

Synthesis calcium-titanate (CaTiO₃)

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Abstract

Ceramic materials have been in use in many different areas of human wellbeing for a very long time. Important domains in ceramic materials are those materials that are applied in electronics. Our research is focused on calcium-titanate (CaTiO₃). Most common way of obtaining this material is by using the process of sintering.

Starting powders of calcium carbonate CaCO₃ and titanium dioxide TiO₂ with a rutile crystal modification were measured to attain the molar ratio of CaCO₃:TiO₂ = 1:1. Mechanical activation of the starting mixture was performed by grinding in a high energy vibro mill in duration of 60 minutes. Depending on the grinding time, four mixtures were used in our work (a non-activated mixture and three differently activated mixtures: 15, 30 and 60 minutes). Calcination for 2 hours at 900°C after what samples were pressed and than sintered at temperatures of 1200°C and 1300°C for 180 minutes. X-ray diffraction is used for observing the evolution of calcium-titanate phase during research. Differential thermal analysis was performed with the purpose of determining characteristic temperatures on which solid-state processes occur.

Based on analysis of all given results it can be concluded that mechanical activation of a mixture of calcium carbonate and titanium-dioxide powders leads to reduction of the size of the material, deformation of the crystal structure of the dispersed material and generation of point and line defects. We noticed temperature drop and time reduction needed for CaTiO₃ sintering when duration of mechanical activation is longer.

Keywords

Calcium-titanate, perovskites, mills, sintering, X-ray methods.

Introduction

A typical representative of the class of modern ceramics materials known as perovskites is calcium-titanate (CaTiO_3). The perovskites with general formula ABO_3 have been widely used for dielectric materials. Dielectric behavior of CaTiO_3 is described in several comprehensive textbooks [1,2]. The most important application begin as capacitors in the electronic circuits [3]. It has been applied in the fabrication of ceramic condensers, microwave resonators and high-frequency filters, radioactive waste detectors. Calcium-titanate is one of the three major constituents of Synroc (assemblage of synthetic titanate based-minerals) that was developed as matrix for immobilizing high-level radioactive waste [4]. For microwave dielectric-resonator applications, dielectric ceramic materials should have high relative permittivity (ϵ_r), a low dielectric loss (high Q value) and a temperature-stable resonant frequency (τ_f). For the CaTiO_3 : $\epsilon_r \sim 170$, $\tau_f \sim +800$ ppm/K [5].

The perovskite CaTiO_3 is ferroelastic with an orthorhombic symmetry at room temperature (space group Pbnm) and undergoes two phases transitions at respectively $T_1 \sim 1398$ K (space group Mmcm) and $T_2 \sim 1523$ K (space group Pm3m) [6].

Sintering presents a process of particle merging due to heating of a disperse mixture of crystal and non-crystal materials. The essence of this process is in qualitative and quantitative changes of contacts between powder particles. In advanced technologies, preparation of powders for the synthesis of new materials is most often performed using mechanical activation – intensive transport of mechanical energy on to powders, in specially constructed mechanical activators (mills). Mechanical activation leads to controlled disordering and destruction of materials. As the reactive capability of materials is the consequence of its structural properties, the processes of disordering and destruction occurring during mechanical activation of powders later influences acceleration of the synthesis process.

Experimental

In this work starting powders of calcium carbonate (CaCO_3 – Kemika, Zagreb) and titanium dioxide (TiO_2 Alfa products, Ventron) with a rutile crystal modification were measured to attain the molar ratio of $\text{CaCO}_3:\text{TiO}_2 = 1:1$. Mechanical activation of the starting mixture was performed by grinding in a high energy vibro mill (CUP Mill Type MN 954/3 KHD HUMBOLDT WEDAG) in a continual regime in air. The grinding times were 15, 30 and 60 minutes. Depending on the grinding time, four mixtures were used in our work. A non-activated mixture is denoted CT-00 and three mixtures activated during 15, 30 and 60 minutes are denoted CT-15, CT-30 and CT-60, respectively. An X-ray diffraction analysis of the starting mixture (non-activated) and activated mixtures was performed first. Investigations were performed on a Philips Analytical PW-1710 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and a graphite monochromator. Investigations were performed at room temperature in the angle range of $5\text{-}60^\circ$ (2θ) a step of 0.02° and holding time of 2 s per step. X-ray diffraction is used for observing the evolution of calcium-titanate phase during research. Differential thermal analysis (DTA) was performed with the purpose of determining characteristic temperatures on which solid-state processes occur. Starting mixture components (CaCO_3 and TiO_2), the non-activated mixture and activated mixtures (for 15, 30 and 60 minutes) were analyzed on a SHIMADZU DTA-50 in nitrogen atmosphere in the temperature interval from room temperature to 1100°C with a constant heating rate of $10^\circ\text{C}/\text{min}$. Sample preparation for calcination by pressing of starting powders was performed in a VEBTHURINGER INDUSTRIEWERK REUENSTEIN hydraulic press. Pressing was two-sided and the pressed samples had a cylindrical shape (radius 12 mm and mass 2 g with applied pressure of 50 MPa). The significance of this operation is understandable if one has in mind that pressing can influence the formation of interparticle contacts, which are of special

significance for this process. Calcination of pressed samples was performed at the temperature of 900°C for 2 hours. Samples were gradually cooled until room temperature. The prepared samples were sintered in a high temperature tube furnace (Lenton Thermal Design Ltf 16 D) in air. The temperatures of isothermal sintering were 1200 °C and 1300°C. The sintering times at the given temperatures were 0, 30, 60 and 180 minutes.

Results and discussion

Fig. 1 shows diffractograms of starting mixtures activated for 15, 30 and 60 minutes and the non-activated mixture. Fig. 2 shows the dependence of peak intensities of the described crystallographic directions for CaCO₃ and TiO₂ powders as a function of the activation time. The decrease of peak intensities (diffraction maximums) in CaCO₃ indicates deformation of its crystal structure, which is the highest in the first 15 minutes. At the same time the peak intensity decrease is accompanied by their broadening. Broadening of diffraction lines indicates that grinding accompanied by generation of crystal structure defects induces high crystal lattice strain. This indicates that mechanical energy was used to break-up existing grains. Peak broadening indicates that after mechanical activation CaCO₃ and TiO₂ have lower crystallinity degrees.

The dependence of the change in crystallite size of starting CaCO₃ and TiO₂ powders on the activation time is given in fig. 3. In the first 15 minutes of mechanical activation reduction in crystallite size in calcium carbonate is most intensive. Newly formed phases can be noted for rutile after 15 minutes of grinding. Further grinding resulted in a reduction in crystallite size.

With the increase of activation time peak widths increase, which means that dislocation density increases causing an increase in micro strain of the crystal lattice. This contributes to higher mobility of ions participating in the reaction, thus increasing the diffusion rate. We know that the diffusion rate to a great extent depends on crystal lattice defects, such as

vacancies and dislocations. During mechanical activation by grinding the structure of both starting powders is disrupted, though the change of micro structural parameters of CaCO_3 is more intensive.

After calcination, X-ray diffraction patterns (fig. 4) show that the calcium titanate phase is present in all mixtures, i.e. calcium-titanate has formed. Fig. 5 shows the dependence of the intensity of characteristic peaks of calcium-titanate and the remaining TiO_2 after calcination as a function of the activation time. Samples with increased crystallinity are obtained by increasing the duration of mechanical activation.

Fig. 6 shows the crystallite size of calcium-titanate and titan-dioxide after calcination as a function of the activation time. During the first 30 minutes of mechanical activation the crystallite size increases in all phases of CaTiO_3 . The crystallite size in rutile decreases with increasing activation time and all rutile is expected to disappear after sintering.

The influence of mechanical activation on the behaviour of the system during thermal treatment can be analyzed in thermograms of differently activated mixtures. The thermogram given in fig. 7 shows clear endothermic processes below 800°C , which are the result of decomposition of calcium carbonate. After 800°C extended exothermal peaks are noted, that is the consequence of the formation of a new phase - CaTiO_3 .

With the increase of the activation time the reaction occurs at a lower temperature in comparison with non-activated samples. This confirms that basic material changes during mechanical activation are related to physical-chemical surface parameters, resulting in the occurrence of changes in the materials reactivity. Decomposition of the material gives an increased specific surface and thus reactive capability. Thus grinding ceramic powders increases their reactivity and accelerates solid-state reactions.

In accordance with the theoretical principles of Gropyanov sintering of crystal powders without a liquid phase occurs by volume diffusion of vacancies. He has shown that kinetics of the sintering process is in general determined by two parameters: the boundary densification degree (C_∞) and sintering rate constant (K); ($C = C_\infty \cdot K \cdot t / (1 + K \cdot t)$). The results obtained after sintering at 1200 °C and 1300 °C show that the boundary densification degree increases with increased activation time and it is also higher at higher sintering temperatures (fig. 8). The density of sintered samples increases with the growth of the sintering temperature. In this paper maximal density was achieved at the sintering temperature of 1300 °C after 180 minutes of sintering of the mixture activated for 60 minutes. It was 75% of the theoretical density ($\rho_t = 4,1 \text{ g/cm}^3$).

Conclusions

Obtaining materials with properties defined in advance is one of the basic tasks of materials science. Based on analysis of all given results it can be concluded that mechanical activation of a mixture of calcium carbonate and titanium-dioxide powders leads to reduction of the size of the material, deformation of the crystal structure of the dispersed material and generation of point and line defects. It was established that after 15 minutes of grinding the influence of mechanical activation can be noted. With an increase of the time of mechanical activation, the sintering process of the $\text{CaCO}_3\text{-TiO}_2$ becomes more rapid and calcium-titanate forms at lower temperatures. We noticed temperature drop and time reduction needed for CaTiO_3 sintering when duration of mechanical activation is longer.

References

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Figure 1. Diffractograms of non-activated mixture (a), and mixtures activated during 15 (b), 30 (c) and 60 (d) minutes.

Figure 2. Dependence of peak intensities of the described crystallographic directions for CaCO_3 and TiO_2 powders as a function of the activation time.

Figure 3. Crystallite size of starting CaCO_3 and TiO_2 powders on the activation time is given

Figure 4. Diffractograms of non-activated mixture (a), and mixtures activated during 15 (b), 30 (c) and 60 (d) minutes after calcination.

Figure 5. Dependence of the intensity of characteristic peaks of calcium-titanate and the remaining TiO_2 after calcination as a function of the activation time.

Figure 6. Crystallite size of CaTiO_3 and TiO_2 after calcination as a function of the activation time.

Figure 7. Thermograms

Figure 8. The boundary densification degree (C_∞) as a function of the activation time.

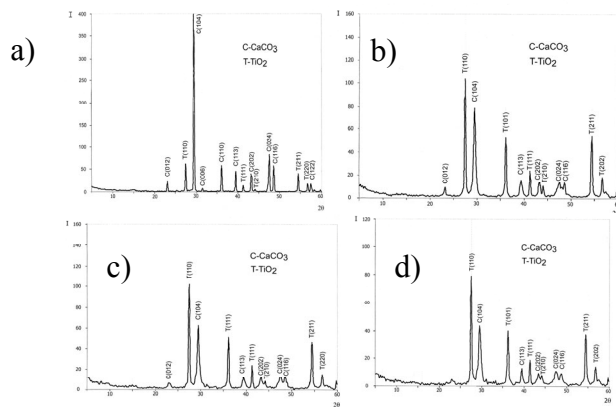


Figure 1. Diffractograms of non-activated mixture (a), and mixtures activated during 15 (b), 30 (c) and 60 (d) minutes.

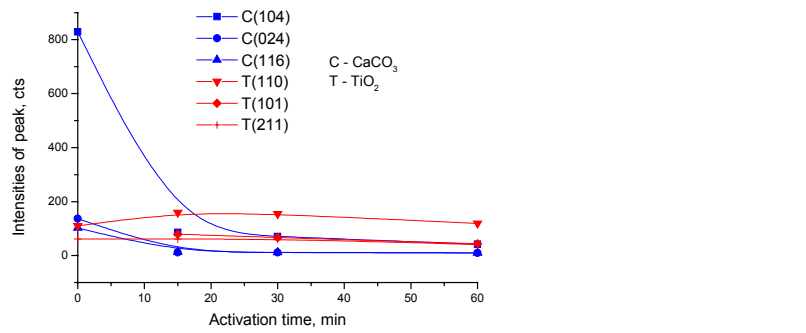


Figure 2. Dependence of peak intensities of the described crystallographic directions for CaCO_3 and TiO_2 powders as a function of the activation time.

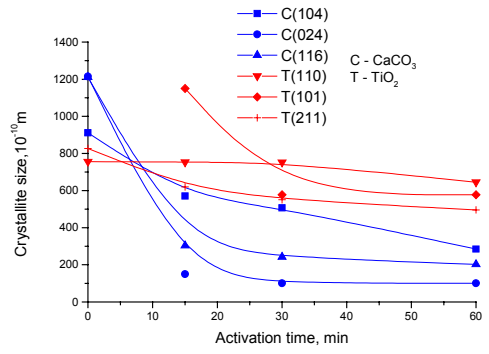


Figure 3. Crystallite size of starting CaCO₃ and TiO₂ powders on the activation time is given.

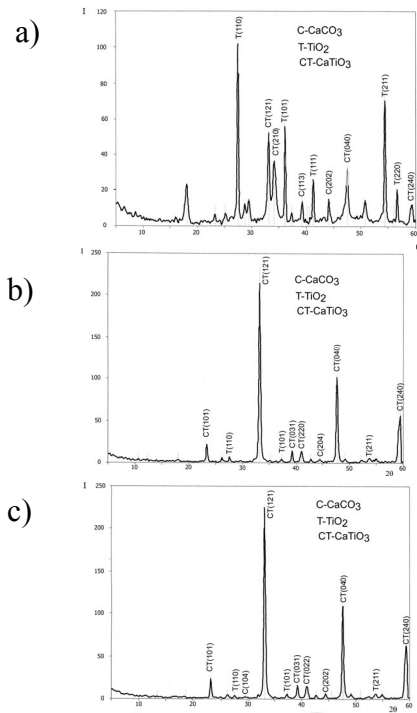


Figure 4. Diffractograms of non-activated mixture (a), and mixtures activated during 30 (b) and 60 (c) minutes after calcination.

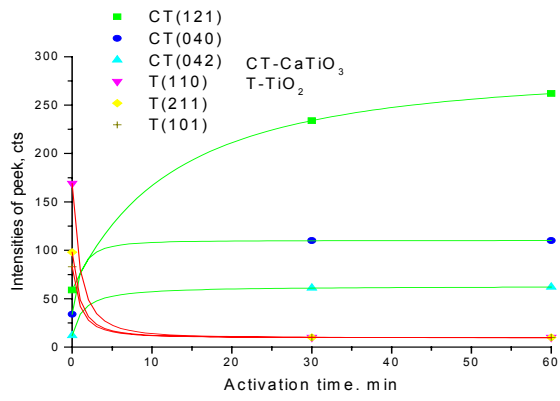


Figure 5. Dependence of the intensity of characteristic peaks of calcium-titanate and the remaining TiO₂ after calcination as a function of the activation time.

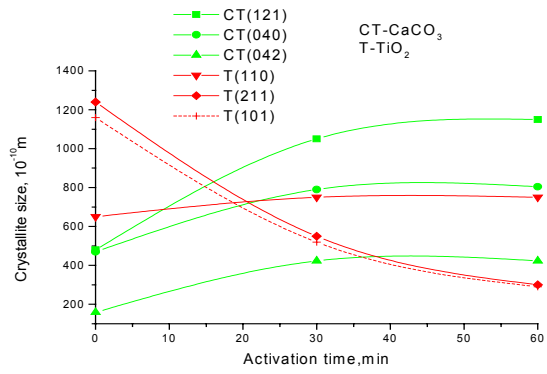


Figure 6. Crystallite size of CaTiO₃ and TiO₂ after calcination as a function of the activation time.

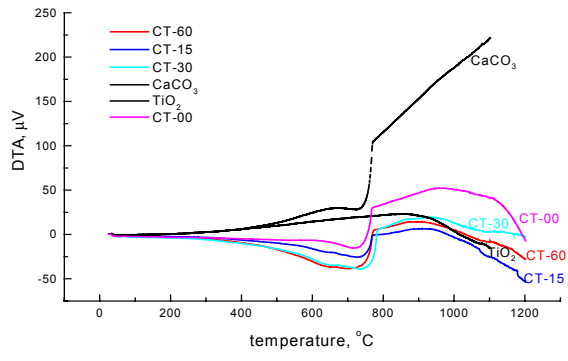


Figure 7. Thermograms

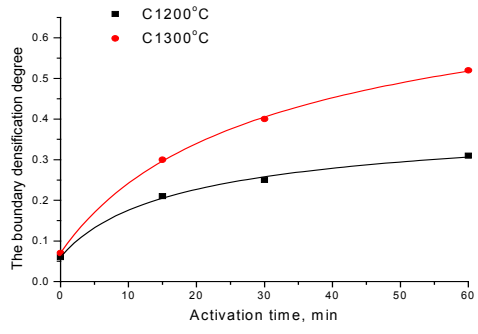


Figure 8. The boundary densification degree (C_{∞}) as a function of the activation time.