

Effects of reagents' nature on mechanochemical synthesis of calcium titanate

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Abstract Because of unique dielectric, piezoelectric, thermoelectric, optical and ferroelectric properties of titanates of alkaline earth metals, they have become an object of many scientific research. This article is concerned with mechanochemical synthesis of calcium titanate as an alternative technique to hydrothermal, sol–gel, thermal methods. The aim of this study was to verify the mechanochemical conditions of CaTiO_3 formation with the use of three calcium oxide precursors— CaO , CaCO_3 and Ca(OH)_2 . The differences in processes of calcium titanate synthesis are presented.

Keywords Calcination · High-energy ball milling · Mechanical activation · Mechanochemical synthesis · Titanates

Introduction

Alkaline earth titanates, such as BaTiO_3 , SrTiO_3 and CaTiO_3 , belong to the important group of compounds with a perovskite structure with different polymorphic forms depending on temperature [1–3]. Because of excellent electrical properties, such as high permittivity, low dielectric loss, ferroelectricity, piezoelectricity and electrical insulation, the above materials are widely used in electronic industry, for production e.g. multilayer ceramic capacitors, thermistors, memory materials and also as sensitive elements

of gas and water vapour sensors, catalyst supports, photocatalysts [4, 5].

In the past, most of the research was focused on ferroelectric ceramic material, BaTiO_3 , which has been utilized in the production of low-frequency electronic devices. Nowadays, the expansion of microwave technologies has resulted in creating the need for a new generation of dielectric materials. For applications in the microwave frequency region, the studies deal with paraelectric rather than ferroelectric materials [6].

Another material that exhibits superior electronic properties for various applications is strontium titanate. The SrTiO_3 is attractive because of its high ion conductivity, good stability in thermal and chemical atmospheres, and its low cost. Therefore, it can be considered as a potential electrolyte material for solid-oxide fuel cells [7–9] and oxygen sensors [10, 11].

A prospective material for communications equipment, operating at microwave frequencies is a CaTiO_3 due to its high dielectric constant, low dielectric loss, and large positive temperature coefficient of the resonant frequency [12–15]. Calcium titanate is also one of the major phases in synroc (synthetic rock), which is widely used for immobilization of high level nuclear waste [16].

Owing to above mentioned wide range of existing and potential applications, significant research effort has been directed towards various synthesis routes to CaTiO_3 and optimization of its properties. Calcium titanate is most often synthesized by heating calcium oxide or calcium carbonate with titanium dioxide powders. This synthesis is difficult because it requires high temperature treatment (about 1350 °C) for a long time. However, it involves several problems associated with the quality of products, such as inhomogeneity and contamination due to impurities with a nonuniform particle size distribution causing the

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decrease of dielectric constant [17, 18]. In order to minimize those problems, wet chemical methods have also been employed to synthesize CaTiO_3 powders, which include sol–gel, co-precipitation, combustion method, organic–inorganic solution technique and hydrothermal process [3, 19–23]. Moreover, there were several attempts made at CaTiO_3 mechanochemical synthesis [24–29].

Mechanochemical treatment realized by high-energy ball milling is a typical example of non-conventional solid-state process. This method has been used for some years in producing ultra fine powders in the range of a sub-micron to a nanometer. Mechanochemical processing can be also used to carry out the reaction of synthesis of new compounds or to activate the solids.

In addition, the mechanochemical treatment can convert the bridging metal–oxygen–metal bonds in the acidic compound into the bridging bonds between the basic and acid compounds. Thus, in the case of the reaction of CaCO_3 , Ca(OH)_2 or CaO with TiO_2 , the Ti–O–Ti bonds are converted into the Ca–O–Ti bonds.

There are many factors influencing the reaction kinetics, as well as physical and mechanical properties of solid products, e.g. the amount of energy delivered during the same period of time to milling system by virtue of using different values of ball-to-powder weight ratio (BPR), the milling atmosphere, media (dry, wet) or gas pressure. The results obtained in different researches are hard to compare, because of employing different types of mills and mechanochemical treatment conditions [30].

The aim of this study is to verify the conditions of CaTiO_3 production using three different precursors of calcium oxide (CaO , CaCO_3 and Ca(OH)_2) maintaining the constant technical parameters of high-energy ball milling.

Experimental

Materials

The initial reagents were: CaCO_3 (calcite, purity 99.9%), Ca(OH)_2 (purity 99.9%), CaO (purity 99%) and TiO_2 (rutile, purity 99.9%). All the reagents were produced by POCH Gliwice Poland Company. Samples to be mechanically treated were prepared as two-component mixtures with the mass of 10 g, in stoichiometric molar ratio $\text{CaO}:\text{TiO}_2$ corresponding to CaTiO_3 formulae.

Method and procedure

The reactive milling process was carried out with the use of a laboratory planetary ball mill Fritsch GmbH *Pulverisette-6* at room temperature. Steel reactor (250 cm^3), and steel balls with a diameter of $d = 10\text{ mm}$ were used. Rotation

speed was kept constant at 550 rpm. Each system was ground in two series differing from each other in BPR values (20:1 and 40:1). The pressure and temperature inside the reactor were monitored using gas–temperature system (GTM). The grinding process was stopped after every 10 or 20 min to prevent excessive increase of temperature in the grinding vessel.

After mechanochemical treatment, the selected samples had been subjected to calcination in air at different temperatures from the range of 300–800 °C.

The phase analysis of synthesis products was performed using the following techniques:

- X-ray powder diffraction (XRD) with the use of diffractometer X'Pert Philips (CuK_α), within the range of 2θ from 10° to 90°;
- Thermal analysis (TG/DTG-DTA curves) in temperature range of 20–1000 °C using TA Instruments SDT 2960 with the heating rate 20 °C min^{-1} ;
- FTIR spectroscopy analysis by the use of spectrometer Digilab Scimitar FTS 2000 S series (tablets with KBr).

Results and discussion

Mechanochemical synthesis of CaTiO_3 in CaCO_3 – TiO_2 system

CaTiO_3 synthesis in CaCO_3 – TiO_2 system is the result of decomposition of calcium carbonate (1) and in consequence of the reaction of calcium oxide with titanium oxide(IV) (2):

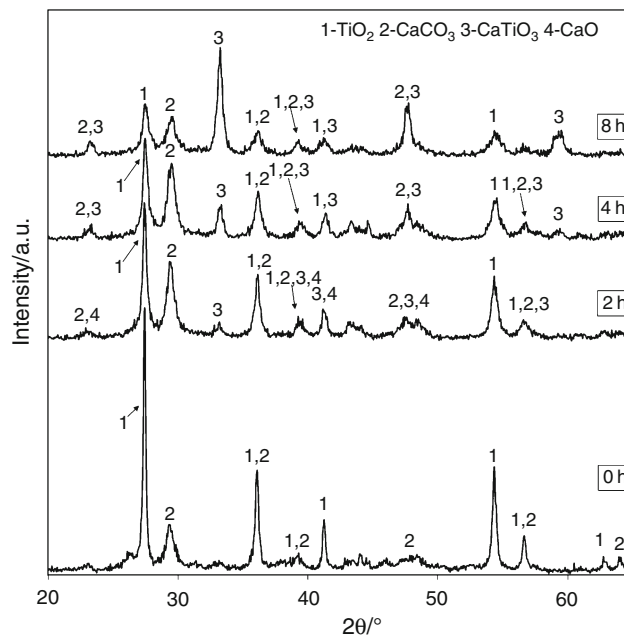
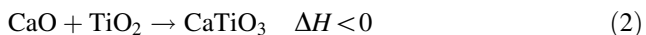
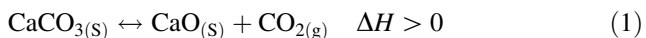


Fig. 1 X-ray diffraction patterns of CaTiO_3 formation in CaCO_3 – TiO_2 system after 0, 2, 4, 8 h of mechanochemical treatment (BPR = 20:1)



The CaTiO₃ begins to form, with a lower energy grinding procedure, i.e. for BPR = 20:1, after 2 h of mechanochemical activation (Fig. 1). CaO also appears indicative of calcium carbonate decomposition (1). However, the completed synthesis has not been achieved even after 8 h of milling, and CaCO₃ is still present (see: FTIR spectrum in Fig. 2).

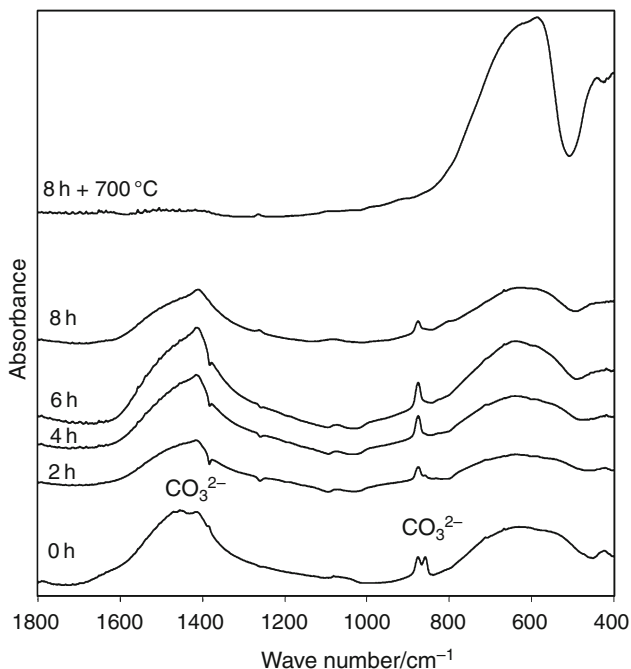


Fig. 2 IR bands of CaCO₃-TiO₂ system before and after mechanochemical treatment (BPR = 20:1) for 2 h, 4 h, 6 h, 8 h and after 8 h of milling followed by calcination at 700 °C (4 h) illustrating lack of CaCO₃

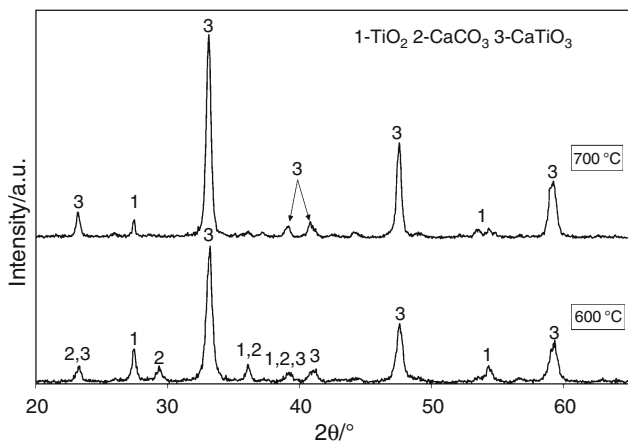


Fig. 3 X-ray diffraction patterns of CaTiO₃ formation in CaCO₃-TiO₂ system after 8 h of mechanochemical treatment followed by calcination at 600 °C and 700 °C (BPR = 20:1)

This milling product was subjected to calcination for 4 h at 600 °C and 700 °C, respectively. The effects are shown by X-ray patterns in Fig. 3. The TG/DTG curves of the milling products for 8 h after calcination at 600 °C and 700 °C indicated that at 700 °C there are only traces of CaCO₃ (Fig. 4). Thus, the temperature of 700 °C seems to be almost sufficient to obtain the monophase system, i.e. CaTiO₃ in the crystalline form. The temperature of 700 °C is much lower than that used in conventional way of CaTiO₃ production by the solely thermal technique, which requires the temperature of 1350 °C [17].

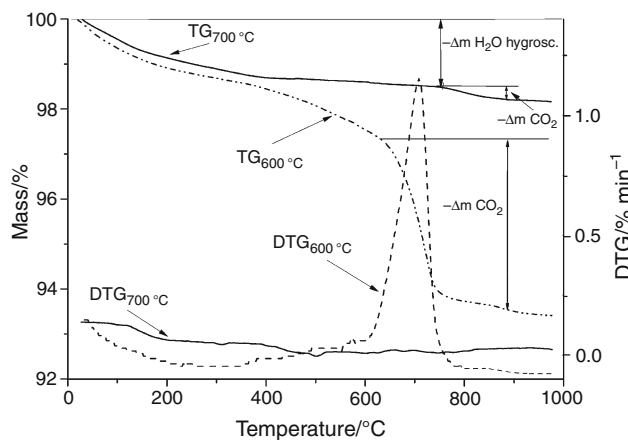


Fig. 4 TG/DTG curves of CaCO₃-TiO₂ system shown in Fig. 3 after 8 h of milling and calcination at 600 °C and 700 °C (BPR = 20:1)

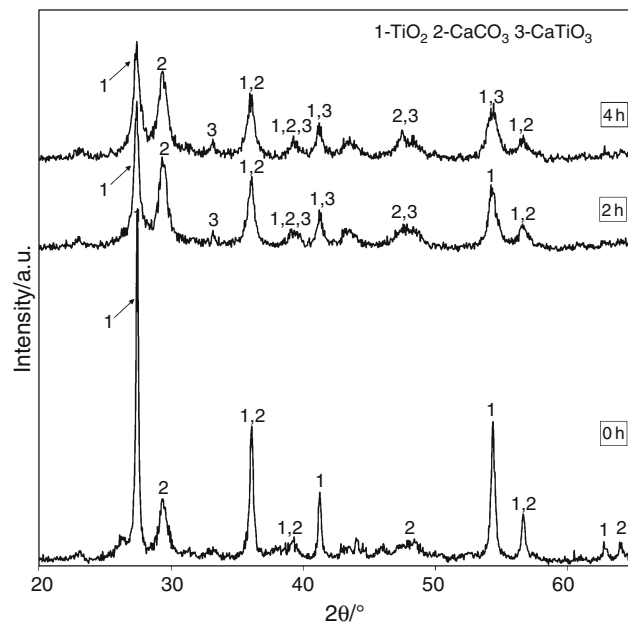


Fig. 5 X-ray diffraction patterns of CaTiO₃ formation in CaCO₃-TiO₂ system after 0, 2, 4 h of mechanochemical treatment (BPR = 40:1)

Increase in delivered energy during the milling process through the change of BPR value from 20:1 to 40:1 accelerated the beginning of CaTiO_3 formation (Fig. 5). The shorter time of calcinations (2 h) at 800 °C was enough to obtain pure crystalline form of CaTiO_3 . This is confirmed by XRD patterns presented in Fig. 6. Moreover, TG-DTA curves shown in Fig. 7 and FTIR bands in Fig. 8 indicate the complete decomposition of CaCO_3 .

Mechanochemical synthesis of CaTiO_3 in $\text{Ca}(\text{OH})_2$ - TiO_2 system

Similar to mechanochemical synthesis of CaTiO_3 in CaCO_3 - TiO_2 system, it was possible to obtain crystalline calcium titanate after mechanochemical activation in the

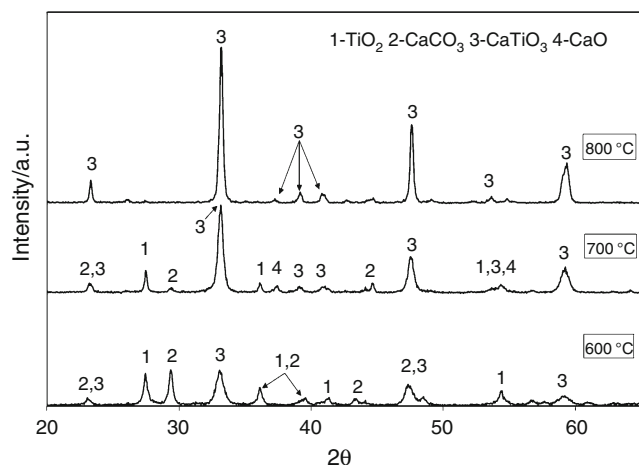


Fig. 6 X-ray diffraction patterns of CaTiO_3 formation in CaCO_3 - TiO_2 system after 4 h of mechanochemical treatment followed by calcinations at 600 °C, 700 °C and 800 °C (BPR = 40:1)

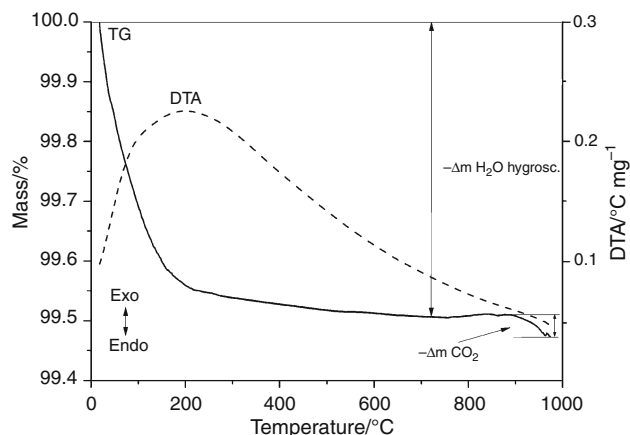


Fig. 7 TG-DTA curves of CaCO_3 - TiO_2 system after milling (4 h) and subsequent calcination at 800 °C (2 h), illustrating completed CaTiO_3 synthesis (BPR = 40:1)

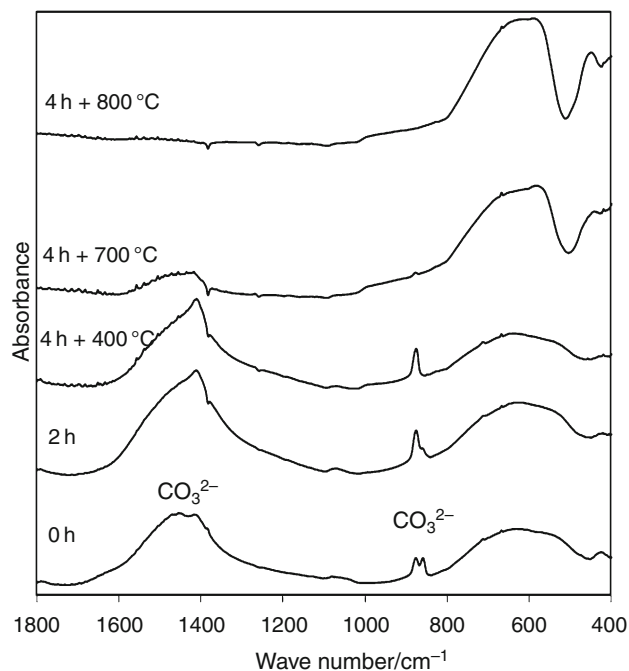


Fig. 8 Set of IR curves illustrating the disappearance of calcium carbonate as an effect of milling followed by thermal treatment in CaCO_3 - TiO_2 system (BPR = 40:1)

powder mixture of $\text{Ca}(\text{OH})_2$ and TiO_2 and subsequent thermal treatment of the milling products. The effects of these two processes are analogous to reactions (1) and (2).

The influence of the more and the less energetic milling is evident. Thus, in the case of BPR value 20:1, 6 h of mechanochemical activation followed by calcination at 700 °C for 4 h produced the crystalline form of calcium titanate (Fig. 9) and with BPR = 40:1, the duration of mechanochemical treatment can be reduced to 4 h (Fig. 10) and the

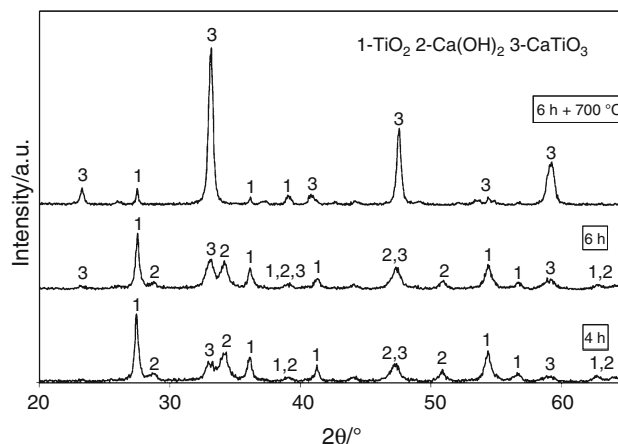


Fig. 9 X-ray diffraction patterns of CaTiO_3 formation in $\text{Ca}(\text{OH})_2$ - TiO_2 system after 6 h of mechanochemical treatment followed by 4 h of calcinations at 700 °C (BPR = 20:1)

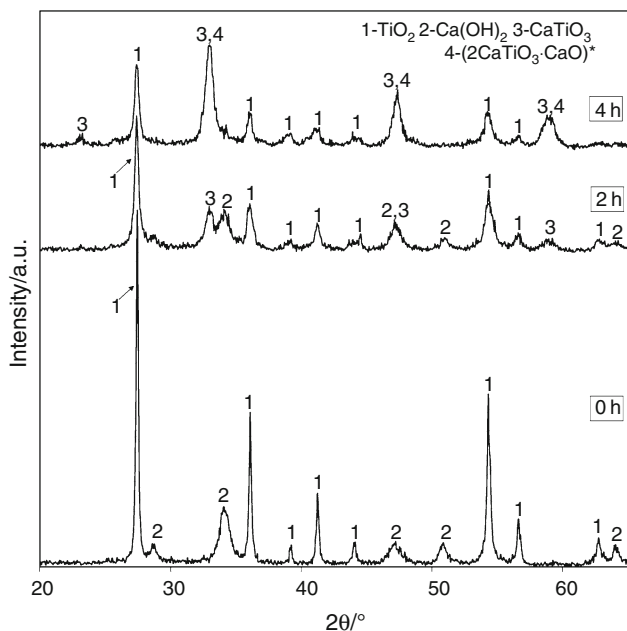


Fig. 10 X-ray diffraction patterns of CaTiO₃ formation in Ca(OH)₂-TiO₂ system after 0, 2, 4 h of mechanochemical treatment (BPR = 40:1); * traces of (2CaTiO₃•CaO)—transition form of CaTiO₃

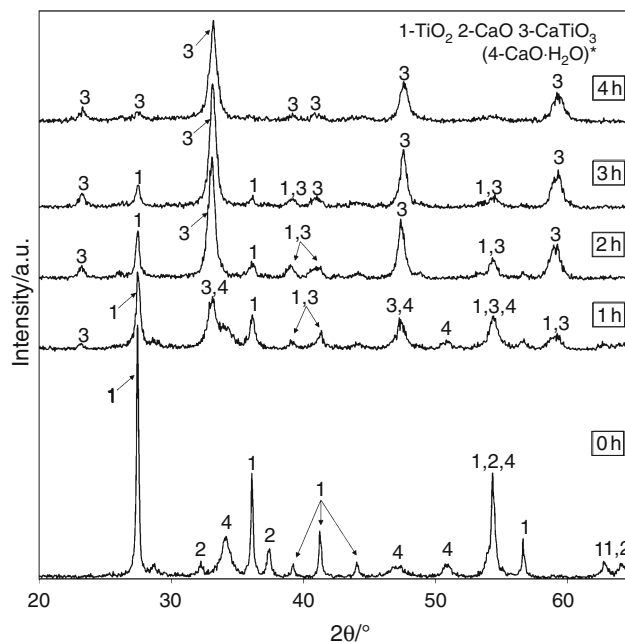


Fig. 12 X-ray diffraction patterns of CaTiO₃ formation in CaO-TiO₂ system after 0, 1, 2, 3, 4 h of mechanochemical treatment (BPR = 40:1); * traces of hydrated form of CaO

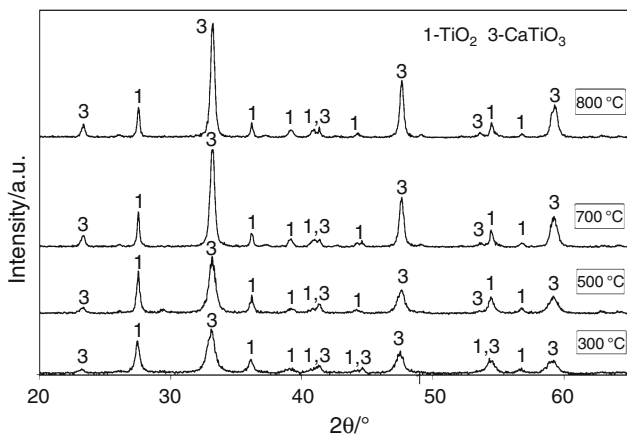


Fig. 11 X-ray diffraction patterns of CaTiO₃ formation in Ca(OH)₂-TiO₂ system after 4 h of mechanochemical treatment followed by 2 h of calcination at 300 °C, 500 °C, 700 °C and 800 °C (BPR = 40:1)

calcination process to 2 h (Fig. 11) although the small amount of reagents would be still present. The syntheses of CaTiO₃ started already after 2 h of milling (BPR = 40:1). Mi et al. [26], applying slightly higher rotational speed of the mill (700 rpm) and average BPR value (30:1), obtained low-crystalline phase of CaTiO₃ after 5 h of mechanochemical activation, and fully crystalline one after its thermal treatment at 625 °C.

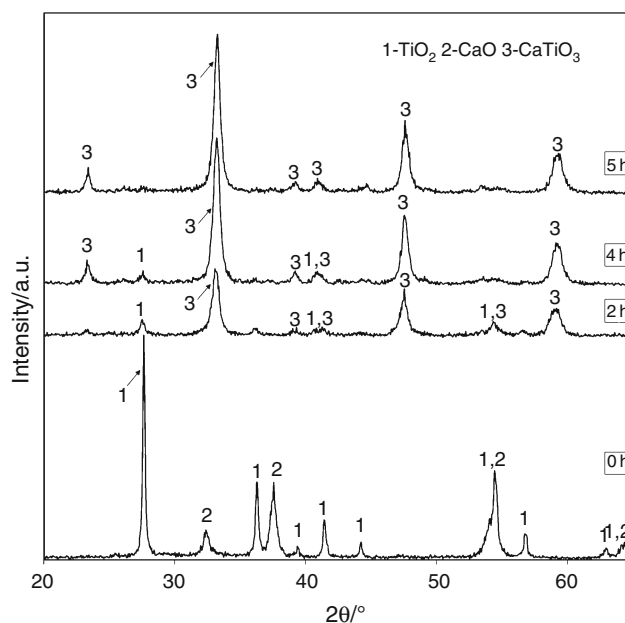


Fig. 13 X-ray diffraction patterns of CaTiO₃ formation in CaO-TiO₂ system after 0, 2, 4, 5 h of mechanochemical treatment (BPR = 20:1)

Mechanochemical synthesis of CaTiO₃ in CaO-TiO₂ system

Calcium titanate synthesis in CaO-TiO₂ system has shown that crystalline product can be obtained with the use of

reactive milling only. The calcination process was unnecessary unlike the synthesis of CaTiO_3 from the two systems described above. It was also shown that the amount of energy delivered to the system in a unit of time significantly influenced the synthesis time. In the case of mechanochemical synthesis with BPR = 40:1, CaTiO_3 formation was already observed after 1 h of milling and the fully crystalline phase after 4 h of milling (Fig. 12). When less energetic milling (BPR = 20:1) was used, longer time was required for achieving the same effect (Fig. 13).

Conclusions

The study presented here, covering the mechanochemical synthesis of calcium titanate from different precursors of calcium oxide, i.e. CaCO_3 , Ca(OH)_2 , CaO and TiO_2 , allows for the following conclusions.

- The process of mechanochemical treatment using planetary ball mill Fritsch GmbH *Pulverisette-6* leads to a complete synthesis of the crystalline calcium titanate only in the case of mixture of CaO and TiO_2 as the reagents, with the application of the following conditions: rpm = 550; for BPR = 40:1 synthesis time = 4 h; for BPR = 20:1 synthesis time = 5 h.
- In two other systems, i.e. CaCO_3 and Ca(OH)_2 with TiO_2 , the mechanochemically activated mixture had to be calcinated. However, the required temperature for this process can be significantly reduced (by about 700 °C) in comparison to the temperature characteristic for high-temperature CaTiO_3 synthesis.
- The known influence on the action of mechanical forces using different BPR values and the resulting transfer of kinetics energy to solids inducing chemical synthesis has been confirmed in CaTiO_3 production.

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