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THERMAL DECOMPOSITION OF $CaCO_3$ IN THE PRESENCE OF CALCIUM FLUORIDE

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The thermal decompositoon of calcium carbonate mixed with calcium fluoride was examined by means of simultaneous TG, DTG and DTA. The temperature range of $CaCO_3$ decomposition shifted to higher temperatures as a result of $CaCO_3$–CaF_2 eutectic formation. The temperature of melting of this eutectic was in the temperature range of $CaCO_3$ decomposition, and therefore all factors which increase the partial pressure of CO_2 (such as the thickness of the sample layer, the shape of the crucible, the heating rate, etc.) influence the amount of the liquid phase. The DTA curves can be regarded as the sum of three endothermic effects occurring almost simultaneously: decomposition of $CaCO_3$ in the solid phase, melting of the eutectic, and decomposition of $CaCO_3$ present in the liquid phase.

The synthesis of calcium fluorochloroapatite from $CaHPO_4$, $CaCO_3$, $CaCl_2$ and CaF_2 has been the subject of significant research interest over the past few decades. However, relatively few contributions have dealt with the influence of the liquid phase formed during the reaction on the formation of the product [1]. In particular, the eutectic melting associated with the $CaCl_2$–$CaCO_3$ system (620°) and the $CaCl_2$–CaF_2 system (650°) results in higher reaction rates of calcium fluorochloroapatite and chloroapatite formation as compared to the rate of formation of calcium fluoroapatite. In the latter case, it has been established [1] that no liquid phase is formed in the course of the reaction. It must be noted however, that the authors did not take into consideration the possibility of the existence of a simple eutectic mixture in the $CaCO_3$–CaF_2 system (64 wt% $CaCO_3$, 36 wt% CaF_2 [2]), which melts at 880°. In previous work [3], we demonstrated that his phenomenon can significantly affect the rate of calcium fluoroapatite synthesis in the $Ca_2P_2O_7$–$CaCO_3$–CaF_2 system.

During thermal analysis in air at 101.3 kPa, calcium carbonate decomposes in the temperature range 630–920° (Fig. 1). Since melting of the $CaCO_3$–CaF_2 eutectic occurs within this range, it seemed interesting to verify the influence of the presence of CaF_2 on the thermal decomposition of $CaCO_3$.

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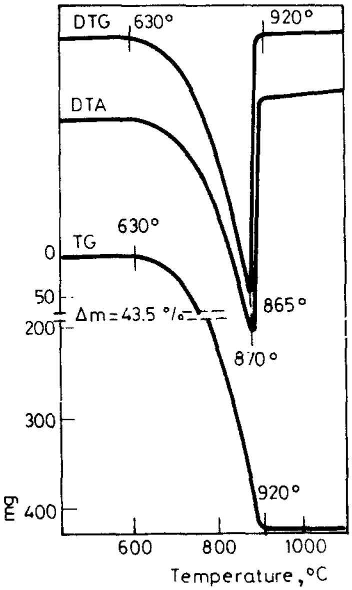

Fig. 1 TG, DTG and DTA curves recorded for pure $CaCO_3$ (air, open crucible) $m=1000$ mg in air atmosphere

Experimental

The calcium carbonate used in all experiments was purchased from Riedel–De Haen (West Germany). Calcium fluoride (Hitachi, Japan) was heated at 1000° for 5 h before being mixed with calcium carbonate.

Simultaneous TG, DTG and DTA experiments were carried out on a Q–1500 D derivatograph (MOM, Hungary), within the temperature range 20–1050°, at a heating rate of 10 deg min^{-1}. Typical samples varied from 500 mg to 1000 mg. High-purity alumina was used as the standard reference material. The experiments were performed either in air or in a CO_2 flow, using open or covered crucibles.

Results

Representative thermal analysis curves obtained for a mixture of 80 wt% $CaCO_3$ and 20 wt% CaF_2, heated in air in an open crucible, are presented in Fig. 2. In the temperature range 635–940°, a significant mass loss, associated with calcium carbonate decomposition, is observed. In the DTA curve, the corresponding

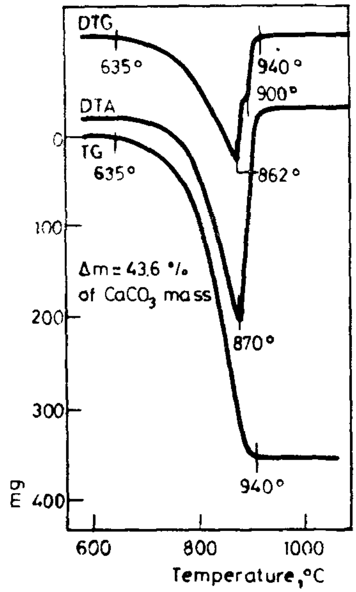

Fig. 2 TG, DTG and DTA curves recorded for the mixture of 80 wt% $CaCO_3$ with 20 wt% CaF_2 (air, open crucible) $m = 1000$ mg in air atmosphere

endothermic peak at 870° as for pure $CaCO_3$, can be seen. The shape of the DTG peak, however, is slightly different since at 900° a small maximum appears. In order to verify whether the observed changes in the DTG shape are due to the dilution of $CaCO_3$ with CaF_2, an experiment was carried out in which an 80 wt% $CaCO_3$ with 20 wt% Al_2O_3 mixture was decomposed under the same conditions. The resulting DTG curve was essentially identical to the one observed for pure calcium carbonate. It may therefore be concluded that the additional maximum, clearly observed in the DTG curve, is not associated with the dilution.

The use of a covered crucible resulted in a shift of the thermal decomposition temperature range recorded for pure calcium carbonate towards higher temperatures. This is due to the fact that under such conditions the diffusion of CO_2 is severely slowed down. As in the former case, no differences were observed in the DTA and DTG curves recorded for pure and Al_2O_3-diluted $CaCO_3$. On the other hand, the addition of CaF_2 to $CaCO_3$ caused a significant change in the shapes of all three thermal analysis curves.

In Figs 3–5 the TG, DTG and DTA curves corresponding to different CaF_2 contents (5, 10 and 20 wt%) are presented. In the DTG curves, two clear maxima are observed for the samples with 5 and 10 wt% CaF_2 contents (878°, 915° and 865°, 920°, respectively), whereas in the case of the 20 wt% CaF_2 sample three

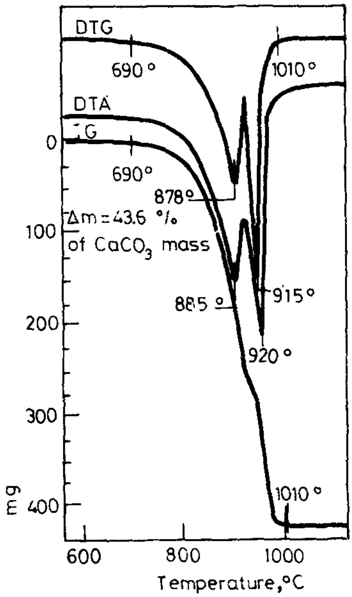

Fig. 3 TG, DTG and DTA curves recorded for the mixture of 95 wt% $CaCO_3$ with 5 wt% CaF_2 (air, covered crucible) $m = 1000$ mg in air atmosphere

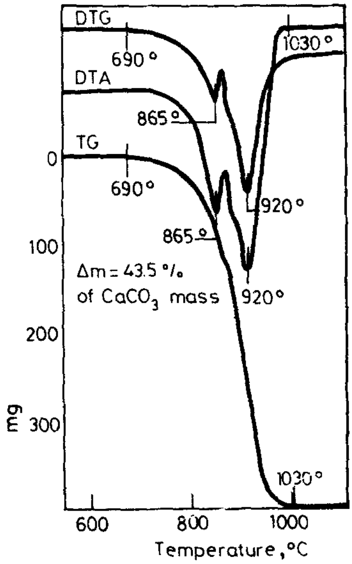

Fig. 4 TG, DTG and DTA curves recorded for the mixture of 90 wt% $CaCO_3$ with 10 wt% CaF_2 (air, covered crucible) $m = 1000$ mg in air atmosphere

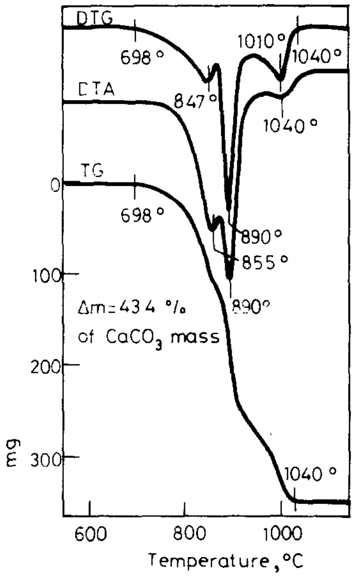

Fig. 5 TG, DTG and DTA curves recorded for the mixture of 80 wt% $CaCO_3$ with 20 wt% CaF_2 (air, covered crucible) $m = 1000$ mg in air atmosphere

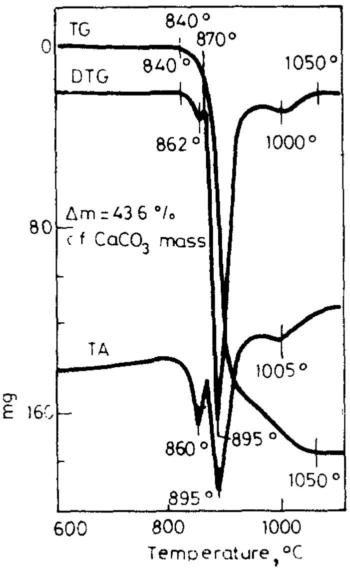

Fig. 6 TG, DTG and DTA curves recorded for the mixture of 80 wt% $CaCO_3$ with 20 wt% CaF_2 (CO_2, open crucible) $m = 1000$ mg in air atmosphere

maxima are present (847°, 890° and 1010°). The ends of the mass losses occur at higher temperatures as compared to the Al_2O_3-diluted sample: 1010° (5 wt% CaF_2), 1030° (10 wt% CaF_2), 1040° (20 wt% CaF_2) and 960° (20 wt% Al_2O_3). In the DTA curves, a strong endothermic effect can be observed in addition to the maximum at ca. 900°. The temperature at which the maximum of this endothermic peak occurs decreases with increase of the CaF_2 content: 885° (5 wt% CaF_2), 865° (10 wt% CaF_2) and 855° (20 wt% CaF_2). At the highest CaF_2 content studied, a third peak of low intensity was recorded at 1010°.

In order to shift the temperature of the beginning of $CaCO_3$ decomposition towards even higher temperatures, the thermal analysis of the 80 wt% $CaCO_3$ and 20 wt% CaF_2 mixture was carried out in a CO_2 atmosphere. Under these conditions, the dissociation of calcium carbonate occurred in the temperature range 840–1050° (Fig. 6). Three maxima can be observed in the DTG curve, at 862°, 895° and 1000°. The first small maximum corresponds to the hardly observed inflection at 870° in the TG curve. The mass loss recorded up to this temperature was 10 mg, which constitutes only 5.6% of the overall mass loss observed for the sample. The reaction occurring in the temperature range 840–870° is manifested in the DTA curve by a strong endothermic effect with maximum at 860°. The area of this peak is anomalously large as compared to the expected thermal effect associated with the decomposition of such a small amount of calcium carbonate. This therefore indicates that the melting of the $CaCO_3$–CaF_2 eutectic contributes to this endothermic effect. Additional evidence in support of this conclusion comes from analysis of the cooling of the sample heated previously to 890°. An exothermic effect, due to the eutectic crystallization which starts at 848° (Fig. 7), can be observed in the cooling DTA curve.

Conclusions

To summarize, the results of the present research unequivocally show that the presence of calcium fluoride causes a significant shift of the end of calcium carbonate decomposition towards higher temperatures. The appearance of a liquid phase, associated with the $CaCO_3$–CaF_2 eutectic, renders the elimination of CO_2 from the system difficult. In addition, the presence of CaF_2 causes a "stepwise" decomposition of $CaCO_3$. In the literature on calcium carbonate, such behaviour has not been reported previously. The shape of the DTA curve recorded for the $CaCO_3$–CaF_2 mixture is the resultant of the overlapping of three endothermic effects: $CaCO_3$ decomposition in the solid phase, $CaCO_3$–CaF_2 eutectic melting, and the decomposition of $CaCO_3$ present in the liquid eutectic phase.

Since one of these effects is associated with a reversible phase transition, it is

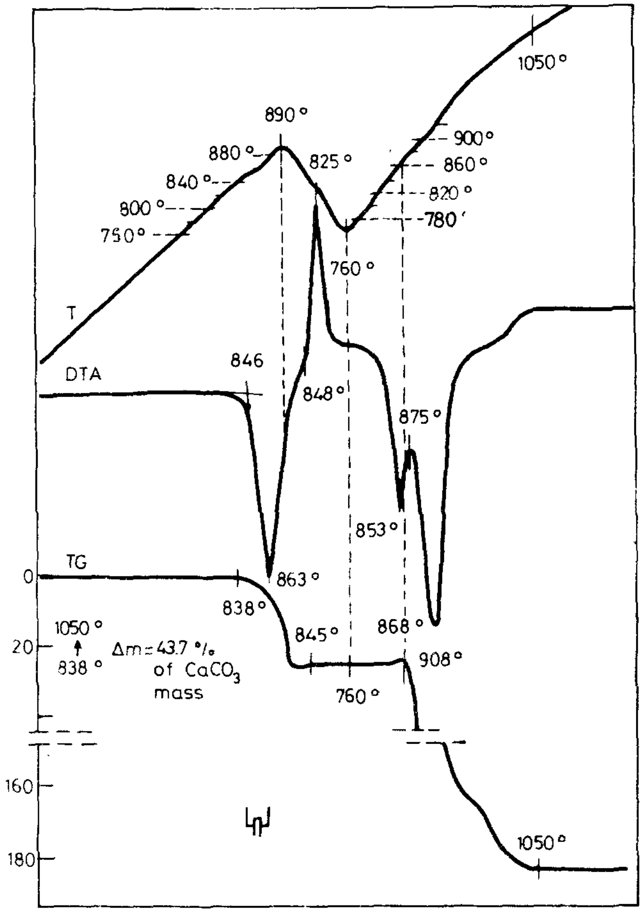

Fig. 7 T, TG and DTA curves recorded during heating and cooling program for the mixture of 80 wt% $CaCO_3$ with 20 wt% CaF_2 (CO_2, open crucible) $m = 524$ mg

possible to separate this effect from the two others by analysis of the cooling curve, which shows a strong exothermic peak due to the crystallization of the eutectic. Such an approach can constitute the basis for a method which allows the application of DTA and TG curves for study of the phase diagrams of systems in which the decomposition temperature of one of the components is close to the eutectic melting point [4].

It seems highly likely that the formation of the $CaCO_3$–CaF_2 eutectic can significantly influence the synthesis of calcium fluorochloroapatite, which, when activated with antimony and manganese, is one of the most frequently fabricated luminescent materials. If the amount of the reacting mixture is large, the temperature range of calcium carbonate decomposition is shifted towards higher temperatures. As a result, a significantly higher content of the liquid phase originating from the eutectic can be expected.

References

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Zusammenfassung — Die thermische Zersetzung von Calciumcarbonat-Calciumfluorid-Mischungen wurde durch simultane TG–DTG–DTA untersucht. Der Bereich der $CaCO_3$-Zersetzung wird infolge der Bildung des $CaCO_3$–CaF_2-Eutektikums zu höheren Temperaturen verschoben. Die Schmelztemperatur dieses Eutektikums liegt im Temperaturbereich der $CaCO_3$-Zersetzung, deshalb haben alle Faktoren, die den Partialdruck des CO_2 beeinflussen (Schichtdicke der Probe, Tiegelgeometrie, Aufheizgeschwindigkeit usw.) auch Einfluss auf die Menge der entstehenden flüssigen Phase. Die DTA-Kurven entstehen durch Überlagerung von 3 endothermen Effekten, die fast gleichzeitig ablaufen: Zersetzung von $CaCO_3$ in fester Phase, Schmelzen des Eutektikums, Zersetzung von $CaCO_3$ in flüssiger Phase.

Резюме — Совмещенным методом ТГ, ДТГ и ДТА исследовано термическое разложение карбоната кальция в смеси с фторидом кальция. Температурный интервал разложения карбоната кальция сдвигается к более высоким температурам, вследствии образования эвтектики $CaCO_3$–CaF_2. Температура плавления этой эвтектики попадат в температурную область плавления карбоната кальция, в связ с чем факторы увеличивающие парцияльное давление CO_2 (толщина слоя образца, форма тигля, скорость нагрева и др.) оказывают влияние и на количество жидкой фазы. ДТА кривые могут рассматриваться как сумма трех одновременно протекающих эндотермических эффектов: разложение карбоната кальция в твердой фазе, плавление эвтектики и разложение карбоната кальция, находящегося в жидкой фазе.