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# Formation of perovskite-related structures $CaMO_3$ (M = Sn, Ti) by mechanical milling

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Nanoparticle calcium stannate ($CaSnO_3$) and calcium titanate ($CaTiO_3$) have been prepared by the mechanical milling of mixtures of calcium(II) oxide with tin(IV) oxide or titanium(IV) oxide. The formation of calcium titanate ($CaTiO_3$) is more easily achieved by milling calcium(II) oxide with the rutile modification of titanium (IV) oxide than with the anatase form. © *2001 Kluwer Academic Publishers*

## 1. Introduction

The formation of alloys by the mechanical milling of elemental transition metal powders has been known for some time [1] and has been used, for example, to synthesise alloys with compositions far from equilibrium [2] as well as metastable solid solutions in immiscible alloy systems [3]. Mechanical milling has, in recent years, been used to produce oxides, such as spinel-related ferrites [4] and we have prepared solid solutions of tin in corundum-related $\alpha$-$Fe_2O_3$ by the mechanical milling of $SnO_2$ and $\alpha$-$Fe_2O_3$ [5].

The preparation of metal stannates and titanates of composition $MSn/TiO_3$ (M = Ca, Sr, Ba) continues to attract attention partly because of their use in thermally stable capacitors. The titanates in particular show ferroelectric and piezoelectric behaviour which renders them important for the production of compact capacitors and ceramic transducers. We report here on the formation of perovskite-related calcium stannate, $CaSnO_3$, (which is normally prepared by solid state reactions at elevated temperatures) by ball milling calcium(II) oxide with a rock salt-related structure and tin(IV) oxide with a rutile-related structure. We also report on ball milling of both the anatase and rutile modifications of titanium(IV) oxide with calcium(II) oxide and the formation of perovskite-related $CaTiO_3$ which is also normally prepared by solid state reactions at elevated temperatures.

## 2. Experimental

A 30 g equimolar mixture of calcium(II) oxide and tin(IV) oxide was dry milled in air in a Fritsch Pulverisette 5 planetary ball mill using a tungsten carbide vial and ten tungsten carbide balls for 116 hours at 200 rpm. The valves were open during the milling such that air was constantly available to the oxide powders. A ball to powder ratio of 20 : 1 was used. Small amounts of the powders were removed at intervals during the milling. A similar procedure was used to mill calcium(II) oxide and the anatase and rutile modifications of titanium(IV) oxide.

X-ray powder diffraction data were recorded with a Siemens D5000 diffractometer using $CuK_\alpha$ radiation. $^{119}Sn$ Mössbauer spectra were recorded at 298 K with a constant-acceleration spectrometer in transmission geometry using a *ca.* 5 mCi $Ba^{119}SnO_3$ source.

## 3. Results and discussion

### 3.1. Calcium stannate

The phases formed from the mixture of calcium(II) oxide and tin(IV) oxide as a function of milling time were deduced from the X-ray powder diffraction patterns (Fig. 1). We note that any contamination from the tungsten carbide balls and vials was below the limit of detection by X-ray powder diffraction and we estimate that, after 110 hours of milling, it to be *ca* 1 at. %.

The results show the appearance of a reflection at 22.5° $2\theta$ characteristic of $CaSnO_3$ after 22 h milling which increases in intensity with increased milling time. The results show a concomitant decrease in the intensity of the reflections associated with CaO and $SnO_2$. The full width at half maximum of the peak at 22.5° $2\theta$ characteristic of $CaSnO_3$ in the material milled for 22 hours was broad (0.49° $2\theta$) indicative of small crystal size or non stoichiometry in the $CaSnO_3$ phase. After 116 hours of milling the narrower peak width (0.36° $2\theta$) suggested a more crystalline or stoichiometric material. The overlap of peaks in the X-ray powder

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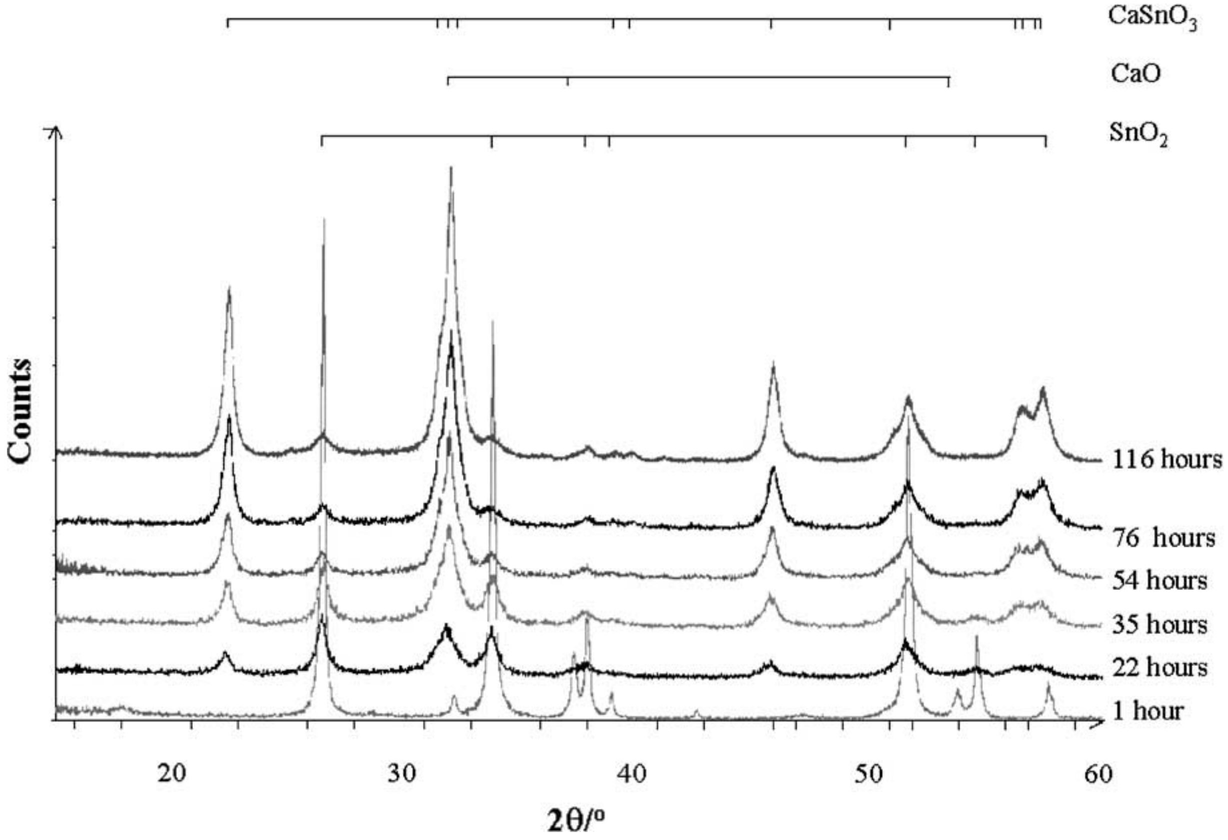

*Figure 1* X-ray powder diffraction patterns showing the transformation of a mixture of CaO and $SnO_2$ to $CaSnO_3$ as a function of milling time.

diffraction pattern precluded the determination of particle sizes. Scanning electron microscopy showed the particle size of the ball milled $CaSnO_3$ (<25 nm) to be smaller than that of $CaSnO_3$ (>50 nm) made by the calcination of CaO and $SnO_2$ at 1400°C for 5 days.

The $^{119}$Sn Mössbauer spectra (Fig. 2) showed the linewidth of the material ball milled for 22 h to be significantly broader ($\Gamma = 2.28(5)$ mms$^{-1}$) than that ball milled for either 1 h ($\Gamma = 1.55(5)$ mms$^{-1}$) or 116 h ($\Gamma = 1.96(5)$ mms$^{-1}$). The results are consistent with the transformation of the reaction mixture containing tin in a single phase ($SnO_2$ after 1 hour ball milling) to a two component mixture of $CaSnO_3$ and $SnO_2$ after 22 h ball milling and finally to the $CaSnO_3$ product containing tin in a single site in the material ball milled for 116 h.

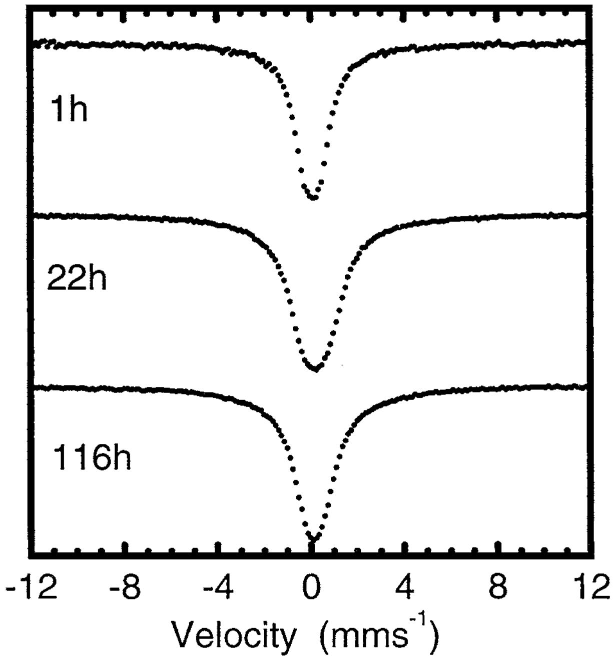

*Figure 2* $^{119}$Sn Mössbauer spectra recorded from a mixture of CaO and $SnO_2$ ball milled for 1, 22, and 116 hours.

### 3.2. Calcium titanate

The phases formed from the mixture of calcium(II) oxide and the anatase modification of titanium(IV) oxide as a function of milling time were deduced from the X-ray powder diffraction patterns (Fig. 3). Calcium hydroxide was present in the reactant calcium(II) oxide and appeared to undergo only limited change in the ball mill as illustrated by the modest reduction in the $Ca(OH)_2$ peaks at *ca* 18.09 and 34.09° $2\theta$ over 110 hours of milling. In contrast, the peaks corresponding to calcium(II) oxide (e.g. *ca*. 37.36° $2\theta$) disappeared in the X-ray powder diffraction pattern recorded from the sample ball milled for 110 h. The peaks corresponding to anatase (e.g. *ca*. 25.29° $2\theta$) showed a gradual decrease in intensity as the milling time increased although, from Fig. 3, it is clear that some anatase was unchanged after 110 hours of milling. The disappearance of peaks corresponding to CaO and the decrease in intensity of reflections corresponding to anatase and $Ca(OH)_2$ with increasing milling time was accompanied by a concomitant increase in intensity of peaks corresponding to $CaTiO_3$ (*ca*. 33.11° $2\theta$). The results suggest that CaO reacts preferentially in the ball mill with anatase to give $CaTiO_3$. It is interesting to note that

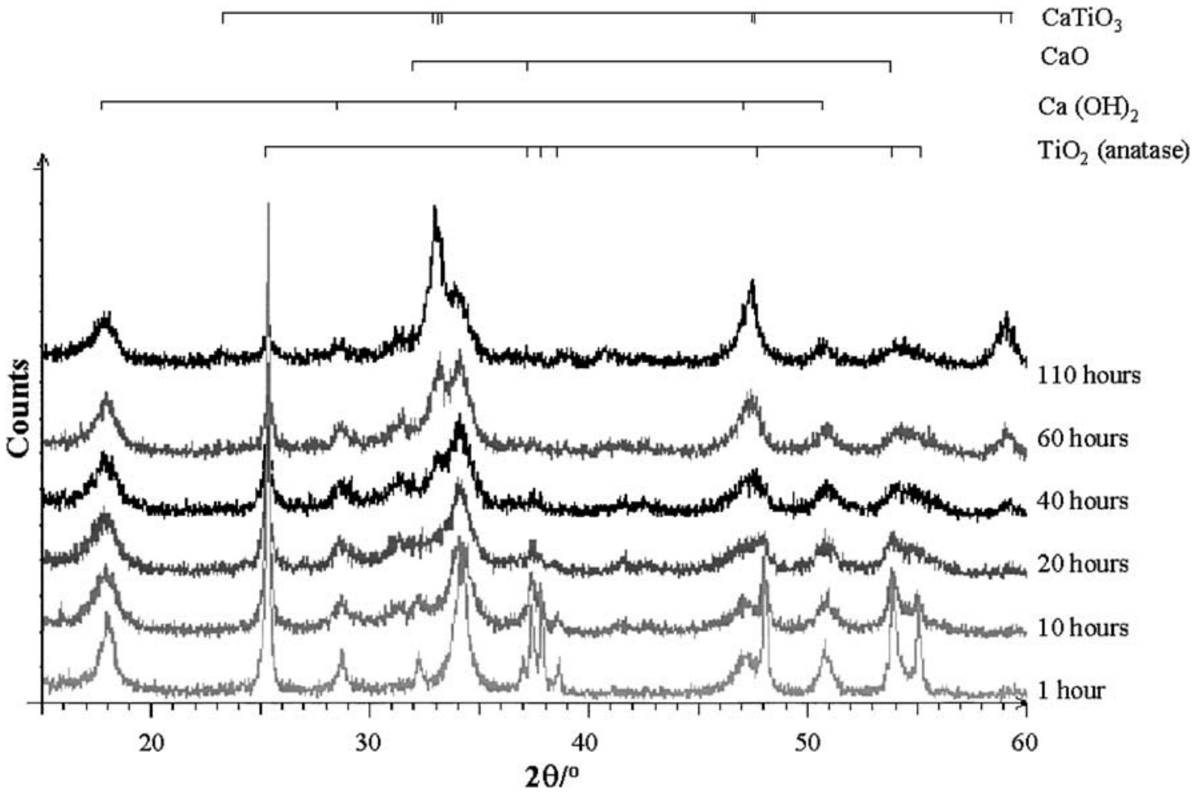

*Figure 3* X-ray powder diffraction patterns showing the transformation of a mixture of CaO and the anatase modification of $TiO_2$ to $CaTiO_3$ as a function of time.

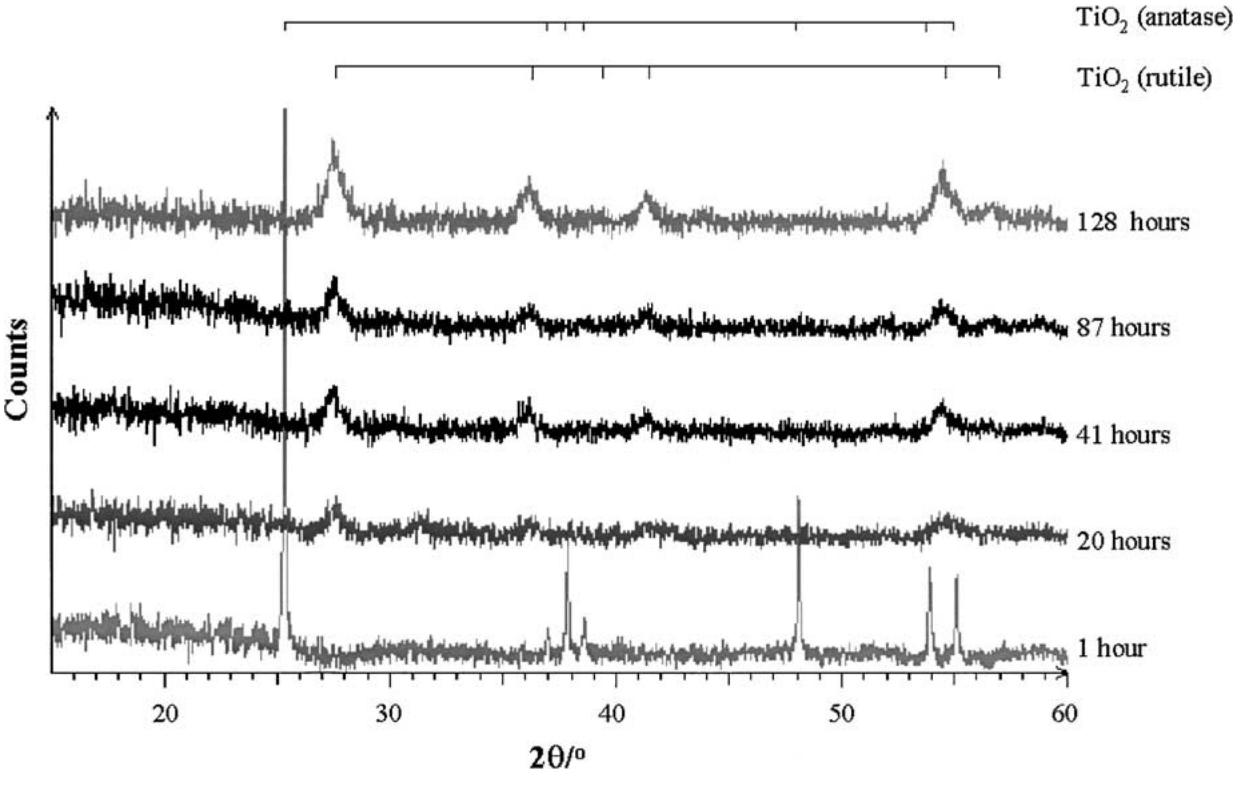

*Figure 4* X-ray powder diffraction patterns showing the transformation of the anatase modification of $TiO_2$ to rutile as a function of time.

the unreacted anatase did not undergo transformation to the rutile modification of titanium(IV) oxide (main peak at 27.44° $2\theta$). This is somewhat surprising since X-ray powder diffraction (Fig. 4) showed that, under the conditions used here, the pure anatase modification of titanium(IV) oxide is converted to the rutile form after 20 hours of milling. Recent reports [6] have shown that the kinetics of the phase transformations of anatase to rutile depend on the powder to ball weight ratio and the nature of the grinding media. Our results, from experiments in which both these parameters were unchanged, suggest that both the kinetics and mechanisms of the

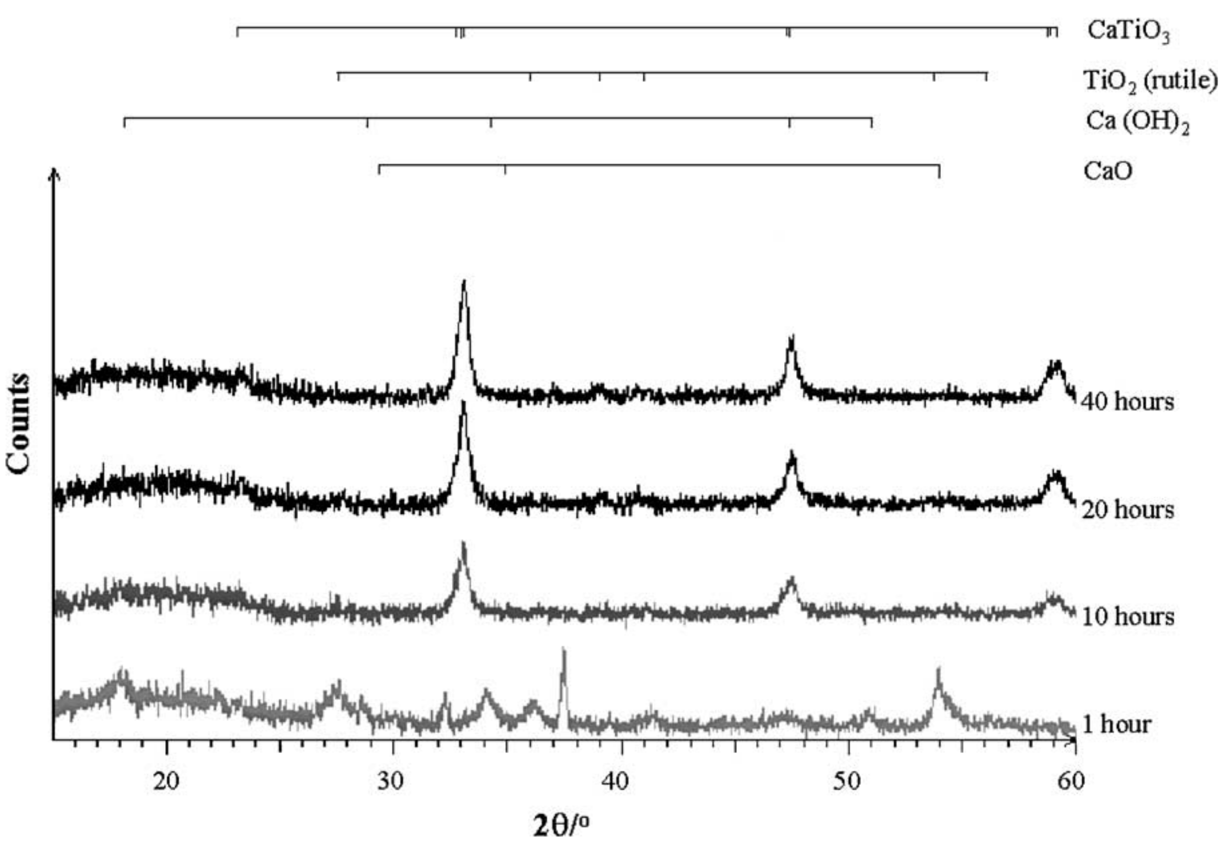

*Figure 5* X-ray powder diffraction patterns showing the transformation of a mixture CaO and the rutile modification of $TiO_2$ to $CaTiO_3$ as a function of time.

phase transformation are complex and are influenced by the presence of other phases.

A striking difference in the formation of $CaTiO_3$ was observed when calcium(II) oxide (which also contained calcium hydroxide contamination) was milled with the rutile modification of titanium (IV) oxide. The X-ray powder diffraction patterns are shown in Fig. 5. The results show that the calcium hydroxide and calcium(II) oxide react with rutile to give monophasic $CaTiO_3$ with a particle size as shown by scanning electron microscopy of $<25$ nm after only 10 hours of milling and demonstrate that the crystal modification of titanium dioxide has considerable influence on the ease by which $CaTiO_3$ can be made by milling $TiO_2$ and CaO.

The results therefore demonstrate that the mechanical milling of CaO with $SnO_2$ and of CaO with either the anatase or rutile modifications of $TiO_2$—all structurally unrelated oxides—gives the formation of perovskite-related $CaMO_3(M = Sn/Ti)$ of smaller particle size than that prepared over comparable timescales by conventional calcination techniques. The enthalpy of formation of $CaMO_3$ ($M = Sn/Ti$) from the component oxides is large [7], for example for $CaSnO_3$ it is $-67.76$ kJ mol$^{-1}$ and the temperatures required for its preparation by solid state methods are large. The results reported here suggest that ball milling enances the interdiffusion rates in the reaction mixture.

## Acknowledgement

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