Thermochimica Acta, 27 (1978) 253–260

THERMAL CONVERSION OF SYNTHETIC CYMRITE INTO HEXAGONAL BARIUM FELDSPAR

CARMINE COLELLA
Istituto di Chimica Applicata, Facoltà di Ingegneria, Università di Napoli (Italy)

ROSARIO AIELLO
Dipartimento di Chimica, Università della Calabria, Cosenza (Italy)

(Received 21 December 1977)

ABSTRACT

The synthesis of cymrite, $BaAl_2Si_2O_8 \cdot H_2O$, at low temperature (140 °C) and autogenous water vapour pressure has been reported. Through the study of its thermal behaviour, by means of TG, X-ray and dilatometric analyses, it has been shown that cymrite turns into hexagonal celsian, owing to the departure of water from the structure and that the process appears to be irreversible at room temperature. A hypothesis on the structure of cymrite*, also on the basis of the water desorption kinetics data, has been worked out. The possibility of obtaining celsian, a material of interest in the Ba-refractories industry, through ignition at 400 °C of synthetic cymrite, has been at last pointed out.

INTRODUCTION

Cymrite, $BaAl_2Si_2O_8 \cdot H_2O$, is a framework silicate mineral, only few occurrences of which have been formerly reported[1–6]. Its X-ray diffraction pattern is very close to those of two synthetic α-(orthorombic) and β-(hexagonal) polymorphs[7,8] of celsian (barium feldspar), $BaAl_2Si_2O_8$, although the scant availability of the mineral has not allowed until now the complete explanation of the relationships between cymrite and these compounds. Cymrite has been, on the other hand, synthesized either at high temperatures (200–500 °C) and very high pressures (1–30 Kb)[9,10], or, but not as a pure phase, at low temperature (80 °C) under autogenous water vapour pressure[11,12].

The purpose of this work is therefore both to define the most suitable physicochemical conditions for the synthesis of cymrite at low temperatures and, successively, to study its thermal behaviour in order to investigate the structural relationships between cymrite and celsian.

---

* See Addendum, p. 398.

EXPERIMENTAL

Syntheses were effected at temperatures ranging between 80 and 140 °C in sealed Teflon containers (capacity ~100 ml) containing the reaction mixtures and rotated in a thermostated oven. The usual time allowed for crystallization was 3 days. Metakaolinite (MTK), obtained through ignition of MERCK Kaolin (water loss ~14%) at 600 °C, was used as source of silica and alumina.

The mixtures were prepared from weighed amounts of solution of reagent grade LiOH* with appropriate amounts of metakaolinite and reagent grade $Ba(OH)_2 \cdot 8H_2O$, added as solid because of its limited solubility in water at room temperature. The mole fraction BaO/(BaO + Li_2O) ranged between 0.2 and 0.5. Water was also added to adjust the total hydroxide molality at values ranging each time between 0.8 and 1.2 m. The weight ratio MTK:H_2O was maintained at 1:25 in each run, normally arranged on the basis of 1 g of MTK.

Reaction products were separated from mother liquors by filtration, washed and dried overnight at 80 °C. They were then stored over saturated $Ca(NO_3)_2$ solution at 20 °C (R.H. = 56%) before X-ray, chemical and thermal analyses.

Guinier X-ray powder photographs were subjected to densitometer measurements and cell constants were calculated with the aid of a computer program. The variation of the unit-cell parameters of cymrite with temperature was evaluated by measuring, in a series of densitometer traces taken from a Guinier-Lenné X-ray powder photograph (average heating rate: 0.38 °C min^{-1}), the distance between the positions, at various temperatures, of the (200) and (004) reflections of the synthesized species and, respectively, that of the (102) and (201) reflections at 10 °C, of quartz, employed as reference.

Chemical analyses were made using standard procedures for Si and Al. Atomic adsorption photometry served for analysis of Ba and Li. TG analyses were made with a Stanton-Massflow thermobalance mod. MF-H5 (average heating rate: 6.6 °C min^{-1}). Dehydration kinetics data were collected from TG traces at constant temperatures.

Dilatometric traces were obtained employing a Leitz Dilatometer mod. UBD (average heating rate: 4 °C min^{-1}). Samples were prepared through compaction of cymrite powder in a suitable mould.

RESULTS

Synthesis and characterization

The results of the synthesis experiments widen remarkably the field of physicochemical conditions under which cymrite crystallizes. Its crystallization is in fact possible not only starting from kaolinite, as previously reported[11,12], but also from metakaolinite. The yield is strongly temperature-dependent, so that complete crystallization was obtained only at 140 °C. The most suitable chemical conditions for a

---

* The role played by Li^+ in the reaction environment has been discussed in a previous paper[12].

TABLE 1

CHEMICAL ANALYSIS OF CYMRITE

Compound	*Composition (%)*				
	SiO_2	Al_2O_3	*BaO*	H_2O	*Total*
Synthetic cymrite	30.2	25.6	39.3	4.6[a]	99.7
Stoichiometric $BaAl_2Si_2O_8 \cdot H_2O$	30.51	25.91	39.00	4.58	100.00

[a] Measured from TG trace (see Fig. 1).

TABLE 2

X-RAY DIFFRACTION POWDER DATA FOR CYMRITE AND ITS IGNITION PRODUCT

Synthetic cymrite		*Ignition product*		*hkl*
d(Å)	I/I_0	*d(Å)*	I/I_0	
7.67[a]	25	7.78[a]	38	001
4.62[a]	14	[b]		100
3.961	100	3.949	100	101
2.955	90	2.969	87	102
2.671	100	2.648	75	110
2.557[a]	5	2.596	8	003
2.524	10	2.507	16	111
2.313	37	2.293	27	200
2.241	34	2.259	40	103
2.215	60	2.199	58	201
2.194	20	2.189	23	112
1.982	14	1.975	15	202
1.920	10	1.945	15	004
1.849	33	1.853	40	113
1.775[a]	5	1.790[a]	5	104
1.705	34	1.690	34	211
1.591	38	1.582	35	212
1.558	20	1.567	22	114
1.541	26	1.527	21	300

[a] Reflections not used for the refinement of the unit-cell dimensions.

[b] Zone covered by the reflection (111) of $Pb(NO_3)_2$, employed as internal standard.

TABLE 3

CELL PARAMETERS OF CYMRITE AND ITS IGNITION PRODUCT

Compound	*a(Å)*	*c(Å)*	*V(Å³)*
Synthetic cymrite	5.34(1)	7.68(0)	189.7
Ignition product	5.29(1)	7.78(3)	188.7

complete and reproducible transformation of the reacting magma into cymrite turned out to be: total hydroxide molality = 1.2 m, mole fraction BaO/(BaO + Li$_2$O) = 0.3. These conditions correspond to the following reaction mixture:

metakaolinite	1.00 g
soln. LiOH 1.2 m	18.00 g
Ba(OH)$_2$·8H$_2$O	1.42 g
water	6.86 g

A bulk sample of cymrite was prepared in this way and utilized for all the successive experiments. The chemical analysis of this sample appears in Table I, together with the calculated values for stoichiometric BaAl$_2$Si$_2$O$_8$·H$_2$O. No detectable Li was found in the compound, confirming[11] that during crystallization cymrite is highly selective for Ba^{2+}. The good agreement between experimental and calculated values shows that the synthesized sample has the same composition of the mineral[5].

Table 2 (first two columns) reports the X-ray diffraction powder data for synthetic cymrite. Its diffraction pattern and cell parameters (Table 3) are also very close to those of the mineral[1].

Thermal behaviour

On heating, cymrite gradually loses water, as shown by the TG and DTG traces in Fig. 1. The anhydrous product appears unable to take up water vapour again, even if stored for a long time (e.g. 7 days) in an environment of saturated water vapour pressure, at 20 °C.

Table 2 (last two columns) reports the X-ray diffraction powder data for the ignition product of cymrite. The diffraction pattern is closely related to that of cymrite, apart from a small decrease in the $d_{(hkl)}$ values affecting a-dimension and a small increase in those affecting c-dimension. The pattern is, on the contrary, practically identical to that of the α(low temperature)-form of the synthetic polimorph of celsian[7], with consequent coincidence of the cell parameters (Table 3 and ref. 8).

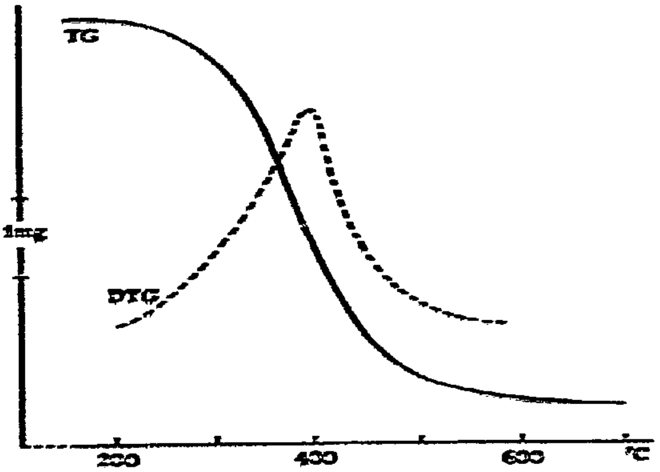

Fig. 1. TG and DTG curves of cymrite. Heating rate: 6.6 °C min^{-1}.

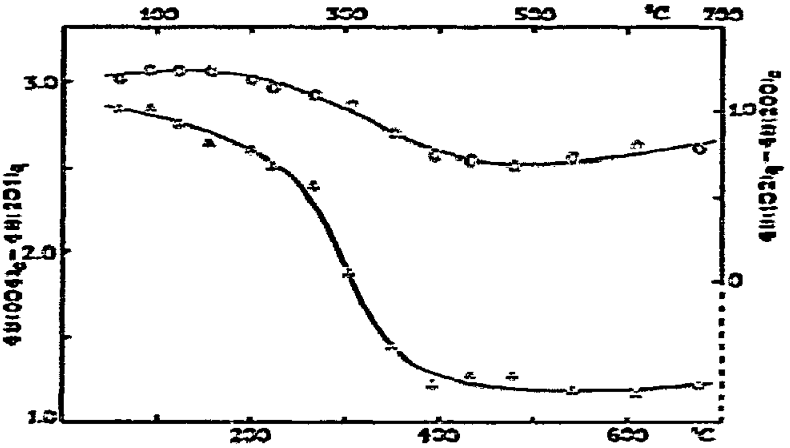

Fig. 2. Shifts on heating of (200) and (004) reflections of cymrite, in respect of the position of (201) and (102) reflections of quartz at 10 °C. Heating rate: 0.38 °C min⁻¹.

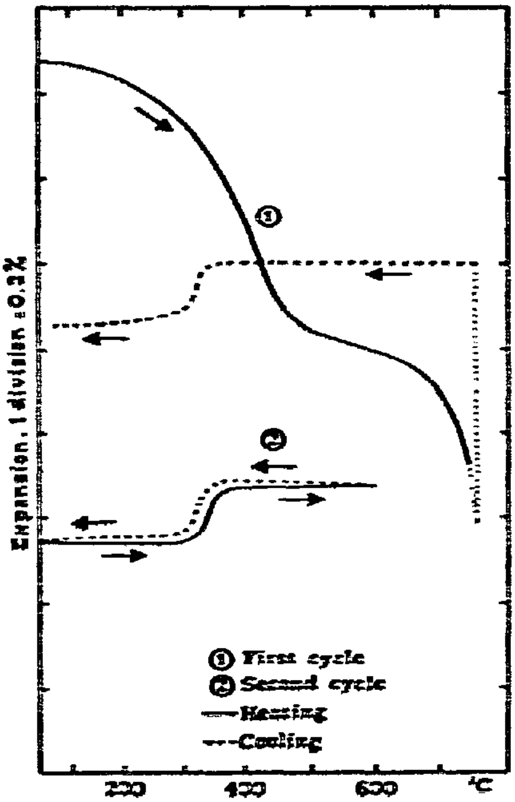

Fig. 3. Dilatometric traces of a compact of cymrite powder. Heating rate: 4 °C min⁻¹.

Figure 2 shows the shifts, on heating, of the (200) reflection (affecting only *a*-dimension) and of the (004) reflection (affecting only *c*-dimension) of cymrite, in respect to the position of (201) and (102) reflections of quartz at 10 °C. It may be noticed, by comparing Figs. 1 and 2, that the gradual water removal causes a continous change in the unit-cell parameters of cymrite, which obviously means that the transformation cymrite → β(high-temperature)-form of synthetic celsian[7] occurs gradually, just as a result of water removal.

Dilatometric traces reported in Fig. 3 confirm the above results and summarize the whole series of transformations: cymrite → β(hexagonal) celsian ⇄ α(orthorombic) celsian[7]. In the first cycle, on heating the sample remarkably shrinks owing to both water departure and tighter arrangement of the powder particles. At temperatures of about 600 °C the transformation into celsian is practically complete (see Fig. 1). On

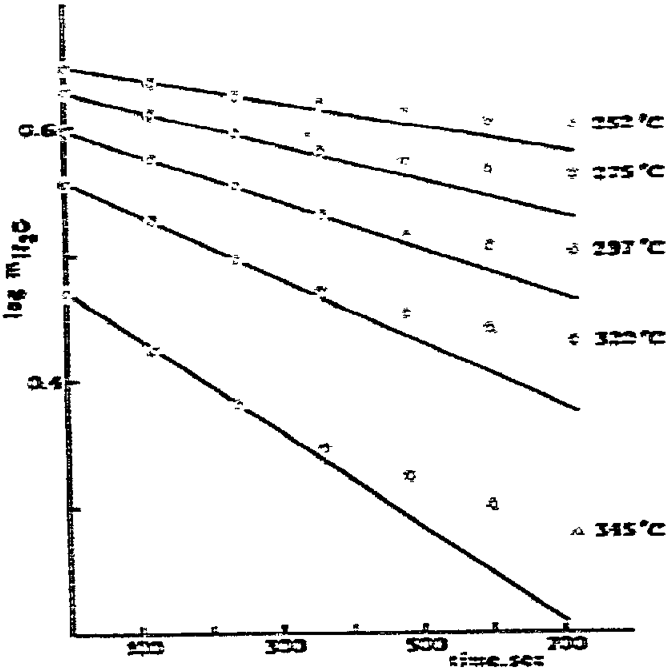

Fig. 4. Kinetics of water desorption process from cymrite. m_{H_2O} is the percent residual water in the specimen.

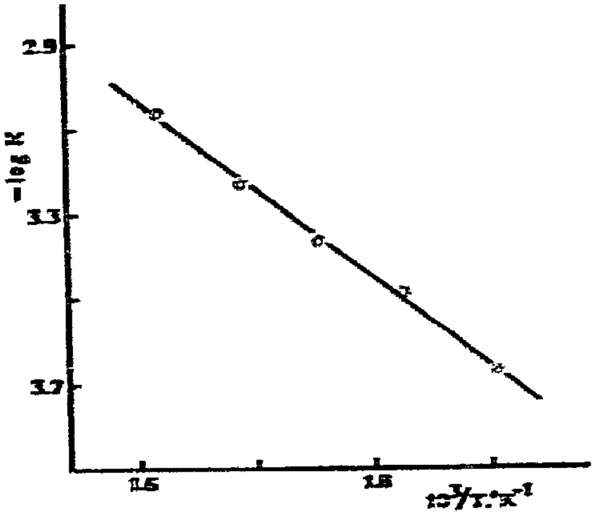

Fig. 5. Arrhenius plot for water desorption process from cymrite.

cooling, in fact, the $\beta \rightarrow \alpha$ inversion of the celsian[7] at about 300 °C takes place and the phase transition $\alpha \rightleftharpoons \beta$ is the only transformation recorded in the second cycle*.

Water desorption kinetics

The gradual departure of water from cymrite, although it appears to be an irreversible process, considerably resembles the continuous zeolite dehydration. The plot in Fig. 4 shows that, as for zeolite[14], the water desorption process of cymrite, until the point at which the saturation of the powder layer in the thermobalance hinders the water removal, is a first-order reaction. By plotting (Fig. 5) the reaction rates calculated from the data of Fig. 4 against temperature, according to the Arrhenius equation

$$\ln k = -E_a/RT + \text{const.}$$

a value of E_a, activation energy, for the water desorption from cymrite, of 9.5 kcal mole^{-1} has been obtained. E_a for the water desorption from zeolite A[14,15] is about 7 kcal mole^{-1}.

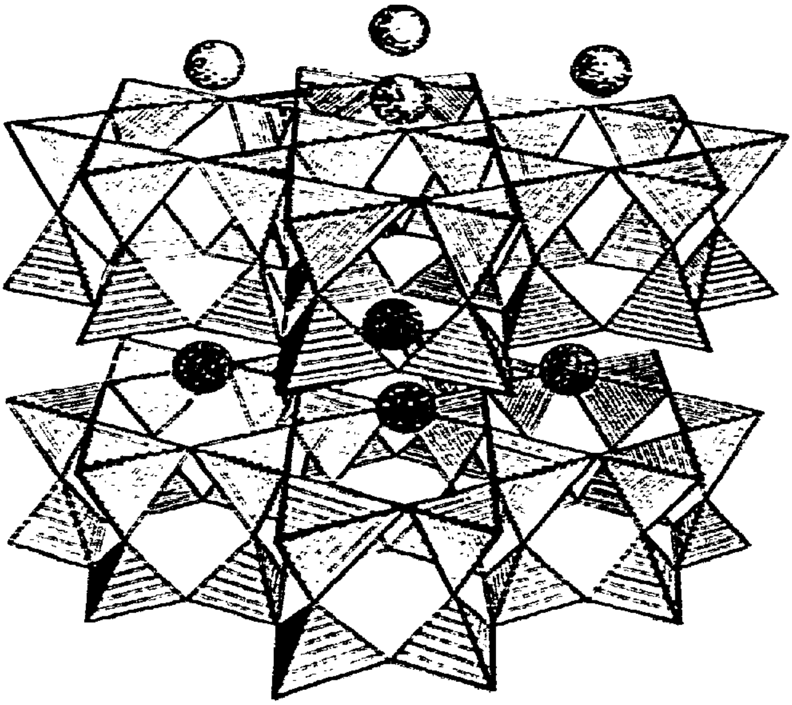

Fig. 6. Structure of high-temperature form of synthetic celsian[7].

---

* It has to be noticed that, because of the metastability of the α- and β-forms of synthetic celsian[13], the high-temperature form can, at higher temperatures, turn into the stable polymorph (monoclinic celsian). The transformation temperature of this *non*-thermodynamic transition is of course strongly dependent on the heating procedures. With a heating rate of 0.38 °C min^{-1} this transformation takes place at about 850 °C.

DISCUSSION

The whole of the above data allows a hypothesis to be worked out on the structure of cymrite. The structure of the high-temperature form of synthetic celsian[7,8] (Fig. 6) is characterized by double-sheets of linked tetrahedra held together by Ba layers. The structure could be described as well on the basis of linked double six-ring (D 6-R) polyhedra with a ratio D 6-R/Ba equal to 1. Being in the cymrite the mole ratio H_2O/Ba exactly 1, the compound could be regarded as a hydrated hexagonal celsian and therefore each water molecule be located in a hexagonal prism, as it sometimes occurs in zeolite structures. Such position of water could explain the magnitude of the E_a value for the desorption process, similar to that of zeolites. The irreversibility of this process could be justified by considering that water molecules (critical diameter 3.2Å), which pass with difficulty through a six-membered ring even at high temperature, are no more adsorbable at room temperature after the structure shrinkage along the *a*-axis, due to the dehydration (see Table 3).

CONCLUSIONS

The results of the syntheses experiments provide a method for obtaining cymrite at low temperature (140 °C) starting from metakaolinite. This may be of interest for researchers in the field of refractories, if one considers that, through ignition at about 400 °C, cymrite turns into celsian, a material of noticeable use in the field of Ba-refractories, otherwise produced by electrofusion method[7,16].

ACKNOWLEDGEMENTS

The Authors wish to thank A. Annetta for technical assistance and helpful discussions.

REFERENCES

1 W. Campbell Smith, F. A. Bannister and M. H. Hey, *Mineral. Mag.*, 28 (1949) 676.
2 W. P. Brosgé, *U.S., Geol. Surv. Prof. Pap.*, 400B (1960) 351.
3 M. K. Carron, M. E. Mrose and A. N. Reiser, *Geol. Soc. Am., Spec. Pap.*, 82 (1964) 26.
4 D. D. Runnels, *Am. Mineral.*, 49 (1964) 158.
5 E. J. Essene, *Am. Mineral.*, 52 (1967) 1885.
6 P. R. De Villiers, *Mem. Dep. Mines South Africa*, 59 (1970) 1.
7 B. Yoshiki and K. Matsumoto, *J. Am. Ceram. Soc.*, 34 (1951) 283.
8 Y. Takeuchi, *Mineral. J. (Tokyo)*, 2 (1958) 311.
9 Y. Seki and G. C. Kennedy, *Am. Mineral.*, 49 (1964) 1407.
10 D. B. Hawkins, *Mater. Res. Bull.*, 2 (1967) 951.
11 R. M. Barrer, R. Beaumont and C. Colella, *J. Chem. Soc., Dalton Trans.*, (1974) 934.
12 C. Colella, *Rend. Accad. Sci. Fis. Mat., Naples*, 40 (1973) 303.
13 H. C. Lin and W. R. Foster, *Am. Mineral.*, 53 (1968) 134.
14 G. Polverino, *Laurea Thesis*, Faculty of Engineering, University of Napoli, 1969.
15 D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *J. Am. Chem. Soc.*, 78 (1956) 5963.
16 F. Singer and S. S. Singer, *Industrielle Keramik*, Vol. III, Springer-Verlag, Berlin, 1966, p. 221.