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THERMAL DECOMPOSITION OF A HYDRATED PYROCHLORE CONTAINING MIXED-VALENCE BISMUTH(III, V) AND POTASSIUM

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ABSTRACT

The study of the pyrolysis of the pyrochlore $[K_{1.13}Bi^{3+}_{0.34}]\,[Bi^{3+}_{0.22}Bi^{5+}_{1.78}]\,O_{5.86}(H_2O)_{0.97}$ by DTA, TGA, gas chromatography and high temperature X-ray diffraction shows a three-step decomposition: an internal redox reaction involving Bi^{5+} and OH^- ions, a dehydration and finally an internal redox reaction involving Bi^{5+} and O^{2-} ions. The structure remains of the pyrochlore type up to 310°C, despite the creation of a large amount of vacancies in the octahedral framework.

INTRODUCTION

Compounds with a pyrochlore-type structure have been widely studied over the last few years. The structure can be described as the interpenetration of an octahedral framework (B_2X_6) with a tetrahedral cuprite like A_2X' net [1]. When stoichiometric, the compounds can be formulated $A_2B_2X_6X'$, but large possibilities of vacancies in the A_2X' array enable the existence of non-stoichiometric phases. Most of them were prepared by solid state reactions. However, we showed that the synthesis of such compounds could be achieved by wet methods: we succeeded [2] in preparing a pyrochlore phase containing bismuth, potassium and protons. Its structure was investigated by means of X-ray powder diffraction [3]: the B sites appear to be fully occupied by bismuth atoms while the A sites accommodate the remaining bismuth and potassium atoms. These sites contain a large number of vacancies and it was shown that their occupancy factor was limited to 0.75, probably to optimize the K–X' distances. When heated, the phase loses weight: this was ascribed to the evolution of both oxygen and water, the latter being easily shown up by condensation. Quite surprisingly, the pyrochlore structure remains unaffected by this loss of weight most of the time. Moreover, a survey of the literature shows that little information can be obtained about the mode of decomposition of materials containing the Bi^{5+} ion. We consequently decided upon a further investigation of this decomposition by means of traditional thermal methods (TGA, DTA, high temperature X-ray diffraction = HTXRD) combined with gas chromatography.

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EXPERIMENTAL

The synthesis of the potassium bismuth pyrochlore was previously described [2,3].

The TGA and DTA experiments were carried out with a thermoanalyzer (Netzsch 429); the sample (about 300 mg) is contained in an alumina crucible and heated in a stream of dried argon at atmospheric pressure. Calcined alumina was used as a standard for the DTA experiments.

A chromatograph (Intersmat IGC 5) was used to analyze the gases evolved during the pyrolysis.

The temperature of the column (Porapak Q) was fixed at 75°C which enabled a good separation of oxygen and water. The sample (~ 200 mg) was heated in a closed U tube; the gases were swept out at regular intervals of time by a stream of dried helium. A similar procedure was used to standardize the apparatus: sodium perchlorate was chosen as a standard for oxygen and sodium oxalate monohydrate for water.

The structural changes occurring during pyrolysis were investigated by means of a Guinier-Lenne (Nonius) camera in dried nitrogen at atmospheric pressure. The sample was spread on a gold grid; the X-ray pattern of gold, corrected for thermal expansion, was used as an internal standard for lattice parameter determinations.

The thermal expansion of the pyrochlore phase was evaluated by comparing the cell parameter at a fixed temperature with the one obtained at room temperature after a fast quenching of the phase.

A uniform heating rate of $100°\mathrm{C\,h^{-1}}$ was chosen for an easier comparison of the results of the different methods, with the exception of the DTA experiments, which were performed with a rate of $300°\mathrm{C\,h^{-1}}$ in order to decrease the spreading of the peaks.

RESULTS

A typical set of experimental curves is shown in Fig. 1. The analytical characterization of the sample is given in Table 1. In accordance with our previous work [3], the phase can be formulated

$$[\mathrm{K}_{1.13}\mathrm{Bi}^{3+}_{0.34}]\ [\mathrm{Bi}^{3+}_{0.22}\mathrm{Bi}^{5+}_{1.78}]\ \mathrm{O}_{5.86}(\mathrm{H_2O})_{0.97}$$

The shapes of the TGA (Fig. 1a) and DTA (Fig. 1b) curves indicate that the phenomena taking place during the pyrolysis are rather complex. The TGA curve shows that the loss of weight begins at about 40°C and ends at 340°C. Endothermic peaks appear on the DTA curve: the first spreads from 150°C to around 200°C while the second one seems to be a composite peak.

The reasons for this complexity are clearly shown by the curves (Fig. 1c) which give the quantities of oxygen and water evolved during the rise in temperature. Quite obviously, we notice a single step evolution of water between 40 and 260°C, whereas the evolution of oxygen takes place in two stages: the first $\mathrm{O_2}$ emission (about 7% of

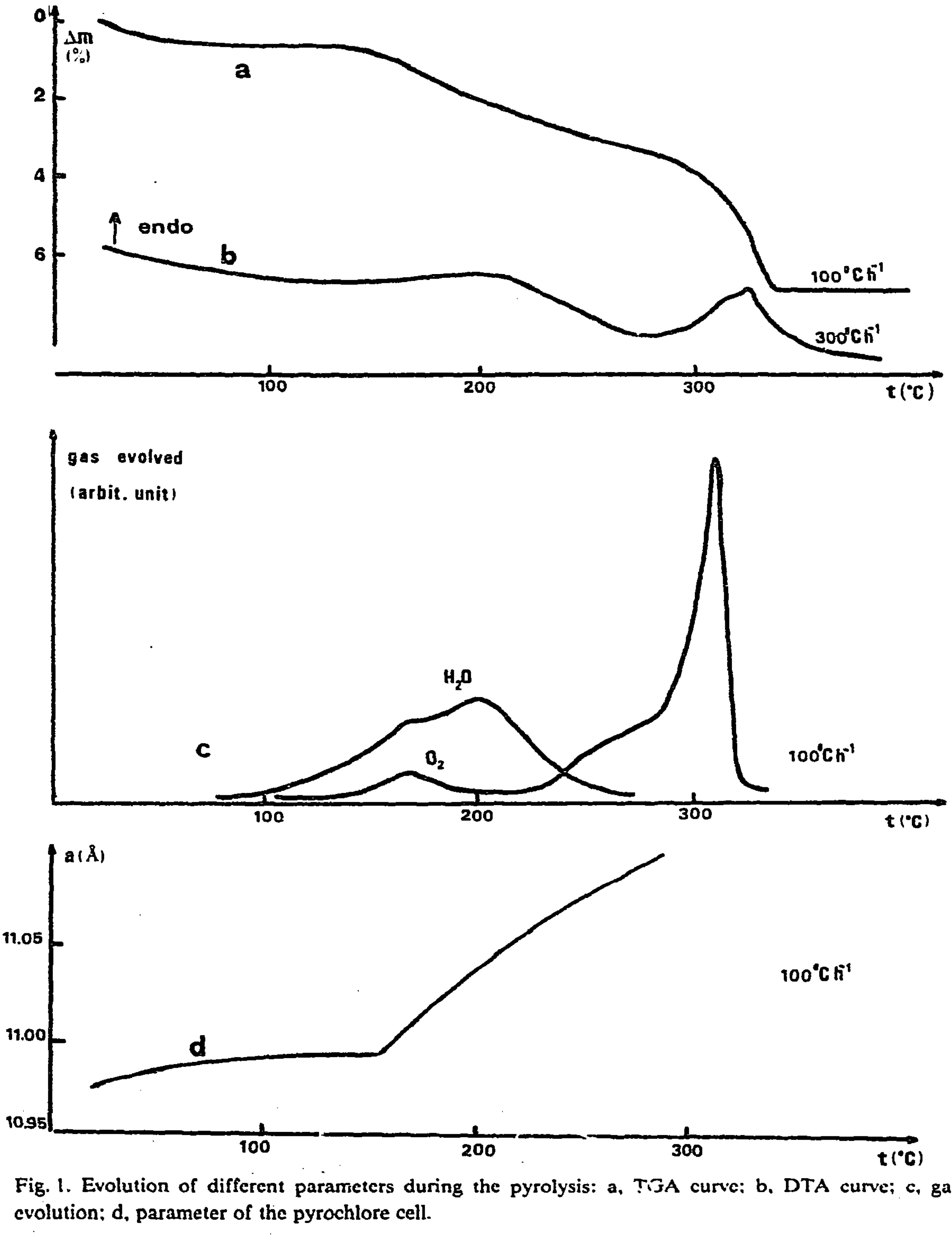

Fig. 1. Evolution of different parameters during the pyrolysis: a, TGA curve; b, DTA curve; c, gas evolution; d, parameter of the pyrochlore cell.

the total O_2 emission) is concomitant with the water emission whereas most of the oxygen is lost between 230 and 320°C.

The HTXRD pattern shows that the pyrochlore structure is retained up to about

TABLE 1

Analytical results

Bi^{5+} (10^{-3} M g^{-1})	2.73
Bi^{3+} (10^{-3} M g^{-1})	0.90
K^{+} (10^{-3} M g^{-1})	1.73
Weight loss at 450°C (%)	7.05
Specific gravity (g cm^{-3})	6.50
Cell parameter (Å)	10.971 (1)
O (chromatography) (%)	4.7
O (calculated) (%)	4.4
H_2O (chromatography) (%)	2.7
H_2O (calculated) (%)	2.7

310–320°C, when it changes into a tetragonal phase ($a = 10.168$ (3), $c = 5.710$ (2) Å at 340°C) that decomposes at 370°C into a mixture of Bi_2O_3 and K_2O. This mixture then reacts at 500°C to give a compound which has been identified as $K_2Bi_4O_7$ [4]. Figure 1d shows the variation of the pyrochlore cell parameter vs. temperature: between room temperature and 160°C, a slight increase followed by a stabilization is observed: a large change of slope occurs at 160°C and a quasi-linear increase is noticed before the pyrochlore structure breaks down. As the slope changes, the intensities of the odd reflections of the f.c.c. cell come to zero giving rise to a fluorite type pattern.

DISCUSSION

The emission of oxygen, as well as the decrease of the oxidizing power (as measured by iodometry on partially decomposed samples), clearly show that a redox reaction occurs when the pyrochlore phase is heated. This reaction must involve Bi^{5+} and oxygen ions (with or without associated protons) belonging either to the octahedral or the cuprite-like networks.

The first step of the pyrolysis is rather complex. The shoulder at about 160°C, which can be noticed on the water evolution curve, coincides with a maximum emission of oxygen. This is consistent with the assumption that, in this temperature range, two superimposed reactions take place, i.e. the beginning of a dehydration process with a maximum at about 220°C, and an internal redox reaction which can be written as

$$Bi^{5+} + 2\,OH^{-} \rightarrow Bi^{3+} + \tfrac{1}{2}O_2 + H_2O$$

The existence of OH^{-} ions has been confirmed by other methods, particularly NMR [5] and XPS experiments reported elsewhere.

The second step is simpler and can be interpreted as the occurrence of the reaction

$$Bi^{5+} + O^{2-} \rightarrow Bi^{3+} + \tfrac{1}{2}O_2$$

The relatively low temperature of decomposition is probably due to the presence of OH^- ions which induce it. When prepared by solid state reactions, the stability of the compounds containing Bi^{5+} ions is increased whatever mode of preparation is chosen: either at atmospheric pressure for $Na_3Bi_4O_7$ [6] and the presumed $Sr_3BiO_{5.5}$ [7,8] or under high oxygen pressure for $KBiO_3$ [9] or $Sr_2Bi_2O_7$ [10].

The most original feature observed during the pyrolysis concerns the evolution of the pyrochlore structure. Up to 160°C, the evolution of the cell parameter results from two opposite variations

(i) an increase imputable to the thermal expansion of the pyrochlore framework

(ii) a decrease consistent with the dehydration, as previously described by other authors for $KTaWO_6 \cdot H_2O$ [11] and $K_{1+x}(Ta_{1+x}W_{1-x})O_6, n\,H_2O$ [12] for example.

After 160°C, the sudden increase coincides with the creation of vacancies in the octahedral network as described elsewhere [13], the structure remaining of the pyrochlore type. It turns into a fluorite structure undoubtedly involving a redistribution of the ordered cations among the different sites. The quadratic form taking place at about 300°C has not been seriously investigated since it cannot be quenched in large enough quantities to undertake an X-ray diffraction study. It probably contains alkaline cations and an excess of oxygen as in the phase $BiO_{1.5+x}$ called $\beta\,Bi_2O_3$ previously described by Gattow and Schutze [14].

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