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Investigation on possibility of mechanochemical synthesis of $CaTiO_3$ from different precursors

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Abstract

Recently, mechanochemical synthesis was widely used in preparation of perovskite type of materials, such as $BaTiO_3$, $PbTiO_3$, PZT, etc. In this work, the possibility of mechanochemical synthesis of $CaTiO_3$ from different precursors, such as $CaCO_3$ or CaO and TiO_2 was investigated. Intensive milling of mixture of CaO and TiO_2, under optimal milling conditions, resulted in synthesis of single phase $CaTiO_3$. It was also found that intensive milling of powder mixture containing $CaCO_3$ and TiO_2 only activate the powders for the sintering process; hence the $CaTiO_3$ could be obtained at lower temperatures of sintering. To complete reaction of $CaTiO_3$ formation during milling it is necessary to reduce CO_2 partial pressure, i.e. it is necessary to change the atmosphere inside the vials during milling. In this work, an explanation for difference in milling behavior of different precursors was proposed and discussed.

Keywords: Milling; Powders-solid state reaction; Perovskites; X-ray method

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1. Introduction

Calcium titanate, $CaTiO_3$, belongs to the important group of compounds with a perovskite structure. Its most important features are high dielectric constant, large positive temperature of the resonance frequency, but also high dielectric loss that could be decreased by substitution of the A-site with trivalent ions.[1] It is promising material for microwave tunable devices and is also used for modification of ferroelectric perovskites, such as $PbTiO_3$ or $BaTiO_3$, for various applications.[2,3] Calcium titanate is mostly prepared by a solid state reaction between $CaCO_3$ or CaO and TiO_2 at 1350 °C, but also by some other methods such as sol–gel processing, thermal decomposition of peroxo-salts, and mechanochemical synthesis from different precursors, such as $CaCO_3$, $Ca(OH)_2$ or CaO, with TiO_2.[4,5] It was found that is possible to obtain pure $CaTiO_3$ by mechanochemical synthesis from CaO and TiO_2, but is very difficult from the other two precursor mixtures.[4–6] Mechanochemical treatment of the $CaCO_3$ and TiO_2 lead to partial formation of $CaTiO_3$, but the reaction was not completed and major part of $CaCO_3$ and TiO_2 remained unreacted. Also, there are some differences if the anatase or rutile modification were used, but neither enables formation of pure $CaTiO_3$ starting from $CaCO_3$ or $Ca(OH)_2$.[4,5] On the other hand intensive milling of $CaCO_3$ or $Ca(OH)_2$ with TiO_2 resulted in highly activated powder mixtures, so the sintering could be performed at lower temperatures in comparison to unmilled powder mixtures. The similar results were found in synthesis of $BaTiO_3$ from $BaCO_3$ or BaO, and TiO_2.[7]

Instability of CaO because of exothermic reaction $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$ causes some difficulties in maintaining desired stoichiometry of the system $CaO–TiO_2$. Because of that it would be more convenient to perform mechanochemical synthesis starting from $CaCO_3$. The aim of this work is to compare results of mechanochemical synthesis of $CaTiO_3$ from different precursors, to explain the observed differences, and finally to propose possible routes for complete synthesis starting from carbonate precursor.

2. Experimental

Starting reagents were $CaCO_3$ (calcite, modification, Kemika, p.a. 99%), CaO and TiO_2 (rutile modification, Alfa Product Ventron, p.a. 99.8%). CaO was obtained from $CaCO_3$

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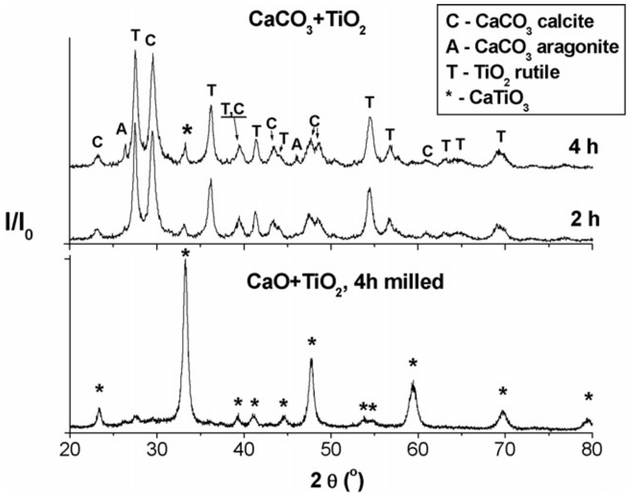


Fig. 1. XRD patterns of the powders obtained after "closed vial" milling of different precursors: CaO and TiO_2, or $CaCO_3$ and TiO_2.

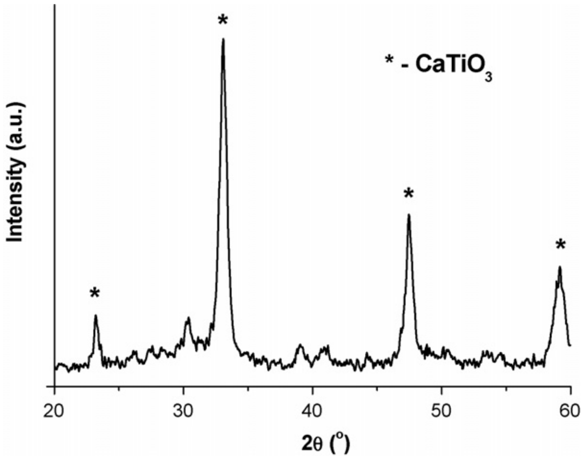


Fig. 2. XRD pattern of the "opened vial powder" obtained after 4 h of milling of mixture of $CaCO_3$ and TiO_2.

by thermal treatment at 1200 °C for 4 h. Equimolar mixtures of CaO and TiO_2 or $CaCO_3$ and TiO_2 were intensively dry milled in planetary ball mill (Fritsch Pulverisette 5) under the following milling conditions: zirconium oxide vials ($V = 500\,\text{cm}^3$) and balls ($d = 10$ mm), ball-to-powder weight ratio was 40:1, air atmosphere, rotation speed of discs with vials was $396\,\text{min}^{-1}$ and milling time was 4 h.

Phase composition of the milled powders was determined by X-ray powder diffraction analysis (XRD) on Philips PW 1710 powder diffractometer with graphite monochromator using Cu Kα radiation. Non-isothermal sintering of the investigated mixtures was followed by a sensitive dilatometer (Bahr Geratebau GmmH) up to 1300 °C with a heating rate of 10 °C/min. TG/DTA was performed on SDT Q600 (TA Instruments) in temperature interval 25–1000 °C with heating rate 20 °C/min.

3. Results and discussion

According to XRD data shown at Fig. 1, a pure, well crystallized, $CaTiO_3$ was obtained after milling the mixture of CaO and TiO_2 for 4 h. On the other hand, milling of mixture of $CaCO_3$ and TiO_2 resulted in formation of small amount of $CaTiO_3$, but reaction wasn't completed. These results are in accordance with results already reported by some other authors.[4,6]

The first step in formation of $CaTiO_3$ from $CaCO_3$ and TiO_2 is decomposition of $CaCO_3$:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g). \quad (1)$$

This reaction is followed by exothermal reaction of $CaTiO_3$ formation,[6] which occurs at the same moment in which CaO is formed and because of that it is not possible to see CaO peaks on XRD pattern:

$$CaO + TiO_2 \rightarrow CaTiO_3. \quad (2)$$

The equilibrium constant of reaction (1) depends only on CO_2 partial pressure, so the amount of the produced CaO will also depend on CO_2 partial pressure. Formation of only small amount of $CaTiO_3$ will dramatically increase partial pressure of CO_2 because of small volume of closed vial. As the partial pressure of CO_2 increases the direct reaction will be suppressed. Therefore, it is very difficult to reach high yields in the reaction performed in a closed vial. The same explanation could be applied on mechanochemical synthesis of $BaTiO_3$.

In order to solve the technical problem of performing intensive milling with the open vials, the other possibility was considered. The mill was stopped every 15 min of milling and vials were opened to change the inner atmosphere. In further text these powders will be assigned "opened vial powder" in contrast to "closed vial powder", which were milled continually 4 h without opening. The results were very encouraging. Almost single phase $CaTiO_3$ was obtained after 4 h of milling in contrast to closed vial powder mixture that was continually milled in a closed vial for the same time period (Fig. 2). As it could be seen on the XRD pattern of closed vial powder there are small $CaTiO_3$ peaks but the intensive peaks of the starting phases indicated that reaction was not completed. According to TG/DTA curves the both powders significantly differ from the simple, physical mixture of unmilled starting powder (Fig. 3). In temperature interval from room temperature to 1000 °C, the unmilled mixture lost 24% of weight during the endothermic reaction of $CaCO_3$ decomposition at 753 °C. The reaction (2) of formation of $CaTiO_3$ from CaO and TiO_2 is exothermic, but there is no exothermic peak on DTA curve that can confirm that this reaction occurred. The exothermic peak on DTA curves of this powder is probably hidden under the endothermic peak of $CaCO_3$ decomposition.[6] This is more obvious from the Fig. 3b (closed vial powder) where the exothermic peak is superposed on endothermic peak, giving impression of two endothermic peaks. Powders milled in a closed vial lost about 13% of weight during the endothermic process in a large temperature interval from 480 to 690 °C. The opened vial powder lost only 3% of weight in the same temperature interval. The last one didn't show neither endothermic nor exothermal effects. This is because reactions of decomposition of $CaCO_3$ and formation of $CaTiO_3$ were almost completely finished during milling.

The high-energy milled powders often show the presence of agglomerates.[8] These agglomerates can be "soft" if they consist

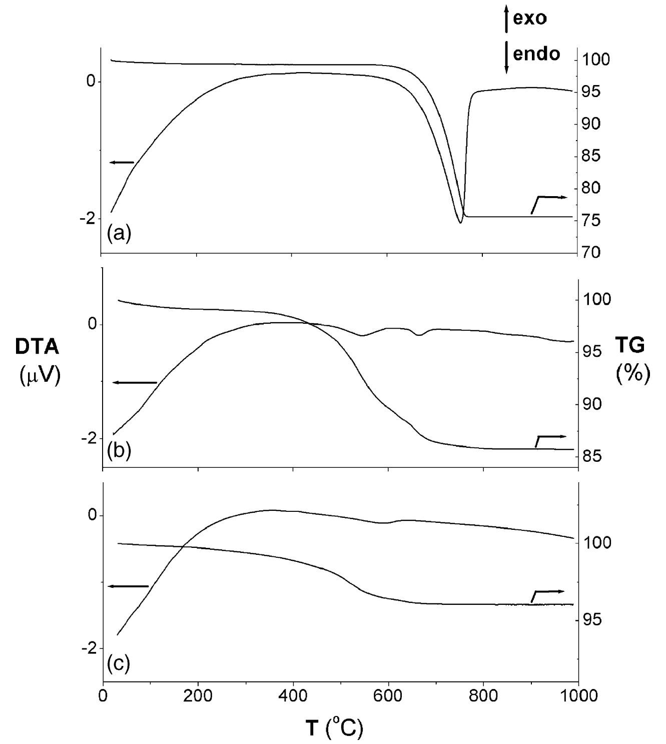


Fig. 3. TG/DTA of the powder mixtures: (a) unmilled, physical mixture of $CaCO_3$ and TiO_2, (b) mixture of $CaCO_3$ and TiO_2 milled for 4 h in closed vial, (c) mixture of $CaCO_3$ and TiO_2 milled for 4 h in opened vial.

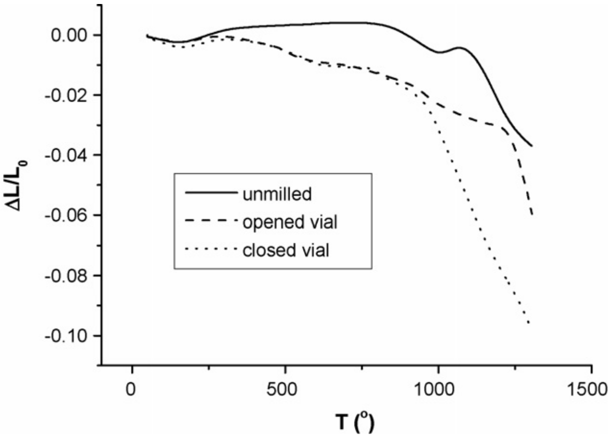
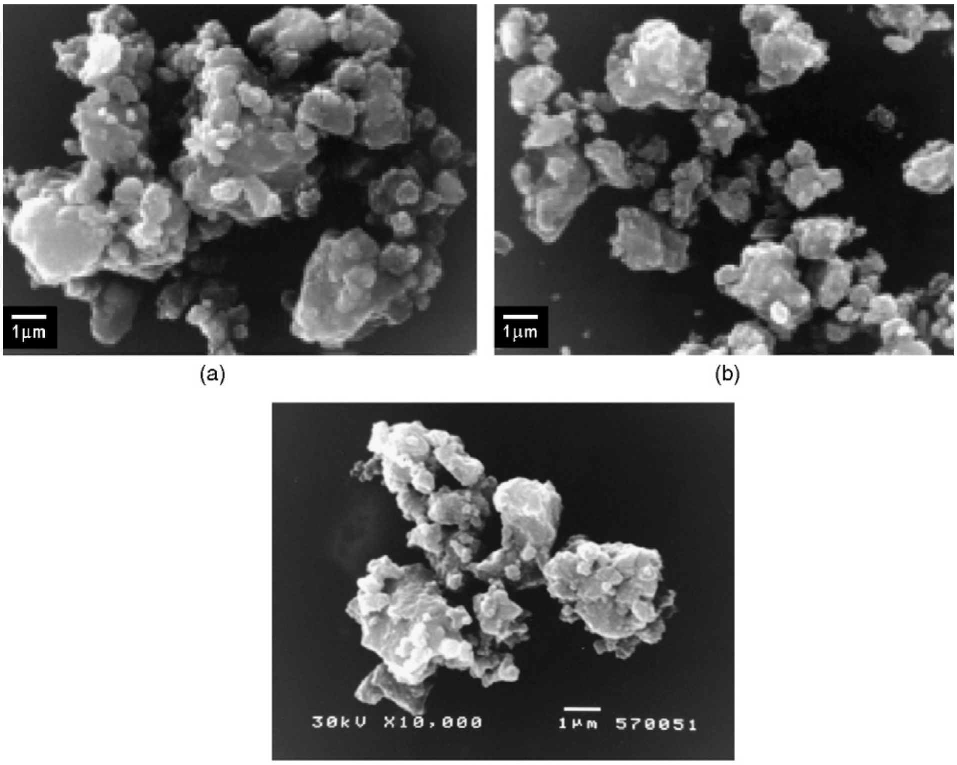


Fig. 4. Relative shrinkage of the unmilled powder in comparison to powders milled in opened or closed vials for 4 h.

of a number of particles held together by weak Van der Waals forces or "hard" if the particles inside the agglomerates are held together by stronger chemical or sintering bonds.[9] The presence of hard agglomerates leads to worse densification during sintering and formation of porous bodies.[10] In our study comparison of relative shrinkage of the samples obtained from opened and closed vials showed that the closed vial powder is more activated for sintering process (Fig. 4). Since there was no noticeable difference in morphologies of investigated powders (Fig. 5) some other explanations for differences in densification behavior of the investigated samples should be considered. The both curves are identical up to 900 °C. At this temperature began prominent



(a) (b)

(c)

Fig. 5. SEM micrographs of the powders milled for 4 h: (a) "closed vial powder" mixture, (b) "opened vial powder" mixture and (c) mixture of CaO and TiO_2.

densification of the closed vial powder. Pronounced densification of the opened vial powder began at higher temperature of 1210 °C. In the case of the closed vial powder we can talk about reaction sintering, because formation of $CaTiO_3$ takes place simultaneously with densification. During sintering of opened vial powder no reaction occurred. Because of solid-state reaction that occurred during milling of "opened vial powder", the hard agglomerates were formed (Fig. 5). Also, formation of $CaTiO_3$ leads to relaxation of defects accumulated in material during intensive milling. As the consequence of the presence of hard agglomerates, as well as due to relaxation of defects, this powder is less activated for sintering.[10,11] To improve sintering of these powders it is necessary to prolong milling process in order to reduce agglomerate size and activate powder for sintering. In closed vial powder the agglomerates are also formed due to intensive milling and large amount of energy that was introduced to the system. Nevertheless densification of this powder occurs at lower temperature because these agglomerates are softer.[10,11]

Obviously, change of CO_2 partial pressure during milling of starting powder mixtures can significantly intensify the reaction of $CaCO_3$ decomposition and consequently reaction of $CaTiO_3$ formation. Change of vial atmosphere during milling also prevent carbon deposition that was also observed in some powders milled in closed vials. Therefore the proposed technique of milling can solve the problem occurring during mechanochemical synthesis of $CaTiO_3$ from $CaCO_3$ and TiO_2, but also in some other reactions where the carbonates are used as precursors. Also, the proposed method, based on controlling of partial pressure of CO_2, enables preparation of powders with desired properties: either $CaTiO_3$ directly during mechanochemical synthesis or highly activated powder containing mixture of phases for low temperature sintering.

4. Conclusion

Mechanochemical synthesis of $CaTiO_3$ was performed from different precursors: $CaCO_3$ and TiO_2 or CaO and TiO_2. While the synthesis reaction was completed within 4 h of milling of oxide precursors, powder mixture of $CaCO_3$ and TiO_2 milled for the same time contained only small amount of $CaTiO_3$. The problem of synthesis of $CaTiO_3$ from the $CaCO_3$ was discussed in the sense of partial pressure of CO_2 formed during decomposition of $CaCO_3$. It was found that only changes of atmosphere inside the vial, either by opening of the vial during milling or milling under certain air flow, could lead to reduction of CO_2 partial pressure and consequently to mechanochemical synthesis of pure $CaTiO_3$. Following this idea $CaTiO_3$ was successfully synthesized from $CaCO_3$ during 4 h of intensive milling in planetary ball mill. Also, the proposed method enables preparation of powders with desired properties: either $CaTiO_3$ directly during mechanochemical synthesis or highly activated powder containing mixture of phases for low temperature sintering.

Acknowledgments

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