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# THERMAL BEHAVIOUR OF SYNTHETIC AKAGANEITE UNDER DIFFERENT EXPERIMENTAL CONDITIONS

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## ABSTRACT

The products of the thermal decomposition of β-FeOOH in air and vacuum are compared. While hematite is the only product in air, $N_2$ and $O_2$, the akaganeite sample leads to a different product in vacuum. This product is characterized by X-ray diffraction and chemical analysis, being identified as poorly crystallized maghemite with traces of magnetite. The DSC curve of this product shows a multiple exothermal effect that causes its conversion to hematite.

## INTRODUCTION

The thermal decomposition of synthetic akaganeite, β-FeOOH, has been extensively studied by several authors (1-6) but the characterization of the products obtained under different experimental conditions is still uncertain in some cases. In this way, the decomposition product in vacuum was identified as maghemite by Gonzalez Calbet and Alario Franco (4) while other authors (5) find an amorphous solid with ultrafine microcristals of undecomposed β-FeOOH On the other hand, the dehydroxylation product in air, $O_2$ and $N_2$ was recently identified as poorly crystallized hematite (6) which undergoes a recrystallization process at ca. 510°C.

In the present paper, the decomposition product of synthetic akaganeite in vacuum is compared with that obtained in air atmosphere. This study was carried out for a sample of known chlorine content in order to have control on the influence of this content on the final products (2). The characterization of the product is complemented with the study of DSC measurements.

## METHODS

Synthetic akaganeite was obtained by the hydrolysis of a 2 % in weight solution of $FeCl_3$ at 70°C. The precipitate was aged for 15 days and washed until peptization occured. The chlorine content of this sample was determined by potentiometric titration with AgNO . in a Metrhom E 536 potentiometer. This content was estimated to be

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4.5 % in Cl.

Decomposed samples in static air atmosphere, $N_2$ and $O_2$ flux and vacuum ($10^{-4}$ torr) were prepared by heating the original akaganeite at 350°C for 1 hour. Fe(II) content was determined by titration with $KMnO_4$.

The X-ray diffraction patterns were obtained with a Phillips PW 1130 diffractometer with $CoK_\alpha$ radiation and Ni filter. Differential scanning calorimetry measurements were performed in a Mettler TA 3000 system under $N_2$ flux at 8°Cmin$^{-1}$ and TG traces were recorded in a Cahn RG electrobalance.

## RESULTS AND DISCUSSION

The X-ray diffraction patterns of the various decomposition products and the original akaganeite are shown in Fig. 1. This sample shows exclusively reflections of β-FeOOH. When akaganeite is heated at 350°C in $O_2$, $N_2$ and air, the only detectable product is hematite in contrast with the observations of Paterson et al. (3) (Fig. 1b).

On the contrary, the thermal decomposition in vacuum yields a product different to hematite which is ferromagnetic and shows the diffraction pattern in Fig. 1c. The diffractogram is characterized by the presence of highly broadened profiles with appreciable intensities. These data differ from those reported by Naono et al. (5). On the other hand, some spacings observed in the diffraction pattern are similar to those corresponding to akaganeite, but the relative intensities are not consistent with this phase (1). In this way, the maximum intensity line is placed at ca. 2.52 A. This reflection could be ascribed to the presence of maghemite or magnetite. However, some lines as that observed at 5.31 A seem to indicate that akaganeite is still present. This akaganeite content may be related to the observations in (5) that are interpreted in terms of the presence of microcrystals of undecomposed akaganeite although the product cannot be considered as amorphous.

In order to analyze the possible presence of magnetite in the decomposed sample, the Fe(II) content was determined. The results indicate that a 2.7 % is present in the product. If this content is associated to magnetite, it represents a 12 % $Fe_3O_4$ ~~that~~ may contrite to the ferromagnetism of this sample.

On the other hand, the presence of maghemite in the decomposition product was studied on the basis of a simulation of several

X-ray diffraction patterns of this sample. This analysis was carried out by using a microcomputer program based in that of Sato and Machii (7). The shape function used for describing the profiles was a Cauchy type and the structure factors used in the calculations were those collected in (8). This procedure leads to the diffraction pattern in Fig 1d. As the profiles are highly broadened, the superestructure lines of maghemite cannot be observed and the pattern shows basically two groups of reflections which are similar to those observed in the diffraction pattern of the decomposition product (see Fig. 1c and d).

From the above considerations, the presence of a poorly crystalline phase structurally related to maghemite may not be discarded in the decomposition product of akaganeite in vacuum.

The thermal behaviour of this product was also examined by the recording of the DSC and TG traces. The DSC curve shows a complex exothermal effect placed at ca. 440-510°C. This result is basically in agreement with the diagram obtained by Gonzalez Calbet and Alario Franco (4) which was explained by the transformation of maghemite to hematite. In order to characterize the exotherm, two samples were prepared by interrupting the DSC experiment at 440 and 470°C, temperatures corresponding to the starting and mid points of the exotherm. The X-ray diffraction lines of these samples (Fig. 1e and f) show that the product at 440°C is similar to

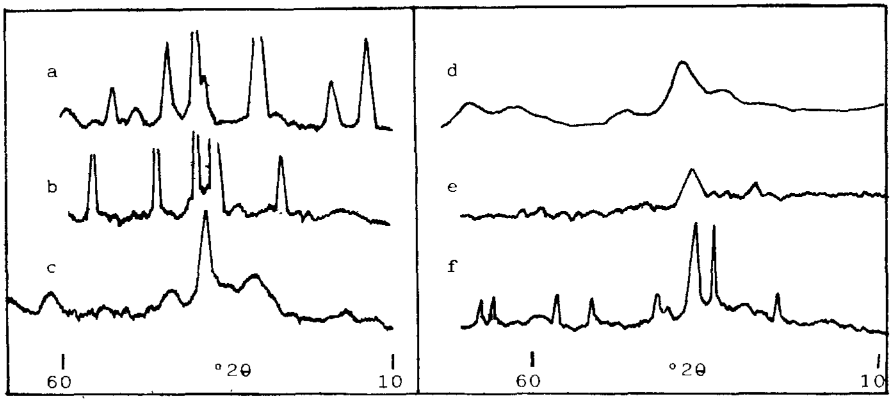

Fig. 1. X-ray diffraction patterns of akaganeite (a), decomposed samples (b,d-f) and simulated of maghemite (c).

the original decomposition product although the lines are more broadened and some reflections (5.31 A) cannot be observed. These changes may indicate that the akaganeite content in low proportion prior to the exotherm is eliminated without giving place to any noticeable thermal effect in the DSC curve. This decomposition process is also evidenced in the TG traces of the original product which shows a continuous weight loss up to 500°C with a maximum placed near 380°C. The remaining lines in Fig. 1e are again consistent with poorly crystalline maghemite.

The X-ray diffraction pattern of the sample obtained by interrupting the DSC curve at 470°C (Fig. 1f) shows exclusively lines belonging to hematite of low crystallinity. This product decreases line broadening throughout the conclusion of the exotherm.

The above results allow us to conclude that the exotherm is due to the transformation of poorly crystalline maghemite to hematite, that increases its crystallinity simultaneously to its formation, probably contributing to the evolved heat.

Moreover, the temperature of this transformation is higher to that corresponding to the transition $\gamma\text{-}Fe_2O_3 \rightarrow \alpha\text{-}Fe_2O_3$ when maghemite has higher crystallinity as that obtained by the thermal decomposition of lepidocrocite (9). In this respect, it has been recently evidenced that maghemite derived from the mechanical dehydration of lepidocrocite increases its thermal stability (10). These facts may indicate that the crystallinity or previous history of the samples affect the temperature of its transformation.

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