Thermochimica Acta, 72 (1984) 159–163
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

COMPARATIVE STUDIES OF STRUCTURAL TRANSFORMATIONS OF CARBONATE AND SILICA MINERALS BY MEANS OF THERMOSONIMETRY AND DIFFERENTIAL THERMAL ANALYSIS

Lønvik, K. [+] and Smykatz-Kloss, W. [++]
[+]Inst. for Eksperimentalfysikk, Univ. of Trondheim, Norway
[++]Mineralogical Inst. of the Univ., Karlsruhe, Germany

ABSTRACT

Many minerals exhibit structural transformations between low- and high-temperature modifications the nature and mechanism of which are not yet completely clear. Physical defects and chemical impurities influence the shape, and temperatures of the transformation effects. Especially the fine-grained, micro-and cryptocrystalline species of silica (e.g. agates, jasper, chrysoprase etc.) show a broadening of the low-high inversion effect, lower intensity (ΔT) of the peaks and lower inversion temperatures, compared with well crystallized quartz crystals. These effects can be measured by DTA. But this technique do not have resolution good enough in case of overlapping effects. This is much better in thermosonimetry (TS).

The combination of DTA and TS enables the exact determination of the nature of structural transformations (DTA) in dependence on the physical defect character of the minerals (TS). The present paper includes the data of the minerals strontianite ($SrCO_3$), witherite ($BaCO_3$) well and badly crystalline quartz (e.g., rose and smoky quartz, jasper, agate, chrysoprase) and cristobalite.

INTRODUCTION

Very recently the transformation behaviour of minerals and other crystalline materials have been extensively studied. The reason for this is due to the possible applicability of such materials exhibiting reversible structural transformations in heat storage techniques (e.g. ELDER; WIEDEMANN and SMYKATZ-KLOSS) or for being temperature standards (e.g. recommandations of the ICTA standardisation committee). A lot of minerals exist which are characterized by spontaneous and reversible structural transformations which can be measured by various thermal methods. The structural transformations are documented at distinct temperatures by sharp endothermic (on heating) respective exothermic (on cooling) effects of considerable intensity (ΔT). The transformation data of sulfides (e.g. argentite, chalcocite, see

0040-6031/84/$03.00

NIESZERY), sulfates (e.g. thenardite, see MEHROTRA et al., WIEDEMANN and SMYKATZ-KLOSS), carbonates, phosphates, silica or silicate minerals (SMYKATZ-KLOSS) are contained in physical handbooks and numerous special publications.

The following table shows the transformation temperatures (due to the literature) of those minerals which were used in this study.

Table 1

mineral	*formula*	*temp. of low-high transformation*
Cryiolite	Na_3AlF_6	562 °C
witherite	$BaCO_3$	810 and 981 °C
strontianite	$SrCO_3$	927 °C
quartz	SiO_2	573
cristobalite	SiO_2	270

COMMENTS TO MEASUREMENTS

These transformation data, however, are influenced by several preparative and apparative factors, e.g. by grinding methods or heating rate etc. Even in differential thermal analyses, which were run under highly standardiced conditions (as far as possible), considerable differences in shape, temperature and ΔT of their structural transformations may occur due to crystal physical defects or crystal chemical substitutions (e.g. SMYKATZ-KLOSS, 1983; NIESZERY and SMYKATZ-KLOSS). Thus, various samples of the mineral strontianite differ strongly in their transformation behaviour: e.g. temperatures between 870 and 935° C will be observed. However, comparable samples (in size, colour etc.) from the same locality do show reproducible results. This fact means that the occuring differences may primary be due to environmental factors during formation.

The same is true for silica minerals: Mainly microcrystalline quartz samples differ in their low-high inversion behaviour, often showing lower transformation temperatures and broad, less intensive effects compared to most macrocrystalline quartz specimens (e.g. those which have been formed in igneous rocks or hydrothermal veins). DTA curves of quartz specimens do sometimes exhibit more than one endothermic peak in the range of the transformation temperature.

This may mean that the inversion behaviour is not well interpreted as a second order transition, as it generally is. There are indeed some hints for the occurence of an additional phase

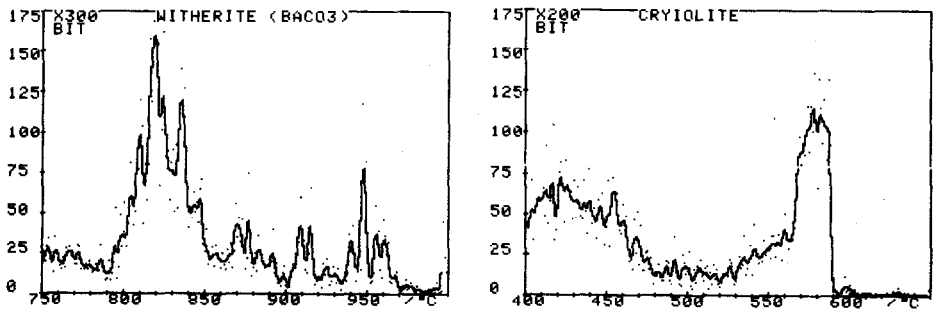
between the α - β phase of quartz, but that is still obscure. This effect, not very well but clearly observed in DTA, becomes much clearer in thermosonimetric curves: the transformation of quartz and strontianite and witherite as well seems to be a process much more complicated in nature than expected and interpreted up to now.

In the case where the transformation temperatures were used and recommended for temperature calibration and standards (quartz!, witherite !, cryiolite!) one has to be careful not to obtain wrong temperatures. The preparation techniques should always be comparable and standardized. It is not possible to take any kind of "quartz" for temperature calibration, because the temperature of this very specimen may differ more than 50° C from the textbook value of 573° C. The same is true for any other mineral. Even the silica species cristobalite, which seems to be the only mineral among the samples studied (compare with its TS curve), exhibiting a very sharp endothermic effect exactly at the "right" temperature of 270° C, may be characterized by much lower inversion temperatures due to crystal... physical defects which occur mainly in case of sedimentary cristobalites.

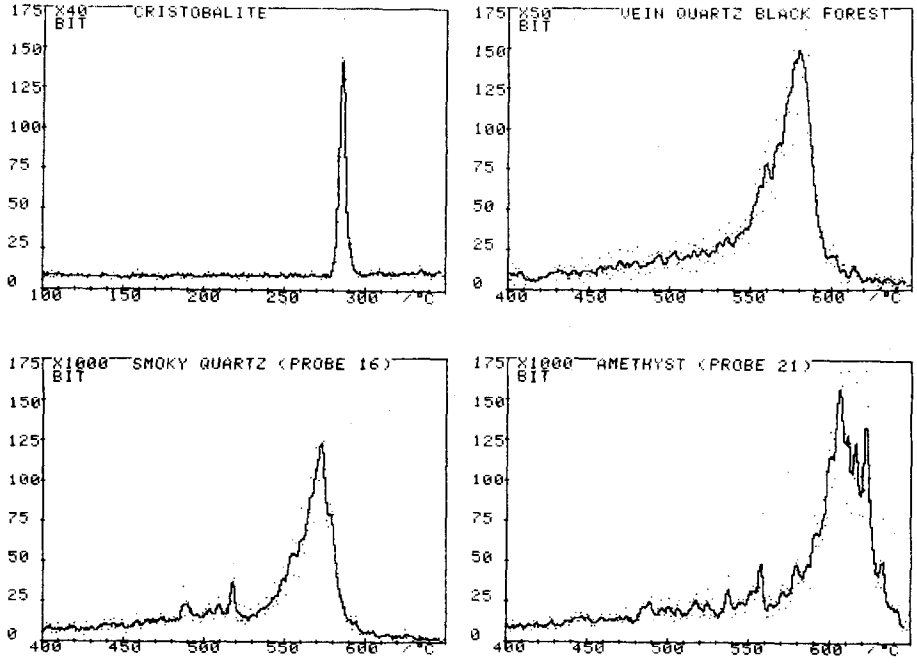
To explain the differences in the transformation behaviour fully, some more work has to be done.

METHODS AND RESULTS

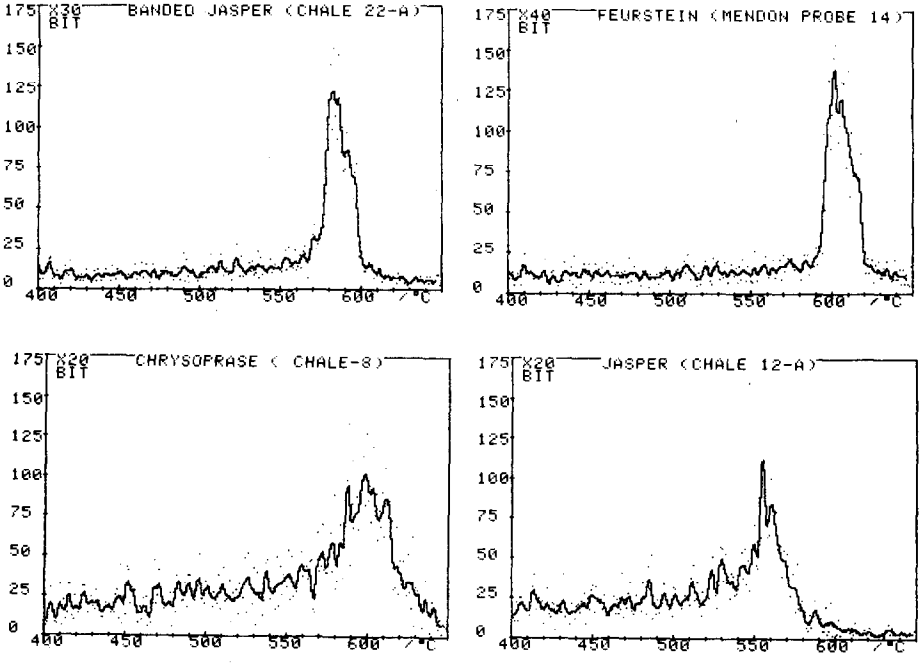
The analytical technique, Thermosonimetry (TS), applied in this investigation, is previously described elsewhere in literature (8). The typical thermosonigram obtained are illustrated by the four following arrangements of pictures.



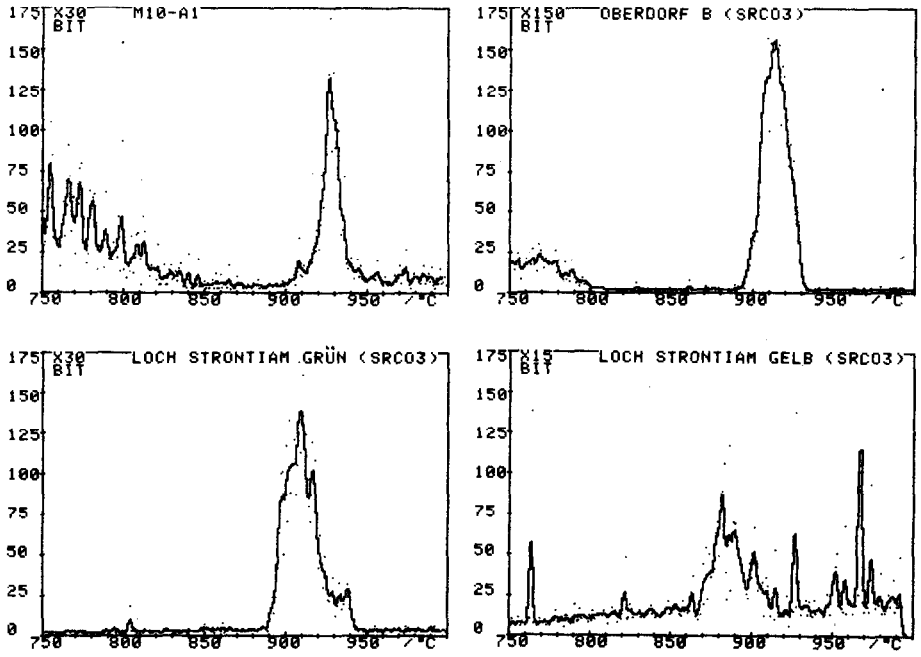
PICT. SERIE 1; EX. OF CRYOLITE AND WITHERITE MINERALS.



PICT. SERIE 2: EX. OF MACROCRYSTALLINE QUARTZ MINERALS



PICT. SERIE 3: EX. OF MICROCRYSTALLINE QUARTZ MINERALS.



The nominal rise of temperature of these recordings have a rate of 10 °C/min. in open air atmosphare.

Conclusion.
This preliminary work confirms that the main feature of the TS-measurements are agreeable compared to those of DTA. The TS-recordings, however, show a more datailed information, suggesting the inversion of minerals to be of a rather more complexed nature than earlyer supposed.

REFERENCES

1 Elder, J. P., Thermochim. Acta 36, 67 (1980)
2 Wiedemann, H.G. and W. Smykatz-Kloss, Thermochim. Acta 50, 17 (1981)
3 Nieszery, K. unpublished thesis, Univ. Karlsruhe, Germany (1983)
4 Mehrotra, B.N., Th. Hahn, W. Eysel and H. Arnold, 10 th Internat. Congr. Crystallogr., Amsterdam (1975)
5 Smykatz-Kloss, W.: Differential Thermal Analysis - Application and Results in Mineralogy. - Springer, Heidelberg (1974)
6 Smykatz-Kloss, W., in: ASTM Special Publ. on Purity Determination (in prepar., 1983)
7 Nieazery and W. Smykatz-Kloss, in:Abstr. of Copenhagen Conf. (1983)
8 Lønvik, K., Thermal Analysis - Vol 3 p 1089 - Proceedings 4th ICTA Budapest 1974