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Formation of zirconium titanate powder from a sol–gel prepared reactive precursor

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A hydroxoperoxo compound of Zr and Ti (HXPZT) was prepared as a reactive powder by a sol–gel method. X-ray diffraction and SEM studies showed it to be formed from small (ca. 10–15 μm) amorphous particles. The effects of progressive thermal treatment were determined by differential thermal analysis, thermogravimetric analysis, temperature programmed desorption, X-ray diffraction, energy-dispersive spectrometry and SEM. The features observed have been attributed to the removal of physically and chemically bonded water and of some nitrogen-containing compound. Crystallization of zirconium titanate occurs at low temperature (650 °C), giving rise to spherical (ca. 2 μm dia.) regular particles.

1. Introduction

Zirconium titanate, ideally $ZrTiO_4$, is a very well-known material for a wide field of applications. The binary system TiO_2–ZrO_2 has been shown to be an effective acid–base bifunctional catalyst [1–3]. Titanates and zirconates constitute one of the most important families of ferroelectric material used in the industrial production of transducer ceramic elements [4, 5]; polycrystalline zirconium titanate has been investigated as a high-dielectric material [6].

However, reactive calcination from oxides leads to synthesizing these compounds at elevated temperatures (1200–1700 °C) [6, 7]. More recently, the sol–gel and alkoxide synthesis routes have been widely investigated to obtain ultrafine, very homogeneous and high-purity materials as ceramics, glasses, glass–ceramics and composites [8, 9]. In these ways it is possible to prepare highly reactive precursors and new synthetic compositions which allows one to lower the sintering temperature and to control the microstructure. The technological applications are of great interest and show the impact of those new processes: monoliths, thin glass coatings, glass refractories, catalysts, fibres and other components in electronics, catalytic and advanced ceramic materials.

On the other hand, hydrated peroxides $MO(O_2)(H_2O)_x$ ($M = Ti, Zr$; $x > 2$) have been precipitated by ammonia from titanium or zirconium solutions containing hydrogen peroxide [10, 11].

In the present work, we report the preparation of zirconium titanate powder at low temperature (ca. 650 °C) from a reactive chemically prepared hydroxoperoxo compound, used as precursor. The effects of progressive thermal treatment on this precursor have been investigated by a series of techniques.

2. Experimental procedure

2.1. Materials

The starting reactive powdered precursor was obtained from an anhydrous methanol solution which contained equimolar amounts of titanium tetrachloride (Merck, 99.99%) and zirconyl chloride (Fluka AG, 43–44% ZrO_2). Hydrogen peroxide (Merck, 30–32 wt % solution in water) was added in excess. The mixing was performed by constant stirring at 0 °C and the hydrolysis was carried out by slow addition of 28% aqueous ammonia (pH = 8–9). The precipitate was allowed to settle and the supernatant liquid decanted after several washings with distilled water; completion of the precipitation was verified by adding alkali to the decanted portions of the solution, until no further precipitation occurred. The powder was repeatedly washed and filtered until the filtrate showed a negative reaction for Cl^- ions ($AgNO_3$ test). Acetone was used for the last washing. The solid was dried slowly for several days under an infrared lamp and finally powdered in an agate mortar. The preparative schedule is summarized in Fig. 1.

The final material was slightly yellow, which is an indication of the formation of peroxo bonds as often found for this kind of oxide [10, 11]. Therefore it seems reasonable to think that a hydroxoperoxo Zr–Ti compound (designated HXPZT hereafter) had been formed.

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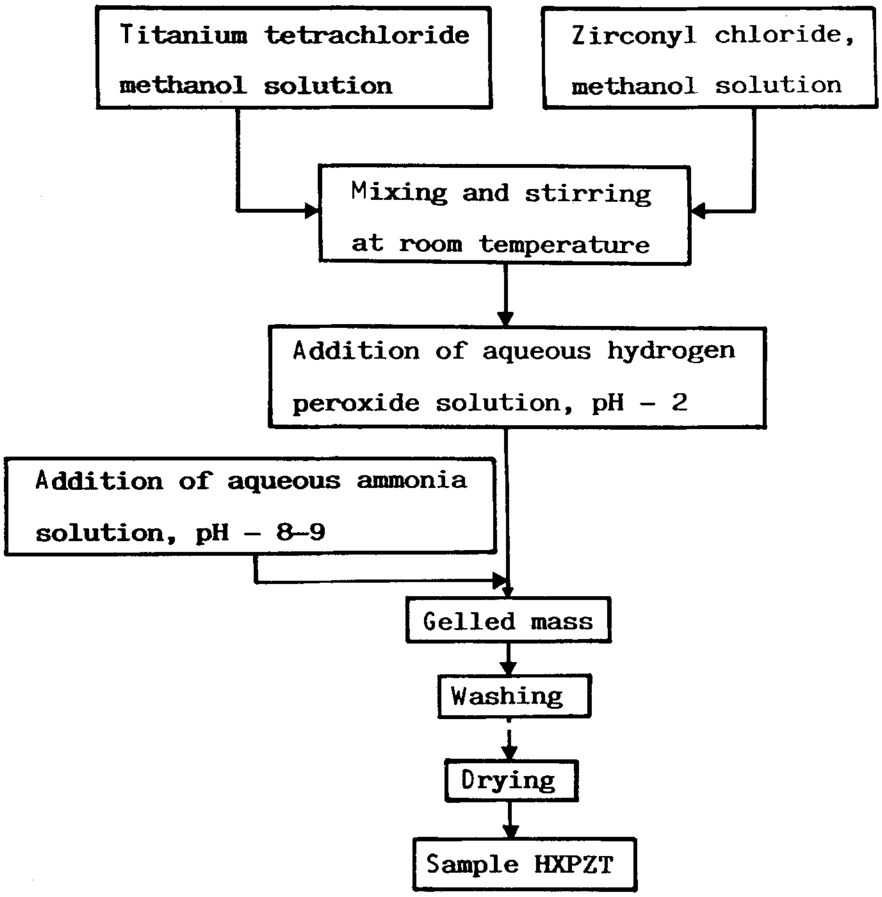

Figure 1 Preparative procedure of the hydroxoperoxo Zr–Ti reactive precursor (HXPZT).

2.2. Techniques

The non-isothermal thermogravimetric (TG) traces were recorded under 10^{-3} torr, using a Cahn electrobalance (model RG) and a heating rate of 4 °C min^{-1}. The analysis of evolved gases during sample heating was performed with a Hewlett-Packard 5992 A quadrupole temperature programmed desorption–mass spectrometer (TPD-MS device). Differential thermogravimetric analysis (DTA) was obtained in static air with a thermal analyser (model PTC-10A, Rigaku Co., Tokyo) at a heating rate of 10 °C min^{-1}. About 20 mg of sample was gently packed in the platinum holder. Calcined alumina was used as reference material. X-ray diffraction (XRD) patterns were obtained at room temperature with a Philips PW 1060 using CuK_α radiation and a nickel filter. Finally, with their surfaces made conductive by gold sputtering, the original precursor and the thermally treated products were examined by scanning electron microscopy (ISI model SS-40). An energy-dispersive X-ray analyser (Kevex model 8000) was fitted to the SEM system.

3. Results and discussion

3.1. TG/TPD-MS and DTA studies

From the TG and TPD-MS data (Fig. 2) the chemical formula of HXPZT was established as $ZrTiO_{3.43}(OH)_{1.13}xH_2O$, thus corresponding to ca. 0.8 ± 0.1 peroxo species per metal ion. By elemental chemical analysis, nitrogen (N = 3.5 wt %) and carbon (C = 0.5 wt %) were found, and traces of N_2, NO_2 and CO_x were detected by mass spectrometry during the TPD experiments. HXPZT was found amorphous by XRD. The DTA analysis (Fig. 3) showed a great endothermic effect at ~ 100 °C which was ascribed principally to water elimination. The simultaneous decomposition of peroxide species could explain the width of this DTA peak. Both processes are represented by Reaction 1:

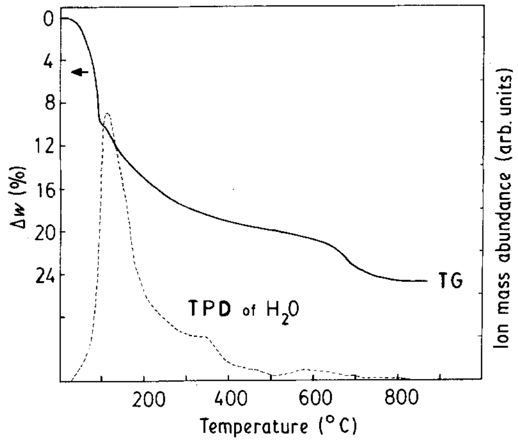

Figure 2 (——) TG and (– – –) TPD (water evolution) diagrams of the HXPZT reactive precursor, β = 4 °C min^{-1}.

$$2H_2O(s) + O_2^{2-}(s) \xrightarrow{\Delta} 2H_2O(g) + O^{2-}(s) + \tfrac{1}{2}O_2(g) \qquad (1)$$

As the temperature increases, the remaining water,

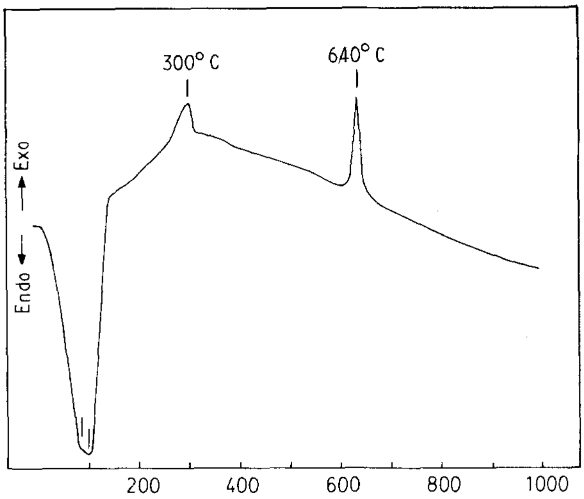

Figure 3 DTA curve of the HXPZT powder, $\beta = 10\,^{\circ}\mathrm{C\,min^{-1}}$.

strongly bonded inside the pores of the particles, can be eliminated.

The exothermal effect at 300 °C could be due to the elimination of ammonium retained during the preparation and its partial or total combustion (Reactions 2 and 3 below) with oxygen from air and possibly also from that formed *in situ* as indicated by Reaction 1:

$$4NH_3 + 7O_2 \xrightarrow{\Delta} 6H_2O + 4NO_2 \qquad (2)$$

$$4NH_3 + 3O_2 \xrightarrow{\Delta} 2N_2 + 6H_2O \qquad (3)$$

The finding of ~3.5 wt % of nitrogen in the original "as-prepared" sample is in favour of this interpretation as well as the detection of very little N_2 and NO_2 by mass spectrometry during the TPD experiments. Finally, the sharp exothermal effect at 640 °C suggests the crystallization of a new phase.

The TG and TPD diagrams (Fig. 2) are consistent with some of the above suggestions. Thus, the main weight loss can be associated with the endothermic effect observed by DTA (Fig. 3) and attributed to water elimination (Reaction 1). After 250 °C, the weight loss continues and is attributed to the progressive elimination of water molecules trapped or bonded into the pores of the solid. The second peak in the TPD diagram could be the result of Reactions 2 and 3. The last weight losses could be due to the faster elimination of the remaining water when the crystallization process takes place. This would indicate that the thermal treatment produces a strong atomic rearrangement that involves water elimination, possibly by condensation of OH groups strongly bonded to Zr and Ti ("structural water").

$$OH^-(s) + OH^-(s) \xrightarrow{\Delta} H_2O(g) + O^{2-}(s) \qquad (4)$$

In fact, the total weight loss obtained after heating up to 800 °C was 24 wt % and the resulting solid showed a high degree of shrinkage.

3.2. Structural information obtained by XRD

The X-ray diffraction diagram of the fresh HXPZT sample and that of the material heated at 250 °C indicates the absence of crystallinity (Fig. 4). The weak diffraction peaks observed after heating at 500 °C reflect the beginning of a structural ordering and nucleation. These peaks correspond to rutile and zirconium titanate (orthorhombic) [12]. For the sample heated at 600 °C, i.e. at a temperature slightly lower than that corresponding to the sharp exothermic DTA peak (Fig. 3), the main X-ray peak of zirconium titanate is much more intense, whereas that of rutile remains weak. The formation of crystalline zirconium titanate (ZT) above 640 °C is shown by sharp X-ray peaks (Fig. 4).

In short, XRD suggests that between 500 and 600 °C the progressive formation of nanometre-sized particles of ZT takes place. This temperature range is low and proves the potential interest of the reactive powdered material [13, 14].

The XRD spectrum of the sample calcined at 1000 °C was identical to that of the sample calcined at 800 °C. This is in contrast with previous results [15] which showed that relatively important amounts of titanium dioxide were separated from zirconium titanate above 850 °C. On the other hand, no crystalline zirconium dioxide was found during our XRD studies, which indicates that all zirconium atoms contribute to the formation of ZT. This could be explained by the

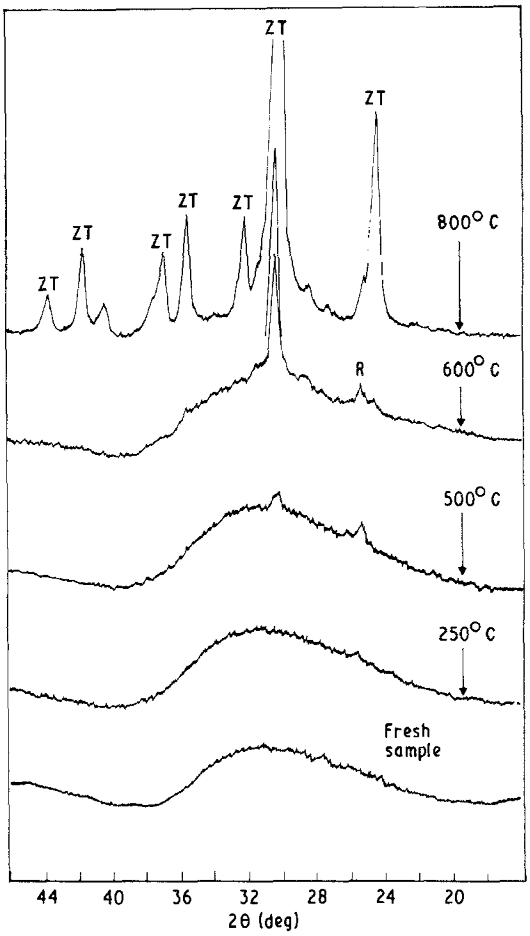

Figure 4 X-ray diffraction diagrams (CuK_α) of the solids obtained after treatment of the HXPZT precursor at the temperatures indicated: (R) rutile, (ZT) zirconium titanate.

existence of $Zr_{1+x}TiO_{4+2x}$ to compensate for the small amount of rutile, as suggested by other authors [15]. Note that the rutile formation is concomitant with the TPD signal tentatively attributed to the condensation of strongly bonded OH groups (Reaction 4).

A complementary extended X-ray absorption fine structure (EXAFS) study of samples heated at 250–500 °C is in progress [16].

3.3. SEM-EDX study

As shown by SEM (Fig. 5) the HXPZT powder is formed from small ($\sim$ 10–15 µm), regular and roughly spherical particles. They are agglomerated, which reflects the high surface energy bonding them. EDX analysis indicates a ZrO_2/TiO_2 ratio of ca. 3.42. This could be due to a coating effect. The possible existence of isolated particles enriched in Ti was not revealed by energy dispersive spectrometry (EDX) analysis (1–2 µm deep).

For the solid material treated at 500 °C (Fig. 6), SEM examination showed a lot of cracks with river structures. These features could be due to the elimination of H_2O. EDX analysis (Fig. 6) indicated a slightly higher proportion of Ti in these particles, as compared with those of the fresh sample (Fig. 5). This fact is in agreement with the formation of TiO_2 and ZT nucleation showed by the X-ray study (Fig. 4).

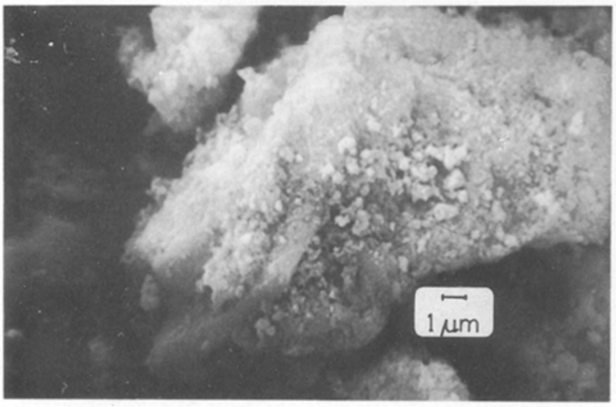

Figure 5 SEM photomicrograph and EDX analysis of the HXPZT fresh sample: TiO_2 22.6%, ZrO_2 77.4%.

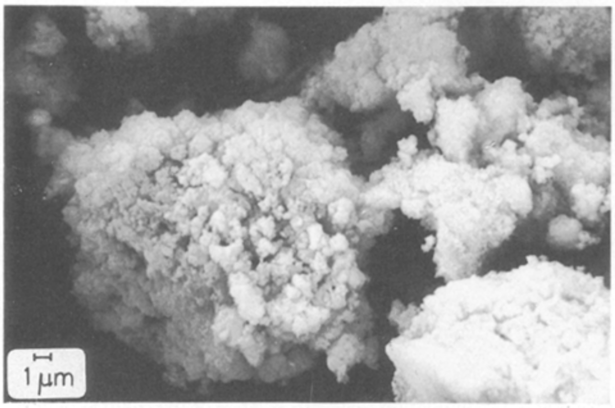

Figure 6 SEM photomicrograph and EDX analysis for the sample treated at 500 °C TiO_2 27.3%, ZrO_2 72.7%.

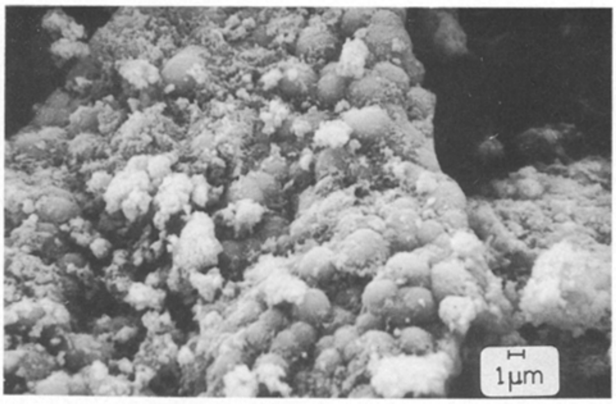

Figure 7 SEM photomicrograph and EDX analysis for the sample treated at 800 °C: TiO_2 50.95%, ZrO_2 49.05%.

After treatment at 800 °C the morphology of the particles is markedly different (Fig. 7). Sintering has taken place. The particles present a smooth surface and are regular and spherical in shape. The progressive sintering process of this reactive powder can also be responsible for the drift of the DTA base line (Fig. 3). EDX analysis confirmed the formation of ZT (Fig. 7).

Work is in progress to study the sintering behaviour of this powder, since enhanced sintering and well-developed microstructures can be obtained by conveniently using the thermally treated HXPZT precursor.

4. Conclusions

A hydroxoperoxo Zr–Ti compound was chemically prepared by treating solutions of $ZrOCl_2$ + $TiCl_4$ in methanol with hydrogen peroxide and ammonium hydroxide aqueous solutions. The thermal treatment of this reactive precursor produces spherical particles of single-phase zirconium titanate with high crystallinity at temperatures as low as 650 °C. The preliminary results of this study show that processing of the HXPZT could be a promising candidate for the synthesis of catalysts, electroceramics and advanced ceramic materials.

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