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Synthesis of magnesium orthotitanate Mg_2TiO_4

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Abstract

The magnesium orthotitanate Mg_2TiO_4 is obtained from a precipitate calcined at 500 °C in a dynamic atmosphere. This precipitate is prepared by coprecipitation of a Ti(IV)–Mg(II) sulphuric solution, at boiling temperature, in a molar ratio 1:2, with an aqueous solution of sodium hydroxide.

INTRODUCTION

Magnesium orthotitanate Mg_2TiO_4 crystallises in a cubic system and has an inverse spinel structure $Mg(MgTi)O_4$.

Magnesium orthotitanate is used in chip impact and heat resistors [1], as microwave dielectrics [2], for temperature compensating capacitors [3], etc. It is also employed as a refractory material.

Only a few papers have been published on the synthesis of magnesium orthotitanate. Billiet et al. [4] prepared very pure Mg_2TiO_4 by heating a mixture of titanium oxide and magnesium oxide at 1300 °C; Navrotsky and Kleppla [5] also obtained Mg_2TiO_4 at 1300 °C by heating the same mixture for 72 h; Popkovich and Sviridov [6] managed to prepare Mg_2TiO_4 at 1000 °C, but with $MgTiO_3$ and MgO impurities.

Thus, so far, the spinel Mg_2TiO_4 has not been stabilised below 1000 °C. In the present study, the synthesis of magnesium orthotitanate was carried out at temperatures of about 500–550 °C by coprecipitating the titanium(IV) and magnesium(II) salts in a Ti^{4+}/Mg^{2+} molar ratio of 1:2. This same technique was previously used to synthesise other titanates.

EXPERIMENTAL

Materials

Titanium (fine powder form), $MgSO_4 \cdot 7H_2O$, H_2SO_4 (95–97%) and NaOH, all from Merck, AnalaR quality, were used.

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Preparation of the sample

Sulphuric solutions of 0.5 M Ti^{+4}/Mg^{2+} were prepared as follows. Titanium (fine powder) was weighed out and boiled with 2 N H_2SO_4 and a few drops of concentrated nitric acid until the powder dissolved. To this solution was added the required amount of $MgSO_4 \cdot 7H_2O$.

Precipitates were obtained by adding a concentrated aqueous solution of sodium hydroxide drop by drop to the sulphuric solution of titanium and magnesium at both room temperature and at the boiling point of the sulphuric solution. The solutions were stirred rapidly during the addition of the sodium hydroxide and the pH was controlled with a pH meter. The white gelatinous precipitates obtained were collected by filtration on a No. 4 porosity filter. The filtrates were analysed for titanium using 2% chromotropic acid and for magnesium by complexometric titration with ethylenediaminetetraacetic acid (EDTA). The analyses were negative, showing that the precipitation was quantitative and that the titanium–magnesium molar composition of the precipitates was also 1 : 2.

The precipitates were washed with cold distilled water until no sulphate was present in the washings. Using atomic absorption spectrophotometry, the washed precipitates were shown to be free of sodium ions.

The precipitates were dried at room temperature, ground (grains size < 95 μm) and kept in closed vessels.

The precipitates were studied by thermogravimetry (TG), differential thermal analysis (DTA), X-ray powder diffraction (XRPD) and infrared reflection spectroscopy (IRRS).

Apparatus

Thermogravimetric (TG) analysis

A Mettler TA 3000 system with a TG50 attachment was used at a heating rate of $600\,^{\circ}C\ h^{-1}$.

Differential thermal analysis (DTA)

A laboratory-constructed system incorporating a vertical furnace and a temperature regulation system, both from Adamel, and a differential chromel–alumel thermocouple were used. The heating rate was $300\,^{\circ}C\ h^{-1}$.

X-ray powder diffraction

A Philips PW 1130 diffractometer was used with a Ni filter and Cu $K\alpha_1$ radiation.

IR spectroscopy

A Perkin–Elmer model 683 spectrophotometer was used. The sample was prepared as a mull using Fluorolube as mulling agent for examination in the region 4000–1500 cm^{-1}, and as KBr pellets for the region 1500–200 cm^{-1}.

RESULTS AND DISCUSSION

The X-ray diffractogram of the 0.5 M Ti^{4+}/Mg^{2+} precipitate obtained at room temperature (RT) indicated a poorly crystallised brucite; the X-ray diffractogram of the precipitate obtained at the boiling point (BP) of the solution showed a poorly crystallised mixture of anatase and brucite.

The IR spectra of the two precipitates are practically identical. Figure 1 shows the IR spectrum of the precipitate at BP. The sharp band at 3700 cm^{-1} is caused by the stretching vibrations of the hydroxyl groups; the wide band at 3400 cm^{-1} is associated with the stretching vibrations of the water of hydration; the bands at 1425 and 1500 cm^{-1} are attributed to CO_3^{2-} which indicates that the precipitate absorbs a little CO_2 from the air; and the wide band at 525 cm^{-1} are due to metal–oxygen vibrations.

The thermal behaviour of the two precipitates is different. Figure 2 gives the TG and differential thermogravimetry (DTG) curves of the precipitate

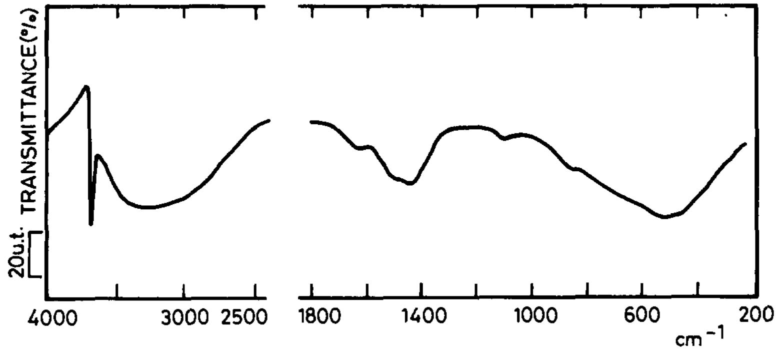

Fig. 1. IR spectra of the precipitate obtained at BP (boiling point).

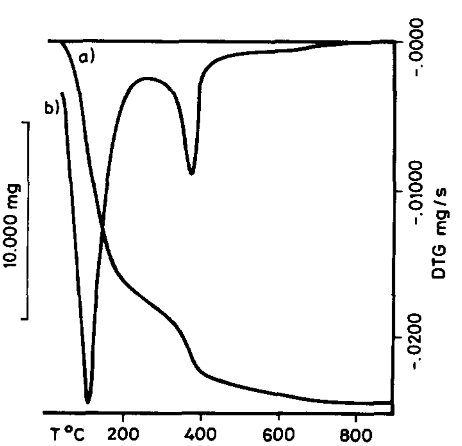

Fig. 2. TG and DTG curves of the precipitate obtained at RT (room temperature). Sample weight 41.076 mg.

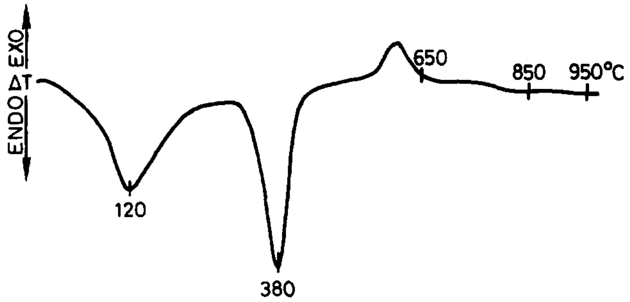

Fig. 3. DTA curve of the precipitate obtained at RT.

obtained at RT. Curve a shows two weight losses: the first loss was 32.6% of the initial weight and corresponds to loss of hydration water; the second loss (12.4% of the initial weight) is attributed to the dehydroxylation of the $Mg(OH)_2$.

The DTG curve (curve b) shows two peaks, the first at 120 °C and the second at 380 °C.

The thermogravimetric results indicate that 85% of the magnesium precipitates separately from the titanium.

The DTA curve in Fig. 3 presents two endothermic peaks, the first at 120 °C, due to the loss of hydration water and the second at 380 °C indicates the dehydroxylation of $Mg(OH)_2$. There is an exothermic peak between 500 and 650 °C.

Identification of the transformation taking place in the samples during heating was made by XRPD. The X-ray patterns of the samples taken at predetermined points on the DTA curve from Fig. 3, are shown in Fig. 4.

The X-ray pattern (Fig. 4, curve a) of the sample taken at 325 °C shows poorly crystallised brucite. The X-ray diagram (Fig. 4, curve b) taken at 500 °C indicates poorly crystallised periclase; the titanium oxide remains amorphous, although at 500 °C the titanium oxide crystallised as anatase. The X-ray pattern (Fig. 4, curve c) taken at the end of the exothermic peak, at 690 °C, indicates the presence of magnesium orthotitanate, Mg_2TiO_4, and geikielite, $MgTiO_3$.

Figure 5 shows the TG and DTG curves of the precipitate obtained at BP. The TG curve (Fig. 5, curve a), presents two weight losses; the DTG curve (Fig. 5, curve b) presents two peaks at 115 and 375 °C. The thermogravimetric results indicate that all of the magnesium precipitated as brucite.

The DTA curve (Fig. 6) shows only two endothermic peaks; the exothermic peak has disappeared.

If the DTA curves are obtained in a dynamic atmosphere of air, oxygen, or argon, the endothermic phenomena occur at lower temperatures, around 60 °C below the static atmosphere temperature range.

The X-ray patterns of the samples taken at predetermined points on the DTA curve (Fig. 6) are shown in Fig. 7.

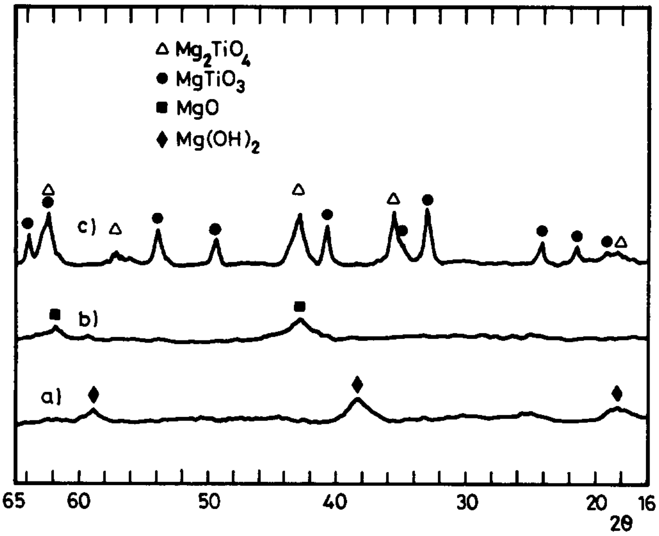

Fig. 4. X-ray diffraction patterns of the precipitate obtained at RT: (a) at 325 ° C; (b) at 500 ° C; (c) at 690 ° C.

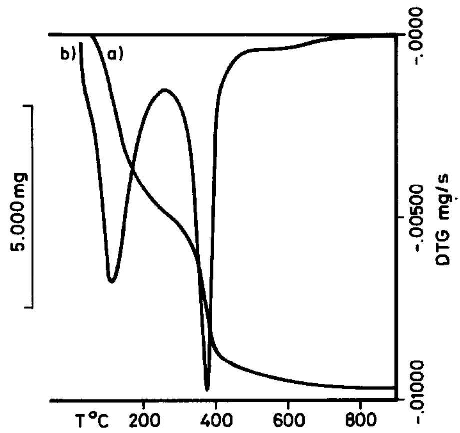

Fig. 5. TG and DTG curves of the precipitate obtained at BP. Sample weight 24.911 mg.

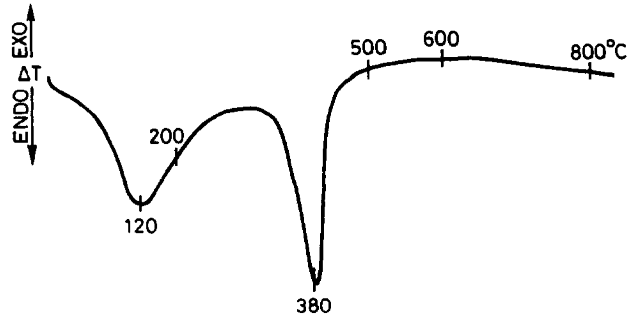

Fig. 6. DTA curve of the precipitate obtained at BP.

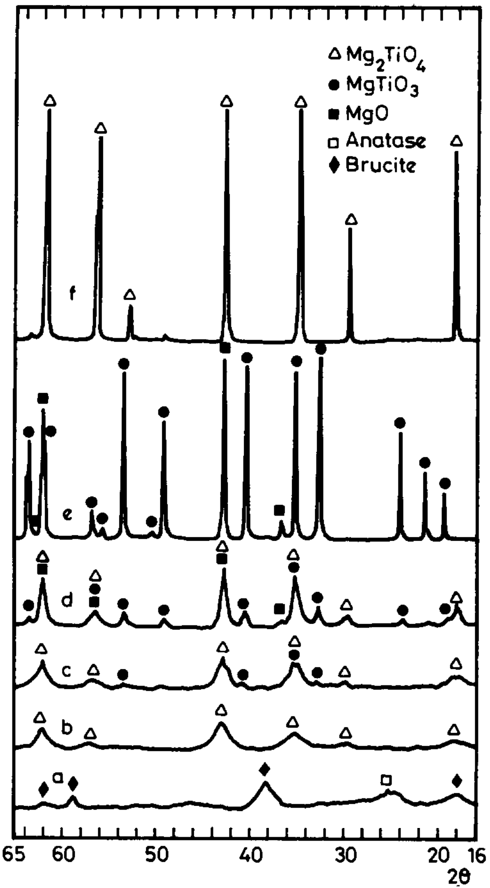

Fig. 7. X-ray diffraction patterns of the precipitate obtained at BP: (a) at 320 °C; (b) at 560 °C; (c) at 560 °C for 4 h; (d) at 740 °C; (e) at 1000 °C; (f) above 1000 °C.

The X-ray pattern (Fig. 7, curve a) of the sample taken at 320 °C shows a mixture of anatase, TiO_2, and brucite, $Mg(OH)_2$, both poorly crystallised. The X-ray pattern (Fig. 7, curve b) taken at the end of the dehydroxylation, 560 °C, corresponds to the magnesium orthotitanate Mg_2TiO_4. The absence of geikielite in the X-ray diagram indicates that the exothermic peak of the DTA curve of the precipitate obtained at RT corresponds to the formation and crystallisation of geikielite.

In order to improve the crystallisation of the magnesium orthotitanate, the precipitate was treated isothermally at 560 °C for 4 h, or calcinated at 740 °C. The X-ray pattern of the sample calcinated at 560 °C for 4 h shows lines of the orthotitanate and of geikielite (Fig. 7, curve c). The X-ray pattern of the sample calcinated at 740 °C shows lines of the orthotitanate, geikielite and MgO (Fig. 7, curve d).

These results confirm that in this temperature interval, the spinel appears to be metastable with respect to the decomposition of $MgTiO_3$ and MgO: $Mg_2TiO_4 \rightleftharpoons MgTiO_3 + MgO$.

The X-ray pattern of the sample calcinated at 1000 °C (Fig. 7, curve e) shows a mixture of geikielite, $MgTiO_3$, and periclase, MgO.

The X-ray pattern of the sample calcinated above 1000 °C (Fig. 7, curve f) corresponds to the magnesium orthotitanate, Mg_2TiO_4.

All these results agree with the phase diagram of the $MgO-TiO_2$ system published by Wechsler and Navrotsky [7].

Finally, the dielectric constant (ε) and the electric resistivity (ρ) of the magnesium orthotitanate obtained in the present study were measured following the same procedure used by the authors for geikielite [8]; the values obtained were $\varepsilon = 15.1$ and $\rho = 6.0 \times 10^9$ Ω cm. These values are similar to the data given in the Handbook of Chemistry and Physics (1983–1984) [9] for titanates of alkaline earth metals.

CONCLUSIONS

The magnesium orthotitanate Mg_2TiO_4 was obtained at low temperatures by coprecipitating a sulphuric solution of Ti^{4+} and Mg^{2+} in molar ratio 1 : 2 with an aqueous solution of sodium hydroxide at boiling temperature. The precipitate obtained was heated in a dynamic atmosphere up to 500 °C.

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