

Ambient-temperature formation of metal titanates from ilmenite (FeTiO₃)

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Alkaline earth metal titanates are an important material in many industrial areas, from dielectric capacitors to ceramics. The present methods of production rely upon purification of the oxides prior to formation. This paper outlines the formation of pure and mixed metal titanates directly from metal oxides and a natural starting material, in the form of the mineral ilmenite (FeTiO₃). The reaction is induced by mechanical activation in a laboratory-scale ball mill and is essentially complete within 50 h for all samples, forming a nanocrystalline titanate and an unidentified iron compound. Annealing studies show that the titanate is formed during milling and can be crystallized at 800 °C. Additionally, the reaction process increases the solubility and separation of iron and titanium from ilmenite and this may have application in the formation of titanium compounds from solution. © 1998 Chapman & Hall

1. Introduction

Alkaline-earth metal titanates are becoming increasingly important in ceramics and electronic components. There are several possible methods of production, e.g., co-precipitation of the oxides from solution [1], sol-gel processing [2, 3] or thermal decomposition of peroxo salts [4]. Mechanochemical synthesis of the metal titanates from titanium dioxide and the metal oxides and hydroxides has also been reported [5, 6]. However, the conventional industrial preparation route is by thermal reaction between a mixture of powders of TiO₂ and oxide (for Mg and Ca) or carbonate (for Sr and Ba) at 1300 °C [7]. The titanium dioxide used is purified from ilmenite (FeTiO₃) by a reduction, leaching, chlorination, distillation and hydrolysis route [7].

A single-process route from ilmenite may prove to be a viable alternative to the current technique. However, a major problem will be with purity owing to the removal of iron from the product titanate. The envisaged route will form an iron product that should be readily leachable from the titanate. The concomitant formation of submicron particles is of considerable value in subsequent sintering operations.

Thermodynamic calculations were made for the following reaction between ilmenite and the metal oxides:



The free energies of reaction, summarized in Table I, indicated the possibility of a solid-state exchange of iron in ilmenite and alkaline-earth metals in oxide form to form alkaline-earth metal titanates, the reaction becoming more favourable with increasing atomic number. However, the metal oxides are known to absorb water and carbon dioxide from the

atmosphere to form hydroxides and carbonates. Calculations for the metal hydroxides showed that only magnesium would be affected with no predicted reaction; the absence of reaction without heating has been shown previously [3]:



The free energies of reaction are more positive than for the unhydrated oxides which may indicate a less facile reaction. Carbon dioxide was a much more significant problem; all four metal carbonates were predicted not to react owing to the stability of the alkaline earth metal carbonates:



A similar trend was noted with other anions such as sulphate, nitrate and halides with the predicted free energy for all these reactions positive with the exception of magnesium chloride. Previous calculations for rutile (TiO₂) showed that all the reactions were more favourable when iron was absent [6].

Ball milling has been used to activate reactions that otherwise require more extreme thermal treatment [8] and to cause reactions to occur under conditions where more conventional processing techniques are ineffective [6, 9]. Thus, the mechanical activation technique was used to investigate the reaction between mineral ilmenite and alkaline-earth metal oxides with a view to forming their titanates.

2. Experimental procedure

The ilmenite was the same as that used previously [8]. The analytical-grade metal oxides, having been stored in air for several months prior to use, were analysed by X-ray diffraction (XRD) and were found to have

TABLE I Calculated values of ΔG at 25°C for reactions (1)–(3) and at 25 and 800°C for reaction (5)

Reaction	ΔG (kJ mol ⁻¹)			
	M \equiv Mg	M \equiv Ca	M \equiv Sr	M \equiv Ba
(1)	-8.58	-65.1	-119	-141
(2)	19.0	-7.31	-36.5	-43.5
(3)	19.4	44.9	42.8	56.6
(5) at 25°C	-128	-185	-239	-260
(5) at 800°C	-82	-145	-196	-208

absorbed water and/or CO₂. Magnesium and calcium were primarily as the oxide but both contained small fractions of their hydroxide; strontium was present as the carbonate and barium was present as the hydroxide. The metal oxides used were heated to 1300°C prior to use under a flowing argon atmosphere to decompose hydroxide and/or carbonate formed during storage [6, 10].

The 6.00 g samples were milled under vacuum for up to 100 h at room temperature in a vertical type 316S stainless steel ball mill using five type 420C stainless steel balls of 10 in (25.4 mm) diameter confined in the vertical plane. Ball motion was controlled by the positioning of magnets radially round the mill [11]. There was no evidence of iron contamination from either ball or mill after milling.

Selected samples of as-milled powder were leached under agitation for 12 h in 3% HCl; the solution was analysed by atomic absorption spectroscopy for iron and titanium to determine whether separation of the elements was feasible.

Samples of milled powders were annealed under inert and oxidizing atmospheres to determine the effect of thermal treatment of the milled powders. The products were analysed by XRD using monochromated CoK α radiation ($\lambda = 0.178896$ nm) with a count time of 2 s per 0.1° step. The crystalline

size was averaged from the four main peaks as measured from the peak broadening of the XRD traces using the Scherrer formula (see, for example, [12]).

3. Results

After milling for 50 h, XRD of the powders showed little evidence of either ilmenite or the metal oxide (Fig. 1), except in the case of magnesium where the *d* spacings of iron and magnesium titanates overlap considerably. Profile fitting of the peaks for 30° < 2 θ < 45° indicated the presence of a single phase, most probably a mixed cation titanate (Fe, Mg)TiO₃, but the presence of the main MgO peak at about $\approx 50^\circ$ confirms that the reaction did not go to completion.

The other milled products showed the alkaline-earth metal titanate but no apparent iron product: other work has demonstrated the difficulty in detecting ferrous products by XRD and the non-detection does not indicate an absence. The milled powder for barium was brown, whereas the other powders were black (the original powders were black and white), suggesting that the extent of reaction was greater for barium than the other metals.

The crystallite size of the milled powders was around 8 nm which is slightly smaller than that of ilmenite milled alone for 100 h which showed a crystallite size of about ~ 10 nm. The metal titanate crystallite size did not change much after milling for beyond 50 h, indicating that the alkaline-earth titanates reached an equilibrium grain size during the milling process. Other work on milled ilmenite [13, 14] has suggested that a similar crystallite size would be achieved by milling for very long times. Thus it appears that there is an equilibrium crystallite size of about ~ 8 nm for this particular crystal structure which is achievable by either reduction or grain growth during the milling processes.

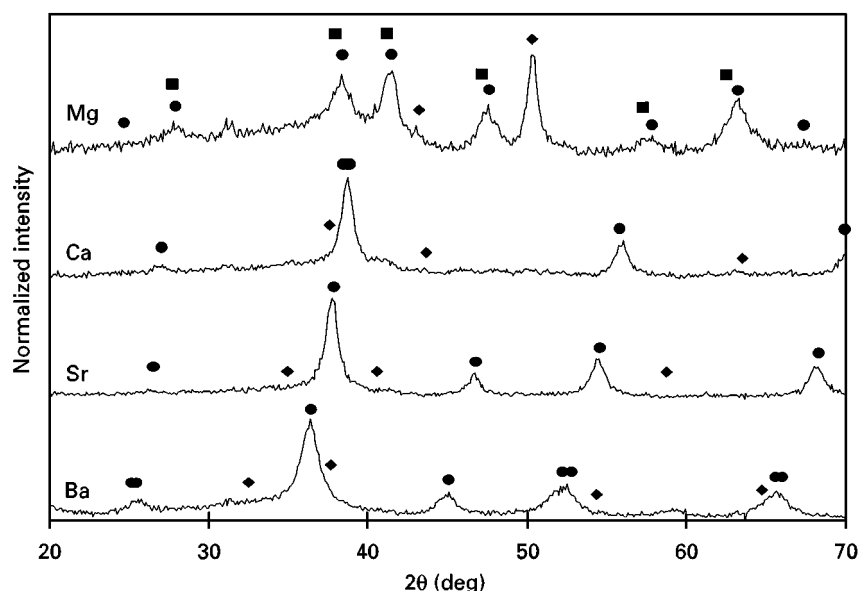


Figure 1 Normalized intensity–2 θ trace of powders milled for 50 h (■) ilmenite; (◆), MO; (●), MTiO₃.

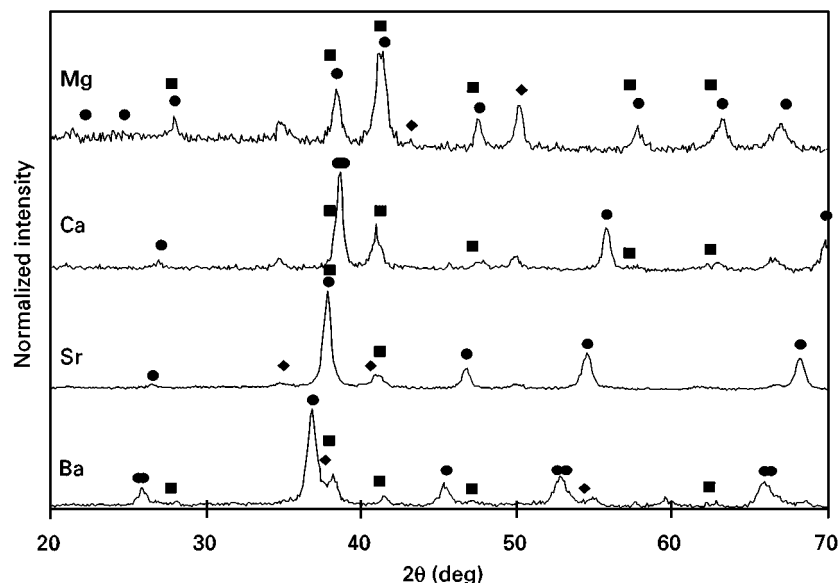
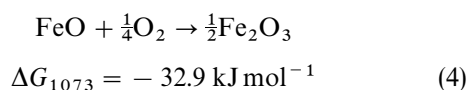


Figure 2 Normalized intensity– 2θ traces of powders annealed at 800°C for 1 h under a flowing argon atmosphere. (■), ilmenite; (◆), MO; (●), MTiO_3 .

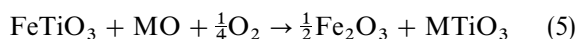
3.1. Annealing

The crystallinity was found to be much greater after annealing at 800°C , the peaks becoming narrower and more intense (Fig. 2). There were small peaks present for ilmenite after annealing in argon (Fig. 2), which were not present after milling. The presence of ilmenite could imply that there was a reversal of reaction (1) with increasing temperature; however, the free energy for reaction (1) becomes more negative with increasing temperature for all metals and the reverse is unlikely. Thus, it would seem that ilmenite remained after milling and had undergone grain growth during annealing; this would suggest that there was insufficient oxide present for complete conversion.

After annealing in air at 800°C the only significant phases were metal titanates and haematite, with the possible exception of barium which showed only very weak peaks. The haematite could be formed by one of two routes, both of which are thermodynamically favourable at 800°C : oxidation of the iron(II) product assumed to be formed during milling according to



or reaction between metal oxide, ilmenite and oxygen according to



The latter route would be partially responsible in the case of magnesium where MgO was present after annealing at under argon (Fig. 2) but absent after 1 h at 800°C in air. Metal oxides were absent after annealing at 800°C in the other powders (Fig. 2); so the first route would be the more likely of the two.

Pseudobrookite (Fe_2TiO_5) was notable by its absence from the air-annealed powders; annealing of milled ilmenite for 1 h in air at 800°C showed pseudobrookite to be the only product. The absence of pseudobrookite would indicate that, although some

ilmenite was present after milling (Fig. 2), the thermal reaction of metal oxides with ilmenite gives a more stable product.

Ilmenite was milled with MgO under an oxygen ambient; the final powder was brown but the only phases detected by XRD were the mixed magnesium–iron titanate and magnesium oxide. After annealing under argon, haematite peaks were revealed, confirming the formation during milling. The relative peak height of MgO compared with that of the MTiO_3 phase was smaller than that for the powder milled in vacuum which suggests that the extent of reaction during milling in oxygen was greater than in vacuum. This observation is consistent with the thermodynamic predictions which show a much more favourable free energy for reaction (5) than for reaction (1) for all metals, even at room temperature (Table I).

3.2. Leaching

The results of leaching in 3% HCl are summarized in Table II and all samples show a considerably greater solubility than milled ilmenite which dissolves congruently under the conditions used, as expected from the nominal composition FeTiO_3 .

The overall solubility increased as the cation size increased, as did the iron solubilization which was approximately linear with total mass loss. The titanium solubility is of more interest with an enormously enhanced solubility compared with that of iron for all alkaline-earth metals.

The dissolution of ilmenite is slow except under much more aggressive chemical and thermal conditions [13]. After milling with metal oxide both the solubility of titanium and the titanium: iron ratio increase dramatically with titanium solubilities of greater than 95% evident for Ca, Sr and Ba oxides. This enhanced solubility under comparatively mild solution conditions may prove to be of use in the

TABLE II Solubility of 1:1 molar MO: ilmenite powders milled for 100 h in 3% HCl after agitation leaching for 12 h

Oxide used	Amount of mass leached (%)	Amount of Fe solubilized (%)	Amount of Ti solubilized (%)
None	6.7	6.5	6.8
Mgo	48	20	70
CaO	67	55	95
SrO	69	63	99
BaO	81	88	95

processing of ilmenite to form pigment-grade TiO_2 or purify the metal titanates by selective precipitation.

3.3. Mixed barium-strontium titanates

The milling of ilmenite with a mixture of strontium and barium oxides was examined to determine the possibility of forming a mixed cation titanate of the general formula $\text{Sr}_x\text{Ba}_{1-x}\text{TiO}_3$. Two different strontium:barium ratios were used: 1:1 and 1:3 (molar) with the stoichiometric amount of ilmenite. After milling the 1:1 ratio, the XRD peaks were about half-way between those of the individual metal titanates, indicating the probability of a mixed metal phase. The 1:3 ratio showed only weak peaks for a phase between the pure metal titanates but closer to BaTiO_3 .

If it is assumed that there is a linear relationship between x , the fraction of strontium in the mixed titanate, and the peak positions, then the composition of the phases can be calculated. For the 1:1 ratio the mean of the four main peaks indicated $x = 0.49$ whereas $x = 0.15$ was found for the higher ratio, which implies a phase richer than expected in barium.

The barium-rich phases have been noted previously after milling the mixed oxides with TiO_2 [6], although the d spacings for the phase became closer to that expected after annealing. There does not seem to be any clear correlation between the presence of iron and the XRD derived stoichiometry detected after milling; the 1:1 ratio was closer in the presence of iron but the converse was true for 1:3 [6].

4. Discussion

Alkaline-earth metal titanates can be formed directly from ilmenite by cation exchange with the earth oxides under mechanical activation conditions although no iron product was detected by XRD. The magnesium product was probably a mixed cation titanate with the XRD peaks between those of the pure ilmenite and MgTiO_3 , especially given the similar size of the cations and the complete solid solution that exists between the end members. The reaction appeared to be complete within 50 h with no evidence of the metal oxides remaining at this time, other than magnesium.

Annealing of the milled powders revealed that ilmenite was almost certainly present in all samples, implying that the reaction had not been completed, possibly owing to insufficient metal oxide addition.

Annealing in air showed oxidation of the iron product to haematite, leaving no evidence of ilmenite which indicated that a thermal reaction had also taken place in which oxidation to iron(III) resulted in a more stable iron oxide which enhanced the cation swap.

For all as-milled powders, the solubility of titanium was considerably higher than iron which confirms the separation of iron and titanium. The titanium in solution was greater than 90% of the total for all elements except magnesium. The low titanium solubility may have been due to the mixed cation nature of the titanate formed during milling, ilmenite being relatively insoluble in the leach solution used.

The standard preparation route of the titanates involves heating of mixed powders to 1300°C ; in the case of Sr and Ba this is essential for the decomposition of the carbonates [10]. The reaction then proceeds by solid-state reaction forming deleterious intermediates, such as MgTi_2O_5 , Ba_2TiO_4 and BaTi_3O_7 [7]. Ball milling shows no evidence that these intermediates are produced prior to annealing at 800°C where grain growth of the titanates is shown to occur. The endothermic nature of the current preparation process results in considerable consumption of energy prior to compound formation; the ability of ball milling to form the titanates at room temperature could result in the saving of some energy. However, on an industrial scale, ball milling is notoriously inefficient and an alternative type of device would be more appropriate for larger-scale operations.

5. Conclusions

Alkaline metal titanates can be formed directly from ilmenite by milling with the appropriate metal oxide. The reaction appeared to be incomplete directly after milling only for magnesium where it was likely that a mixed metal titanate had formed; the other metals showed neither oxide nor ilmenite remaining.

Annealing under argon indicated that there was still a small fraction of ilmenite remaining in addition to the metal titanate, whereas annealing in air showed only haematite and the metal titanate. The thermal reaction between ilmenite and metal oxide is enhanced by the air, which allows formation of a much more stable oxide than that from annealing in argon.

There is an obvious benefit in making alkaline-earth metal titanates directly from ilmenite; however, the removal of iron from the product is the critical step and warrants further investigation under a variety of leaching conditions.

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