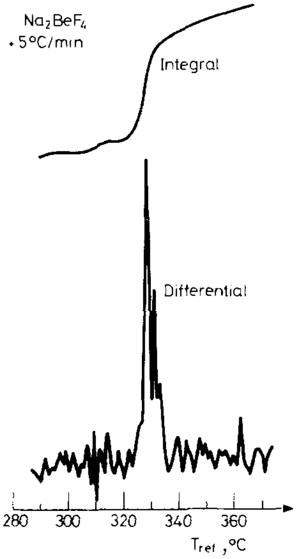

Fig. 7. TS-activity diagram for Na_2BeF_4, heating curve, heating rate 5 deg/min. Transformation from α'-Na_2BeF_4 to α-Na_2BeF_4 is shown.

CONCLUSIONS

From these studies we may conclude that

/1/ thermosonimetry is a very sensitive thermoanalytical method and

/2/ thermosonimetry is particularly a good method for studying transformations where high activation energies are involved, as in the case with the α'-$Ca_2SiO_4 \rightleftarrows \gamma$-$Ca_2SiO_4$ and α'-$Na_2BeF_4 \rightleftarrows \gamma$-$Na_2BeF_4$ transformations.

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This work has been supported by Borgestads Legat IV to J.L. Holm.

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ZUSAMMENFASSUNG – Die polymorphen Umlagerungen von Ca_2SiO_4 *und* Na_2BeF_4 *wurden thermosonimetrisch untersucht. Die für* Na_2BeF_4 *erhaltenen Ergebnisse werden mit Ergebnissen von DSC-Untersuchungen verglichen. Es wird gezeigt, dass die Thermosonimetrie eine gute und empfindliche Methode zur Untersuchung der hohe Aktivierungsenergien erfordernden Festkörperumlagerungen* $\alpha'\text{-}Ca_2SiO_4 \rightleftharpoons \gamma\text{-}Ca_2SiO_4$ *und* $\alpha'\text{-}Na_2BeF_4 \rightleftharpoons \gamma\text{-}Na_2BeF_4$ *ist.*

Резюме – С помощью термосониметрии изучены полиморфные превращения Ca_2SiO_4 и Na_2BeF_4. Результаты для Na_2BeF_4 сопоставлены с результатами ДСК исследования. Показано, что термосониметрия является хорошим и чувствительным методом при изучении твердотельных превращений, протекающих с высокой энергией активации, как например, превращения $\alpha'\text{-}Ca_2SiO_4 \rightleftharpoons \gamma\text{-}Ca_2SiO_4$ и $\alpha'\text{-}Na_2BeF_4 \rightleftharpoons \gamma\text{-}Na_2BeF_4$.