

## An investigation of microsilica by thermoanalytical methods

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### Abstract

It has been shown that the Meråker-type microsilica with SiO<sub>2</sub>-content of ca. 98.5wt% behaves differently from other types of microsilica investigated earlier at our Institute since it does not follow the normal transformation sequence:

microsilica → cristobalite → tridymite

when it is heated at ca. 1000°C. Due to the higher purity of this type of microsilica, it transforms directly either to quartz or cristobalite. However, if small amounts of Li<sub>2</sub>O were added to the microsilica, the following transitions could be observed by using DSC:

low – tridymite  $\xrightarrow{394\text{ K}}$  high – tridymite  $\xrightarrow{444\text{ K}}$  upper high – tridymite

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*Keywords:* DSC; Microsilica; SiO<sub>2</sub>-modifications

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### 1. Introduction

*Microsilica:* Microsilica is the name given to a product obtained through cleaning the fumes from electric arc furnaces. These furnaces usually contain quartz, coal and wood chips and are heated to 2000°C. The fumes go through a unique condensing and filtering process, and the product obtained is a very finely divided silica. The mean particle size is 0.15 μm and the surface area is 22 m<sup>2</sup>/g. The powder obtained is an amorphous non-crystalline or glassy material with an SiO<sub>2</sub>-content usually in the 94–99 wt% range.

*The SiO<sub>2</sub>-system:* It is well known that silica has a multitude of polymorphs which undergo a number of

both displacive and reconstructive transformations, the most important of which are summarized in Fig. 1.

It is generally believed that this is the most accepted diagram for the SiO<sub>2</sub>-system and, therefore, it can be found in many textbooks in ceramics describing the phase relations in the system. For instance, Sosman [1] in his book gives a broad presentation of the problem of stabilities of the different SiO<sub>2</sub>-phases.

In our investigation of microsilica powder from Fiskaa Verk, Norway, some years ago, the so-called FV-type MS, we observed that when the powder was heated in the 850–950°C range between three and seven days, the powder transformed from the amorphous state to cristobalite and then to tridymite in accordance with the Fenner [2] and Sosman [1] diagrams.

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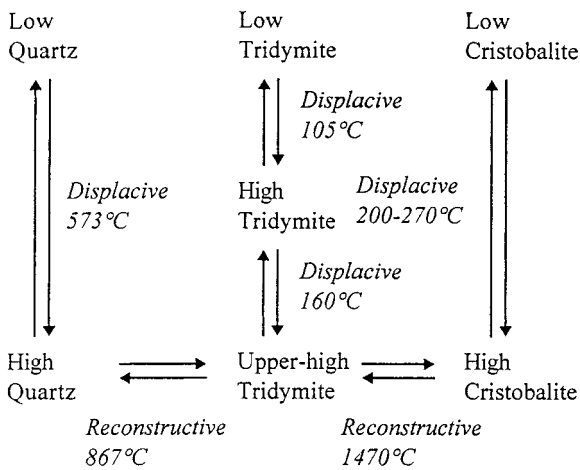
Fig. 1. The polymorphs of SiO<sub>2</sub>.

Fig. 2 presents a DSC-trace from an FV-MS sample heated at 940°C for 28 h. We obtain a peak at 388.5 K, corresponding to the low-tridymite→high-tridymite, and another peak at 472.5 K, corresponding to the low-cristobalite→high-cristobalite transitions.

However, when we started to study a new type of microsilica from Meråker Smelteverk, Norway, we were not able to find any transition corresponding to the tridymite transitions by using the same experimental techniques as in case of previous, DSC and X-ray diffraction (XRD) studies [3]. Instead, we observed that this type of microsilica transformed

on heating into quartz and/or cristobalite. We concluded that this was due to the higher purity (98.4%) of the Meråker-type microsilica as compared to the FV-type (96.4%). We have summarized the results from these comprehensive studies in a free energy or stability diagram shown in Fig. 3.

## 2. Experimental

### 2.1. Chemicals

The chemical analysis of Meråker microsilica is given in Table 1 and compared with the corresponding analysis of the Fiskaa-Verk-type microsilica.

The Li<sub>2</sub>CO<sub>3</sub> used in the present study was Li<sub>2</sub>CO<sub>3</sub> p.a. min. 99% from Merck, Germany.

Table 1

Chemical analysis of the two types of ELKEM microsilica investigated

Meråker		Fiskaa Verk	
SiO <sub>2</sub>	98.4	SiO <sub>2</sub>	96.4
C	0.27	Total C	1.88
Fe <sub>2</sub> O <sub>3</sub>	0.01	Fe	0.10
MgO	0.04	Mg	0.11
CaO	0.19	Ca	0.11
Na <sub>2</sub> O	0.01	Na	0.22
K <sub>2</sub> O	0.10	K	0.54

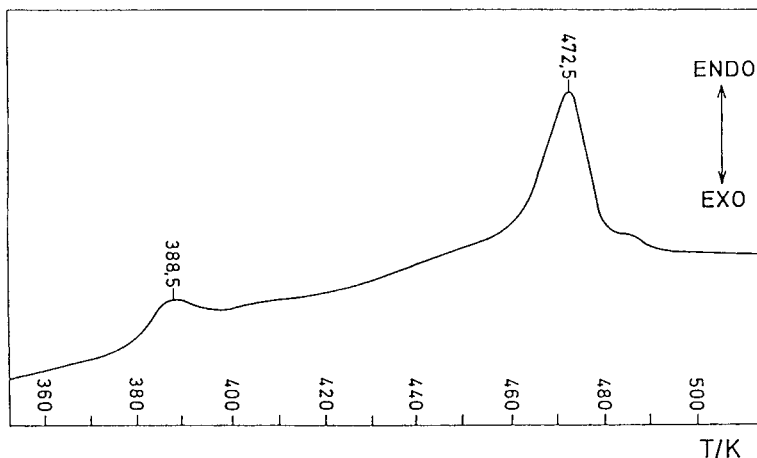


Fig. 2. DSC-diagram (heating rate 20°/min) for microsilica from Fiskaa Verk. Sample heated at 940°C for 28 h.

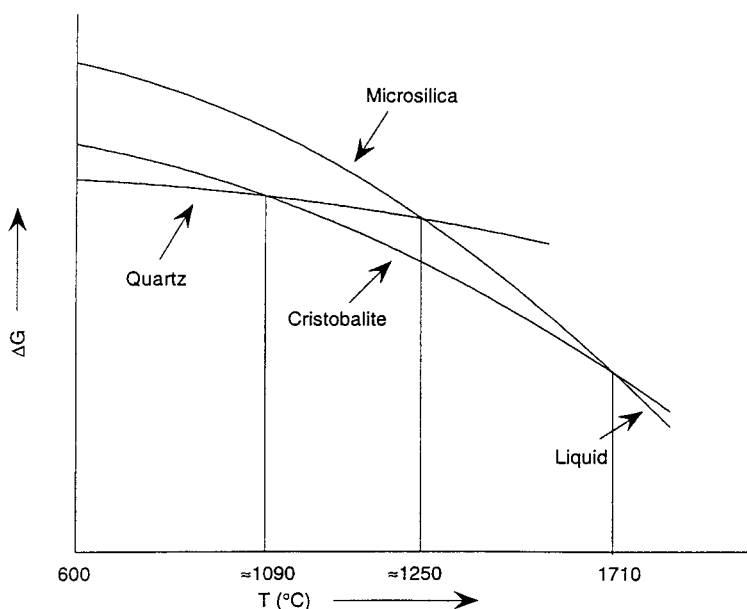


Fig. 3. Free energy or stability diagram for Meråker microsilica, as proposed by the authors.

## 2.2. Preparation of samples

Four samples of the following compositions 0.15, 0.3, 0.6 and 0.9 wt%  $\text{Li}_2\text{O}$  were prepared by mixing  $\text{Li}_2\text{CO}_3$  and microsilica in 100% alcohol. The powder was dried at  $100^\circ\text{C}$  and sintered at  $800^\circ\text{C}$  for 2–3 h. The powder was then pressed into tablets. The tablets were heated at  $900^\circ\text{C}$  for periods from 1 to 4 weeks and at  $1100^\circ\text{C}$  for 24 and 48 h.

## 2.3. Method

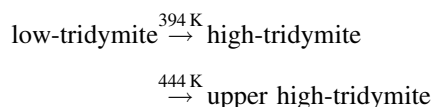
X-ray investigations were carried out by use of a Phillips PW 1730/10 instrument using  $\text{CuK}_\alpha$ -radiation.

The calorimeter was a DSC-2 instrument from Perkin–Elmer. The calibration of the instrument followed the procedure given by ICTAC using metallic indium, tin and zinc as standards. Platinum crucibles were used as containers.

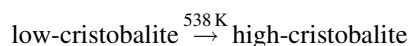
## 3. Results and discussion

*Calorimetry:* Fig. 4 shows a DSC-diagram for a sample containing 0.9%  $\text{Li}_2\text{O}$  and heated for 48 h at

$1100^\circ\text{C}$ . The two peaks in the diagram at 394 and 444 K correspond to the transitions:



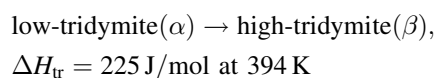
In Fig. 5 are plotted the measured enthalpies of the two transitions as a function of % $\text{Li}_2\text{O}$  added to microsilica as well as the measured enthalpy of the transition:



All samples investigated are heated for 48 h at  $1100^\circ\text{C}$ .

For samples heated at  $900^\circ\text{C}$ , only one transition was found at 394 K, corresponding to the low-tridymite→high-tridymite transition. In Table 2 we give the measured enthalpies for samples containing 0.9%  $\text{Li}_2\text{O}$  and heated between 1 and 4 weeks.

Our values for the enthalpies of transition:



and

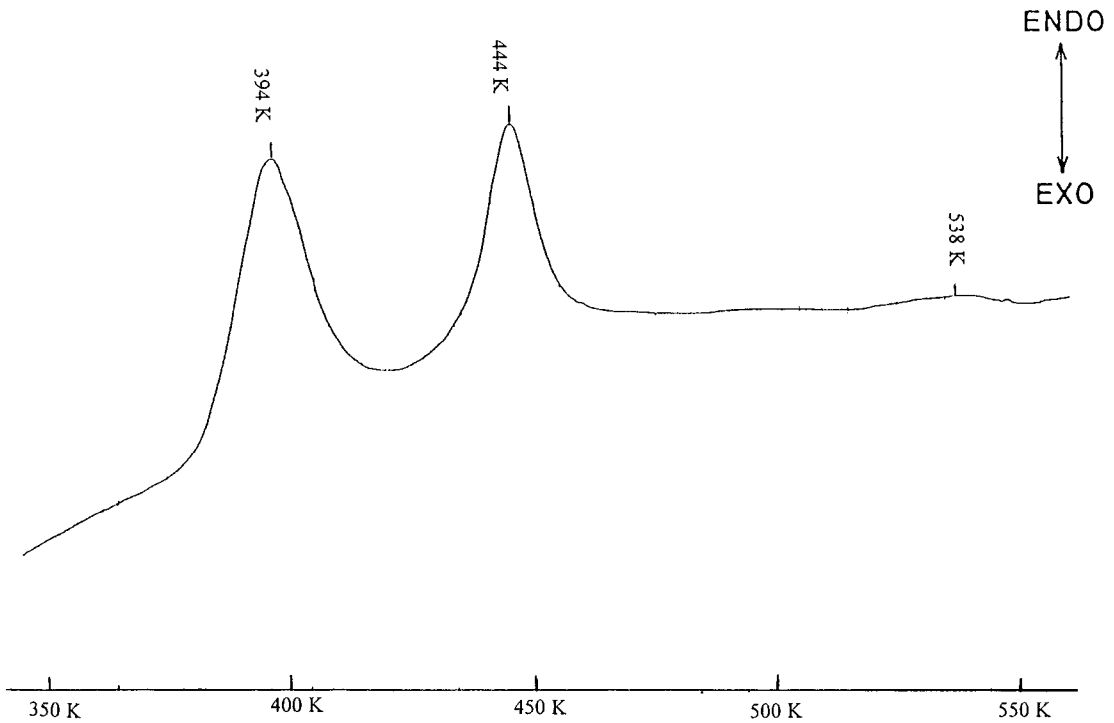


Fig. 4. DSC-diagram (heating rate 20°C/min) for microsilica containing 0.9% Li<sub>2</sub>O. Sample heated for 48 h at 1100°C.

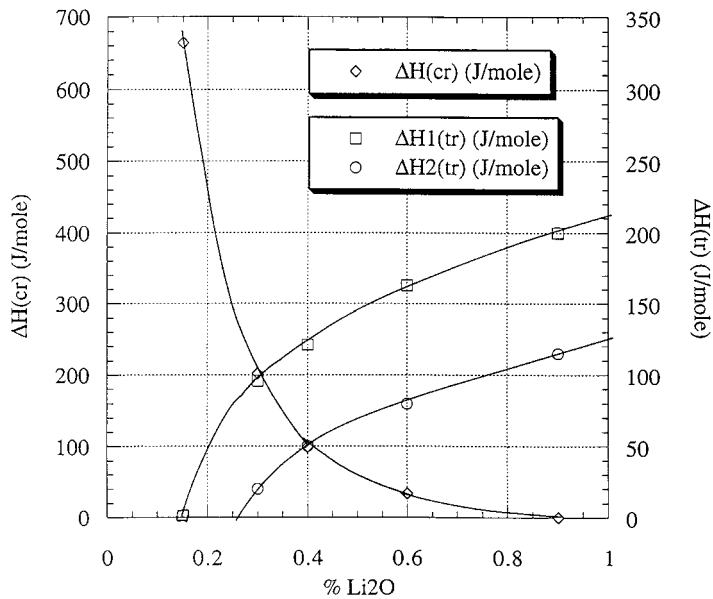


Fig. 5. Measured enthalpies for the three transitions: low-cristobalite→high-cristobalite; low-tridymite→high-tridymite; and high-tridymite→upper high-tridymite. All samples are heated for 48 h at 1100°C.

Table 2  
Enthalpy of the low-tridymite→high-tridymite transition, peak temperature 394 K

Heating time at 900°C	$\Delta H(\text{J/mol})$
1 week	140
2 weeks	164
3 weeks	182
4 weeks	232

Table 3  
Microsilica: phase identification by X-ray and DSC. Q, quartz; C, cristobalite; and T, tridymite

% Li <sub>2</sub> O added	Phases found by X-ray and DSC analysis		
	900°C, 1 week	900°C, 2 weeks	900°C, 4 weeks
0.15	Q	Q+C	
0.3	Q	T+Q+(C)	T+C
0.4	T+Q	T+Q+(C)	T+(C)
0.6	T+Q+C	T+(C)	T
0.9	T+C+(Q)	T+(C)	T

high-tridymite( $\beta$ ) → upper high-tridymite( $\gamma$ ),  
 $\Delta H_{\text{tr}} = 125\text{J/mol}$  at 444 K

should be compared with the values often referred to in the literature by Mosesman and Pitzer [4];  $\Delta H_{\text{tr}} = 293 \pm 84\text{ J/mol}$  at 390 K for the  $\alpha$  to  $\beta$  transition and  $\Delta H_{\text{tr}} = 167 \pm 42\text{ J/mol}$  at 436 K for the  $\beta$  to  $\gamma$  transition.

Knacke, Kubaschewski and Hesselmann [5] report the following values for the enthalpies of transitions; 209 J/mole at 390 K and 188 J/mole at 500 K.

*X-ray investigations:* In Table 3, are summarized the results from the X-ray diffraction investigations together with the results from the DSC-experiments.

These samples were heated at 900°C for 1, 2 and 4 weeks and had different contents of Li<sub>2</sub>O.

#### 4. Conclusion

From the results obtained, we can conclude that the purity of the starting material, the microsilica, as well as the amount of impurities added together with the heating time and temperature, are important parameters both, for the kinetics and thermodynamics of the phase transitions in the SiO<sub>2</sub>-system. The sequence of the transitions at 900°C follow the scheme:

microsilica → quartz → cristobalite → tridymite

The last step will depend on the amount of Li<sub>2</sub>O added to the microsilica.

At 1100°C the sequence of the transitions will be:

microsilica → cristobalite → tridymite

#### Acknowledgements

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#### References

- [1] R.B. Sosman, The Phases of Silica, Rutgers University Press (1965).
- [2] C.N. Fenner, Am. J. Sci. 36 (1913) 331.
- [3] M. Bruno, I. Dynna, J.L. Holm, K. Løvik, Extended Abstracts, 15th Nordic Symposium for Thermal Analysis and Calorimetry, Nov. 13–15, 1996, Helsinki, Finland.
- [4] M.A. Mosesman, K.S. Pitzer, J. Amer. Chem. Soc. 63 (1941) 2348.
- [5] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd. edn., Springer Verlag, Germany, 1991.