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INVESTIGATION OF SOLID STATE REACTION IN THE SYSTEM $Ca_2P_2O_7$-$CaCO_3$-CaF_2

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ABSTRACT

Solid state reactions in the system $Ca_2P_2O_7$-$CaCO_3$-CaF_2 have been studied by thermal, x-ray and chemical analyses. The reaction between $Ca_2P_2O_7$ and CaF_2 proceeds at 700°-1000°C and gives calcium fluoroapatite and gaseous POF_3. It was shown that the latter reacts immediately with $CaCO_3$ (or CaO) and produces solid products: calcium fluoroapatite and CaF_2. The influence of the quantity of $CaCO_3$ in the mixture on course of the reaction was investigated. In the cases where the amount of $CaCO_3$ was insufficient to react with all POF_3 that had been formed, the excess of the latter evolved from the system in a violent endothermic reaction proceeding at narrow temperature range. The formation of the small amount of carbonate apatite, in the reactions carried out in CO_2 atmosphere, has been observed.

INTRODUCTION

Calcium halophosphate phosphor activated with manganese and antimony is obtained in solid state phase by firing a mixture of reactants of which the main components are: $CaHPO_4$, $CaCO_3$ and CaF_2, at the temperature about 1100°C. Calcium fluoroapatite (FA) is produced in the course of the reaction between these compounds, which may be described by the following global equation (including a thermal decomposition of $CaHPO_4$ to $Ca_2P_2O_7$)

$$3Ca_2P_2O_7 + 3CaCO_3 + CaF_2 \longrightarrow Ca_{10}(PO_4)_6F_2 + 3CO_2 \qquad (1)$$

As it was concluded by Rabatin and Gillooly [1] the fundamental process of the synthesis of FA in that system is the reaction between $Ca_2P_2O_7$ and CaF_2 proceeded according to the equation given by Montel [2]

$$18Ca_2P_2O_7 + 14CaF_2 \longrightarrow 5Ca_{10}(PO_4)_6F_2 + 6POF_3 \qquad (2)$$

Studying the possibility of the vapor transport reaction in the formation of halophosphate phosphor Rabatin and Gillooly postulated that FA is produced also in the reaction of gaseous product in the reaction (2) - POF_3 with $CaCO_3$

$$18CaCO_3 + 6POF_3 \longrightarrow Ca_{10}(PO_4)_6F_2 + 8CaF_2 + 18CO_2 \qquad (3)$$

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The influence of quantity of $CaCO_3$ on the course of the reactions in the system $Ca_2P_2O_7$-$CaCO_3$-CaF_2 has been investigated in our studies by thermal analysis.

EXPERIMENTAL

The following reactants were used in our experiments: $Ca_2P_2O_7$ - obtained by heating $CaHPO_4$ (Hitachi, Japan) at 1000°C during 5h, CaF_2 (Hitachi, Japan) - heated in the same conditions and $CaCO_3$ (Riedel-De Haën, West Germany).

The termal analysis was performed by means of the thermoanalyser Derivatograph Q 1500 D (MOM Hungary) at the temperature range 20°-1500°C, with heating rate 7.5°C/min, using the 300mg samples.

The solid products of the reaction were identified by x-ray phase analysis with the aid of diffractometer Dron 20 (USSR) and by IR spectroscopy using Perkin-Elmer 577 (Austria) spectrophotometer.

The amount of CaO in the samples was determined by selective dissolving in 3% NH_4Cl aqueous solution and titration by EDTA in the presence of glyoxal-bis(2-hydroxyanil) (GBHA) as an indicator [3].

RESULTS AND CONCLUSIONS

By means of thermal analysis the studies were carried out with the following molar ratios of the reactants:

I $3Ca_2P_2O_7 + 4CaF_2 + 1.5CaCO_3$
II $3Ca_2P_2O_7 + 4CaF_2 + 2CaCO_3$
III $3Ca_2P_2O_7 + 4CaF_2 + 2.5CaCO_3$
IV $3Ca_2P_2O_7 + 4CaF_2 + 3CaCO_3$

The TG curves (fig.1) showed that the thermal decomposition of $CaCO_3$ occured at the temperature range 580°-840°C. The observed loss of the weight was a bit smaller than calculated from the stoichiometry of the samples: 41.28%(I), 41.59%(II), 43.21% (III), 42.43%(IV) of the weight of $CaCO_3$ in the sample (43.98% - theoretically). During the thermal decomposition of $CaCO_3$ the reaction between $Ca_2P_2O_7$ and CaF_2, usually proceeding at the temperature range 700°-1000°C [4], starts and gives FA and gaseous POF_3. The latter reacts immediately with CaO, therefore the observed loss of the weight was only the result of evolving of CO_2. The presence of $Ca_2P_2O_7$, CaF_2, CaO and small amount of FA was identified by means of x-ray analysis in the products obtained at 840^{o}C.

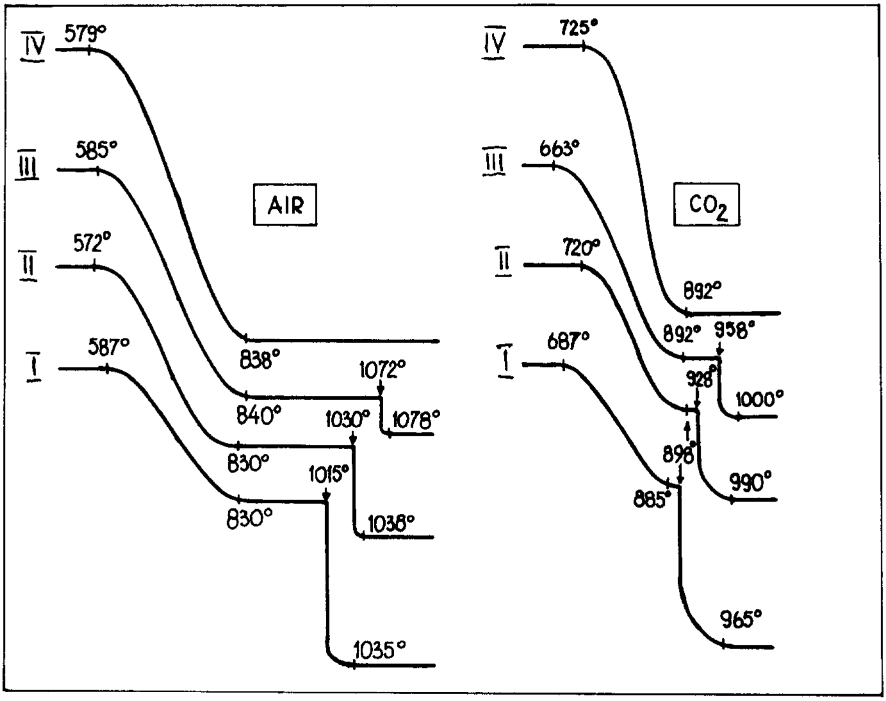

Fig. 1. TG curves obtained for the samples I-IV (see text) in static air and in atmosphere of CO_2. The weight of the samples - 300mg. The heating rate - 7.5^{o}C/min.

Above the temperature 840^{o}C, till the beginning of the vigorous loss of the weight, noted in the experiments I-III, TG curves did not show any changes of weight of the samples. However, x-ray analysis showed that, in this step, the increase of the amount of FA occured which confirmed that both the reactions (2) and (3) took place. The additional evidence that the reaction (3) proceeded was the deacrease of the amount of CaO, which was determined by chemical analysis. The contents of CaO, determined in the samples just before that rapid loss of the weight was over twenty times lower than at the temperature 840^{o}C.

In the experiments I-III at the temperature above 1000^{o}C the vigorous loss of the weight, on TG curves, was observed and that was caused by the evolution of POF_3. Together with the increase of the contents of $CaCO_3$ in reactants the amount of the evolved POF_3 deacreased: 2.98%(I), 1.89%(II), 0.54%(III) of the weight of the sample and this process began at higher temperature. As the contents of CaO, determined just before the rapid loss of the weight, was very slight (about 0.3%) it is obvious that the evolution of POF_3 from the system took place when the whole CaO had reacted.

In the experiment IV, above 1000°C, no vigorous loss of the weight was observed, which proved that the amount of CaO, existing in this sample, was sufficient to react with whole POF_3 formed.

In the experiments I-IV carried out in the atmosphere of CO_2 it was observed that the first step of the reaction occured at the temperature range 663°-898°C. The noted loss of the weight was connected with the reaction of $CaCO_3$ with POF_3 (3). The TG curves shoved that in the atmosphere of CO_2 the loss of the weight was smaller than in the air, and they were as follows: 39.44%(I), 38.62%(II), 38.44%(III), 38.61%(IV) of the weight of $CaCO_3$ in the sample. It indicates that a certain number of anions CO_3^{2-} was built in the lattice of the forming apatite. The two absorption bands which were noted in IR spectra at 1453cm^{-1} and 1429cm^{-1} proved the existence of a certain amount of carbonate apatite [5]. The second loss of the weight connected with the evolution of POF_3 proceeded at the lower temperature than in the air (fig. 1). The observed weight losses were as follows: 3.13%(I), 1.79%(II), 0.95%(III). The most probable explanation of this phenomenon seems to be the acceleration of the reactions which was caused by the melting of the eutectic occured in the system $CaCO_3$-CaF_2 at the temperature 880°C [6].

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