

Transformation enthalpy of the alkali-earths sulfates (SrSO_4 , CaSO_4 , MgSO_4 , BaSO_4)

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Abstract

During the heating of SrSO_4 a structural change occurs at 1413 K. This structural change has effect on the thermodynamic and kinetic properties of the reduction process of SrSO_4 to SrSO_3 . The structural change of the SrSO_4 has not been reported in the literature, hence, it was decided to determine the heat of transformation of this phenomena, using the differential thermal analysis technique. It was found that this structural change also occurs in the sulfates of the alkali-earth metals. In the case of the sulfates of Mg, Ca and Ba, there are not reports of transformation heat data; the literature only reports the temperature at which the transformation takes place. In this work, the heats of transformation of MgSO_4 , CaSO_4 and BaSO_4 were also determined. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nowadays, the main ore of strontium is the celestite (SrSO_4). Some applications of the strontium are as celestite concentrate (SrSO_4); however, its main application occurs as chemical compounds, mainly like carbonate [1,2] and nitrate [1,2], although there are other compounds that have applications on a smaller scale in different industries [3]. The most important strontium compound is SrCO_3 (it is also used as raw material to obtain other compounds), it has two main applications: (1) as an additive in the production of color television screens [1]; and (2) in the industry of magnetic ceramic of ferrite, which are made from iron oxides and Sr and/or Ba carbonates [1].

The SrCO_3 can be obtained by three methods: hydrometallurgical or direct conversion [4]; pyro-

hydrometallurgical [5]; and pyrometallurgical [6]. The pyrometallurgical process starts by reduction of celestite (SrSO_4) to SrS with gases, such as H_2 [7] and CO [8,9] or with a gaseous mixtures of CO–CO₂ [6,9]. The celestite (SrSO_4) transformation by this method, is strongly influenced by the temperature and the atmosphere composition. Literature is scarce and only basic compounds, such as SrSO_4 , SrCO_3 , SrO and SrS, have been studied. The stability of the strontium compounds in atmospheres of CO–CO₂ have been studied [10,11]. Research works [12–15] show that the reduction process mainly depends of the temperature and gas composition. At temperatures higher than 1050 K in a CO–CO₂ atmosphere the celestite (SrSO_4) is transformed to SrS or SrCO_3 or both. The result of this process depends on the concentration of CO–CO₂ in the gaseous phase, i.e. on the pressure of O₂ [12]. When a gaseous mixture of 10% CO–90% CO₂ is used in the temperature range of 1120–1180 K, then SrS is

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produced. With the same mixture of gases, but in a temperature range of 1280–1400 K, a mixture of SrCO₃ and SrS is formed. When a 5% CO–95% CO₂ mixture is used in a temperature range of 1240–1420 K, the product obtained is SrCO₃ [6,9].

The condensed phases present during the process between celestite (SrSO₄) and the gaseous phase CO–CO₂ are SrS, SrO, SrCO₃ and SrSO₄. Another possible product can be SrSO₃, but this is a transition compound not reported in the literature. These compounds are classified into stable and unstable according to their thermodynamic properties.

1.1. Stable compounds

SrS and SrO, these compounds do not undergo structural change or fusion at temperature as high as 1773 K.

1.2. Unstable compounds

SrCO₃ and SrSO₄, these compounds undergo structural changes and decomposition as the temperature increases.

According to the literature [16,17], the SrCO₃ show a structural transition at 1204 K and when it is used in an atmosphere of CO₂ it decomposes at 1553 K.

At high temperature, a structural transformation is shown by SrSO₄ (not reported in the literature). This phenomena has effect on the chemical and kinetic properties of the reactions that take part in the process.

The same phenomena is also present in sulfates of the other metals in the calcium group (alkali-earths): Mg, Ca and Ba.

The structural transformation of SrSO₄ is also present during the cooling. The calorific effect that is present during the heating and cooling of the compound is equivalent to the area of the peaks obtained by the differential thermal analysis (DTA).

2. Experimental procedure

2.1. Materials

Reactive grade SrSO₄ mark Fluka was used. Ultra-high purity argon was used as a purge gas with the purpose of obtaining an inert atmosphere during the

treatments. All the substances used to calibrate the DTA were chemical reagents; the melt temperature of these compounds are in agreement with those reported in the literature [10,11].

2.2. Experimental technique

The heat of transformation of SrSO₄ was determined using a high temperature DTA model 1700 (Perkin–Elmer). Samples of 100 mg in the form of powder were placed in platinum crucibles. Alumina powdered was used as a reference. After placing the samples in the platinum crucibles from DTA, 10 l h⁻¹ flow of argon was passed through the chamber of the analyzer in order to achieve an inert atmosphere. This argon flow was maintained throughout the experiment. The sample was heated, at a constant rate of 10°C min⁻¹, till it achieved a temperature higher than that of melting. The thermal evolution was registered on graphical paper. In order to determine the enthalpy structural transformation of SrSO₄ the DTA had to be calibrated. Ten different substances of known melting point were used to calibrate the DTA. Table 1 shows the substances that were used for the calibration, the melting point from the literature, and experimental melting points. It can be assumed that the area of the peak (S_{Tr}), obtained from the DTA due to the transformation is proportional to the enthalpy value [18,19] (ΔH_{Tr}) according to Eq. (1):

$$S_{Tr} = K(T)[\Delta H_{Tr}] \quad (1)$$

where $K(T)$ = calibration constant and S_{Tr} = peak area obtained by DTA.

The experimental parameters were: sample mass = 100 mg; argon flow = 10 l h⁻¹; heating rate = 10 K min⁻¹; DTA sensitivity = 5 mV; paper speed = 5 mm min⁻¹; $\Delta T = (T_s - T_r) = 10$ K.

From Eq. (1), $K(T)$ value of each substance is determined, then a linear relationship to the temperature is obtained. (ΔH_{Tr}) value was obtain from the literature thermodynamics data and (S_{Tr}) from DTA measured peaks.

3. Results and discussion

The peak limiting curve is described by polynomial series. The value of its area is calculated by integrating

Table 1
Data for DTA calibration

Compounds	Literature data			Experimentals data		
	melting temperature (K)	fusion enthalpy (KJ mol ⁻¹)	fusion enthalpy (J/100 mg)	melting temperature (K)	peak area (cm ²)	calibration constant (cm ² J ⁻¹)
KCl	1045	26.59	35.67	1045	6.47	0.18
NaCl	1074	28.05	47.98	1074	8.31	0.17
Na ₂ CO ₃	1123	29.68	28.01	1124	4.67	0.17
Na ₂ SO ₄	1157	23.03	16.2	1157	2.6	0.16
PbO	1159	27.51	12.31	1160	1.97	0.16
SrCO ₃ ^a	1197	19.68	13.31	1198	2.01	0.15
K ₂ SO ₄	1342	36.84	21.14	1342	2.86	0.14
PbS	1392	36.43	15.24	1394	1.72	0.11
BaF ₂	1563	28.47	16.24	1565	1.54	0.1
CaF ₂	1691	29.73	38.06	1690	1.36	0.04

^a Structural transformation.

within the limits of the peaks. The analysis was repeated four times for each substance, and the average value was calculated.

The melt temperature was determined at a heating rate of 2 C min⁻¹. The calibration data is shown in Table 1. The $K(T)$ function is described by linear type of correlation:

$$K(T) = a + bT \quad (2)$$

where $a = 0.354 \pm 1 \times 10^{-3}$, $b = -1.67 \times 10^{-4} \pm 1 \times 10^{-6}$, standard coefficient of correlation (r^2) = 0.99, and standard deviation of $K(T) = 0.00$.

The Fig. 1 shows the description of $K(T)$.

The error on the value of the transformation enthalpy (ΔH_{Tr}) could be calculated according to the following relationship:

$$\delta \Delta H_{Tr} = \frac{1}{K(T)} \delta S_{Tr} + \frac{S_{Tr}}{K^2(T)} \delta K$$

where $\delta K = \pm 0.004$ and $\delta S_{Tr} = 0.03 S_{Tr}$

This means that the error on measurement of the peak area does not exceed 3% of the value of the total area.

The DTA analysis allows to determine the transformation temperature and the peak area that can be related to the calorific effect of the transformation, by means of the Eq. (3):

$$\Delta H_{Tr} = \frac{S_{Tr}}{K(T)} \quad (3)$$

According to the DTA calibration the $K(T)$ constant is described by the function:

$$K(T) = 0.354 - 1.67 \times 10^{-4}T \quad (4)$$

with standard deviation of ± 0.004

The final calculations to obtain the enthalpy of transformation of SrSO₄ were carried out, resulting the following values: $T_{Tr} = 1413$ K; $K(1413) = 0.12$

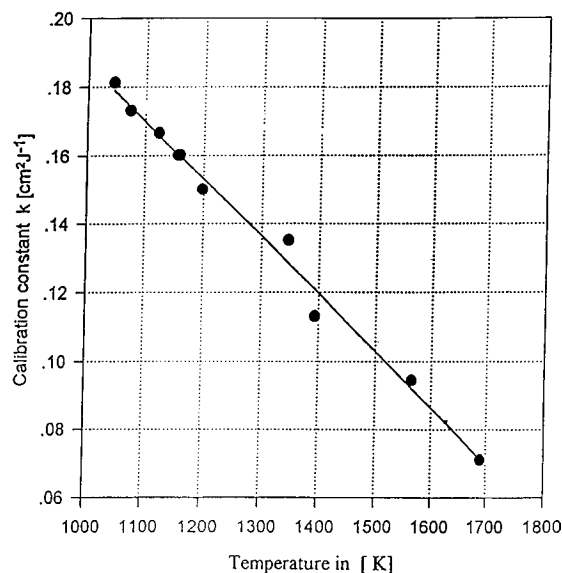


Fig. 1. Relationship of $K(T)$ (calibration constant) with the temperature.

Table 2
Thermodynamic data of MgSO₄, CaSO₄, SrSO₄ and BaSO₄ from the literature [10,11]

Compounds	T_{Tr} (K)	ΔH_{Tr}	T_f (K)	ΔH_f
MgSO ₄	1383	—	1403	14.6
CaSO ₄	1466	—	1723	28.1
SrSO ₄	1425	—	1873	—
BaSO ₄	1423	—	1623	40.6

Table 3
Thermodynamic data of MgSO₄, CaSO₄, SrSO₄ and BaSO₄ obtained experimentally

Compounds	T_{Tr} (K)	S_{Tr} (K)	K (cm ² J ⁻¹)	ΔH_{Tr} (KJ mol ⁻¹)
MgSO ₄	1288	1.97	0.14	18.08
CaSO ₄	1472	2.34	0.11	29.43
SrSO ₄	1413	3.36	0.12	52.22
BaSO ₄	1422	2.81	0.12	56.52

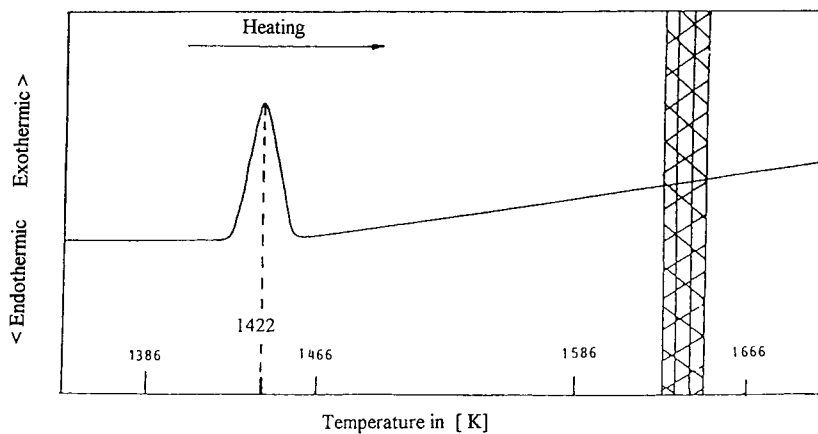


Fig. 2. DTA chart for the transformation of BaSO₄.

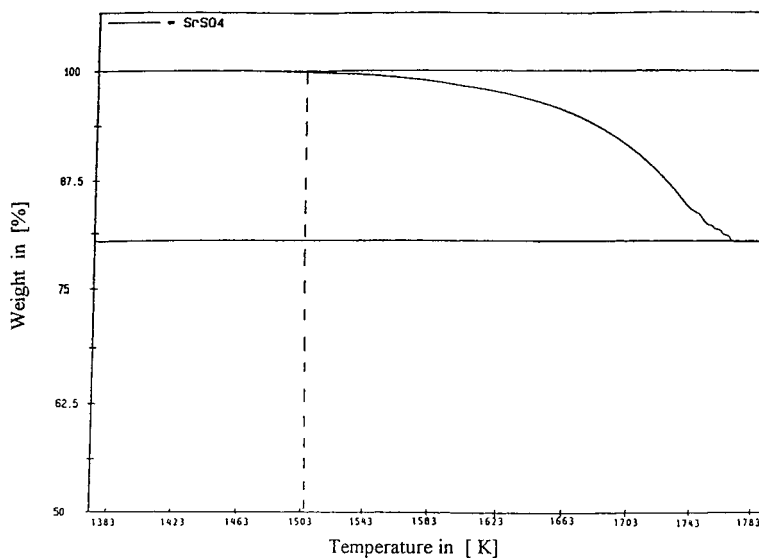


Fig. 3. Decomposition of SrSO₄ under argon atmosphere.

($\text{cm}^2 \text{J}^{-1}$); $S_{\text{Tr}} = 3.36 \text{ (cm}^2\text{)}$; $\Delta H_{\text{Tr}} = S_{\text{Tr}}/K(T) = 28.475 \text{ (J/100 mg)}$; $\Delta H_{\text{Tr}} = 52.22 \text{ (KJ mol}^{-1}\text{)}$.

The structural change is also present in the other metal sulfates of the group IIA (alkali-earths). Some authors [20–24] found that the sulfates from this group also undergo structural transformation, decomposition or melt under certain conditions.

The Table 2 shows the data reported in the literature [10,11]. In this table, the transformation temperature, the melting temperature and the heat of fusion of each

compound are presented; however, the heat of transformation was not found.

Due to the lack of heat of transformation values of the alkali-earths sulfates, the DTA technique was used to determine these values.

The DTA analysis allows the transformation temperature and the peak area to be determined, by which the calorific effect can be calculated using the Eq. (3).

According to the DTA calibration, the constant $K(T)$ is described in Eq. (4). The four sulfate peak areas

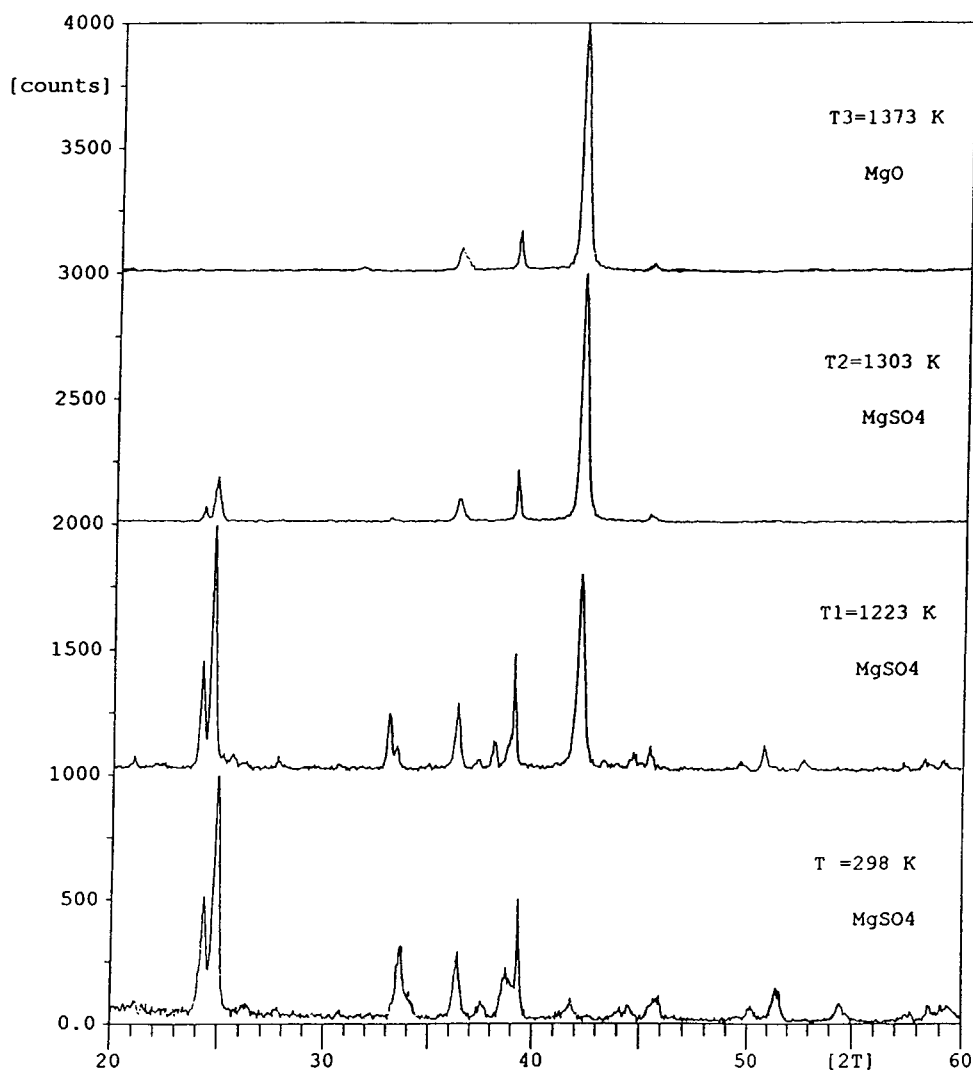


Fig. 4. X-ray diffraction pattern of MgSO₄ at 298, 1223, 1303 and 1373 K.

were determined by the procedure previously explained. The Table 3 shows the experimental data obtained in this work.

BaSO_4 is used in this above described procedure to obtain the value of heat of transformation as an example. Fig. 2 shows the heating curve for BaSO_4 . As it can be seen from Fig. 2 a structural transformation at 1422 K is registered, but the melting point reported in the literature is not observed.

It was also found that, at higher temperatures than the transformation temperature reported in Table 3, sulfates undergo decomposition instead of fusion. This

finding does not agree with the data reported in the literature.

In the case of SrSO_4 , at higher temperatures than the transformation temperature (1413 K), the decomposition also takes place before fusion occurs. In an atmosphere of argon the decomposition begins at a temperature closer to 1500 K, as can be seen in Fig. 3. The decomposition temperature of SrSO_4 decreases considerably in an argon atmosphere.

On the other hand, the structural transformations of these sulfates also occur in the opposite way. Figs. 5–7 shows the X-ray diffraction patterns of MgSO_4 ,

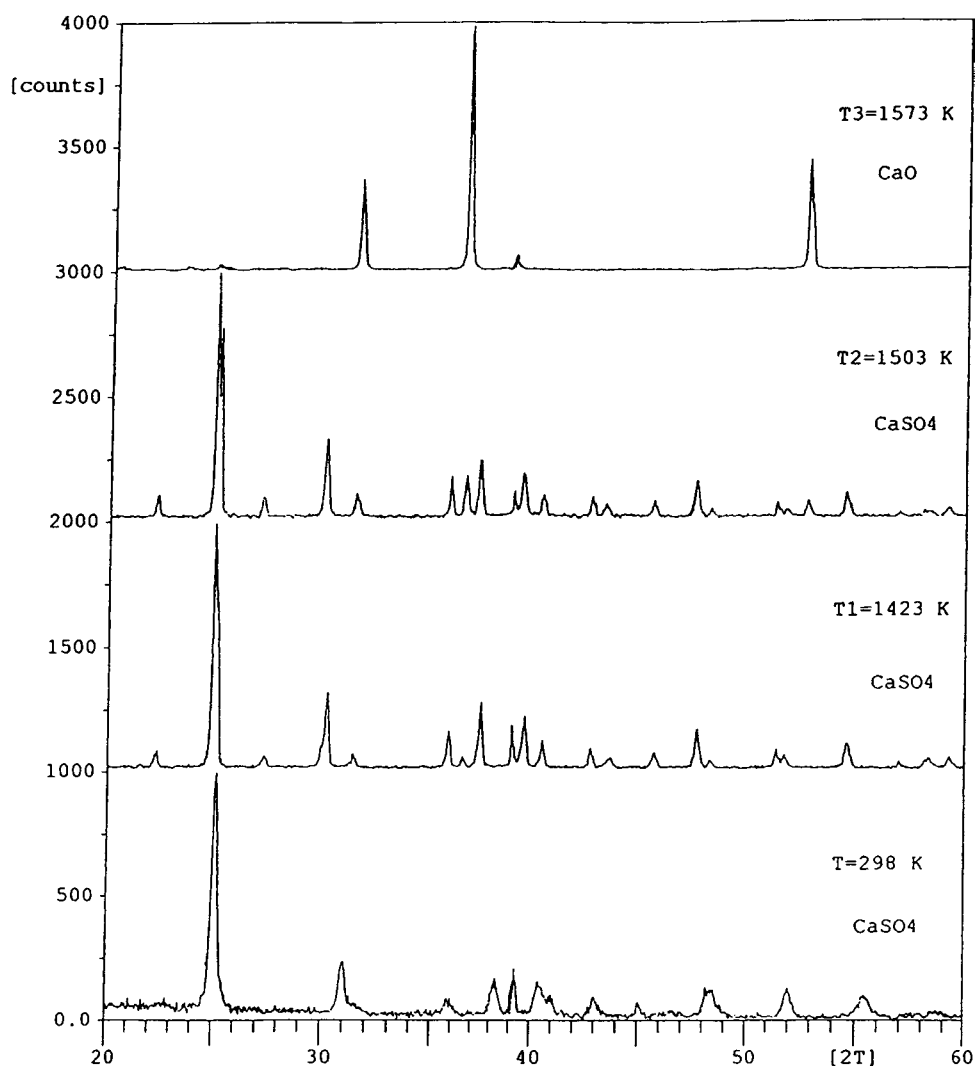


Fig. 5. X-ray diffraction pattern of CaSO_4 at 298, 1423, 1503 and 1573 K.

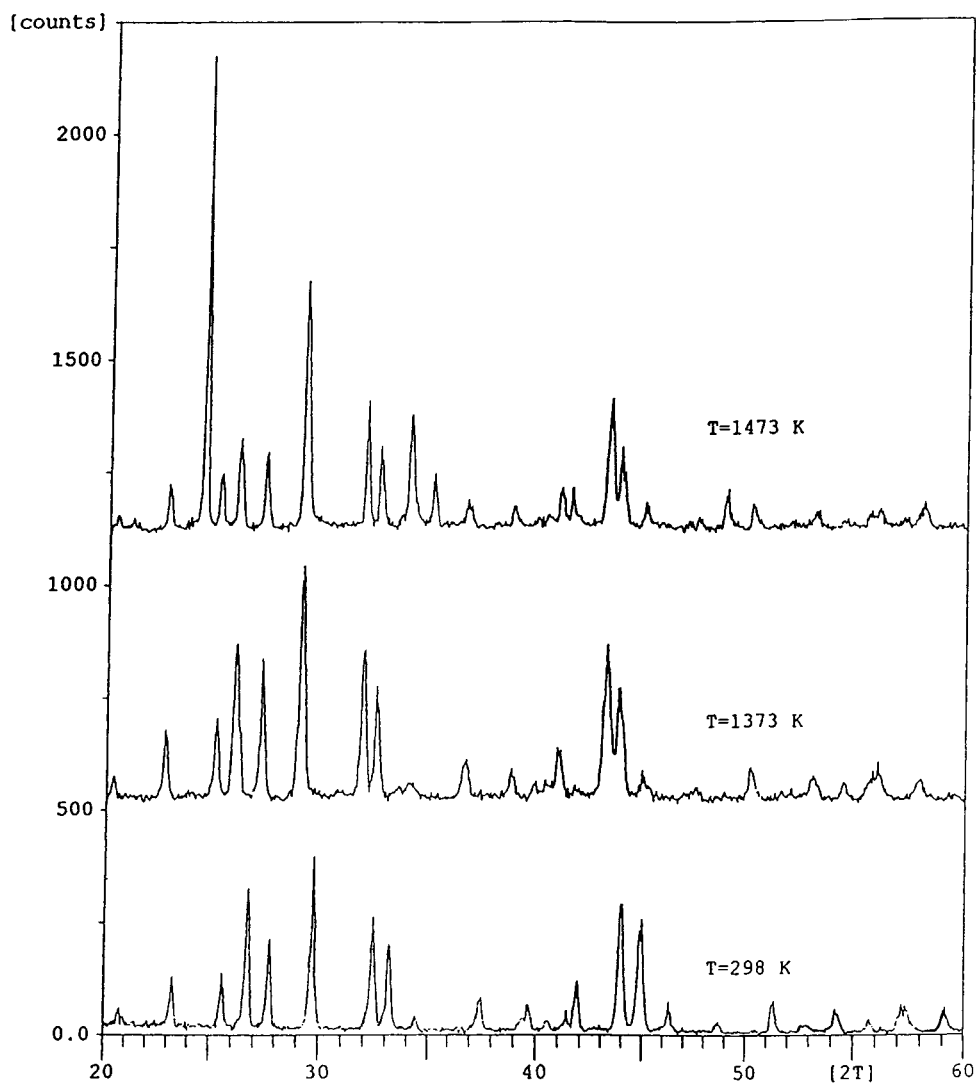


Fig. 6. X-ray diffraction pattern of SrSO_4 at 298, 1373 and 1473 K.

CaSO_4 , SrSO_4 and BaSO_4 carried out at temperatures lower and higher to the transformation temperature. The heating rate was 10 K min^{-1} using an argon flow of 10 l h^{-1} .

The heating cycle used during the experiments is showed in the Fig. 8. According to this heating cycle, T_1 is a temperature below transformation, T_2 a temperature above transformation and T_3 a temperature even higher than T_2 . MgSO_4 and CaSO_4 change to oxides at temperature T_3 as can be seen in Figs. 4 and

5. However, SrSO_4 and BaSO_4 are more stable and they do not change at temperature T_3 as can be seen in Figs. 6 and 7.

4. Conclusions

It has been determined in this work that a structural transformation of SrSO_4 exists, which had not been reported in the literature.

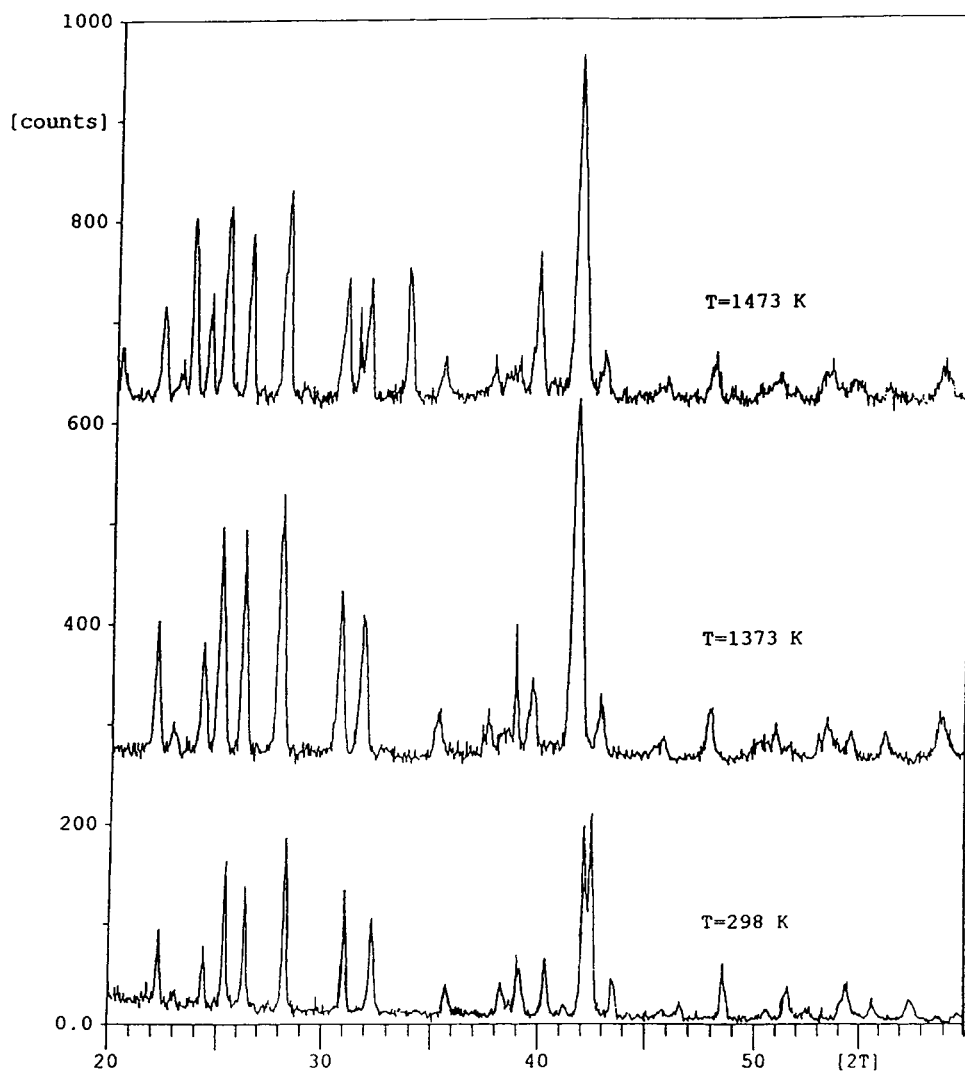


Fig. 7. X-ray diffraction pattern of BaSO_4 at 298 K, 1373 K and 1473 K.

DTA shows that the structural transformation of SrSO_4 takes place at 1413 K.

The enthalpy of this transformation was determined.

The enthalpy of transformation of the MgSO_4 , CaSO_4 and BaSO_4 were also determined; these data had not been reported in the literature.

The experimental evidence shows that melting of these sulfates does not occur as reported in the literature. However, a decomposition process of these compounds was registered instead of melting.

It was found by X-ray diffractometry that the structural transformations of MgSO_4 , CaSO_4 , SrSO_4 and BaSO_4 also occur in the opposite way; i.e. during the cooling process these return to their original condition.

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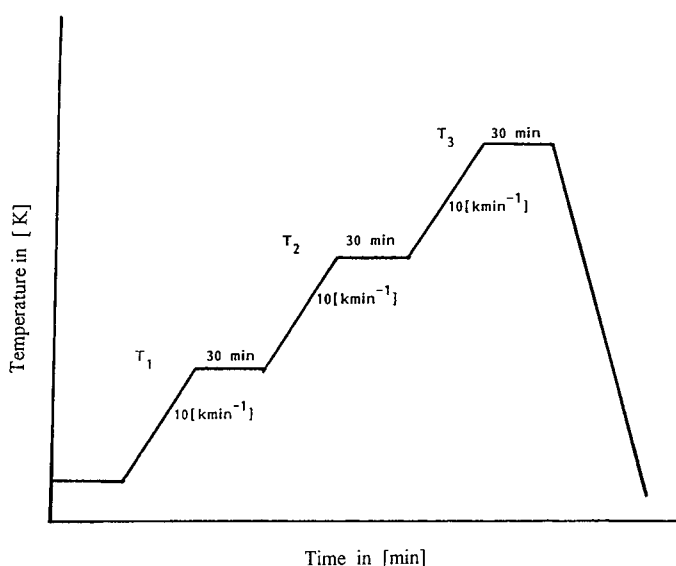


Fig. 8. Heating cycle during X-ray diffractometry experiments.

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