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Influence of milling time on mechanically assisted synthesis of $Pb_{0.91}Ca_{0.1}TiO_3$ powders

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Abstract

$Pb_{0.91}Ca_{0.1}TiO_3$ powders (PCT) were prepared by mechanochemical synthesis from high-energy ball milling process. The influence of milling time on the phase formation, crystal structure, specific surface area, density and powder morphology was observed. We adopted the Rietveld refinement technique to investigate the crystal structure of the PCT powders. Scanning electron microscopy (SEM) analysis revealed that PCT powders milled for 5 h showed a wide distribution of particle agglomerates while milled for 35 h showed a decrease in agglomerates size. Further prolongation of milling time resulted in the agglomerates growth.

Keywords: A. Milling; B. X-ray methods; D. Perovskites

1. Introduction

Lead calcium titanate (PCT) materials are of significant commercial and industrial importance because of their excellent dielectric, ferroelectric and piezoelectric properties [1–3]. The $[Pb_{0.9}Ca_{0.1}]TiO_3$ (PCT) is a promising material for high frequency applications, such as ultra-sonic diagnostic imaging and non-destructive evolution, because of its unusually large anisotropic piezoelectric response as compared to $Pb[Zr_{1-x}Ti_x]O_3$ (PZT) ceramics [4]. The ferroelectric behavior of PCT persists up $x = 0.5$ as confirmed by the presence of a ferroelectric hysteresis loop [5]. In order to achieve a dense and uniform microstructure, a fine powder of perovskite phase with a low degree of particle agglomerations is necessary as starting material.

Many researches have thus focused on the processing of PCT powders by several chemistry-based novel preparation routes. Unfortunately almost all these chemistry routes require that precursors be calcined at a temperature ranging from 700 to 850 °C, in order to develop the designed PT-phase. Intensive milling in high-energy mills could be a probably solution to these problems, i.e. mechanical treatment of starting powders can activate them for sintering process [6,7]. Further, mechanical treatment of ceramic powders can reduce particle size resulting in the production of nanocrystalline powders.

A novel mechanochemical processing route has been developed for the production of nanocrystalline powders [8–11]. Mechanochemical activation has been employed to synthesize several ceramic materials, including lead magnesium niobate (PMN), lead titanate (PT), barium titanate (BT), lead zirconate titanate (PZT) and lead calcium titanate (PCT) [12–18]. The reactivity of starting materials could be improved significantly after an appropriate milling treatment, whereas the subsequent calcinations stages at high temperature can be avoided [19]. More recently, a high-energy mechanochemical milling process has also been successfully employed to synthesize nanosized oxides and compounds [20–22].

The mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for the ceramic powder preparation for several reasons. It uses low-cost and widely available oxides as starting materials and skips the calcination step at an

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intermediate temperature, leading to simplified process [22,23]. Furthermore, the mechanically derived powders possess a much higher sinterability than those synthesized by conventional solid-state reaction and most of wet-chemical processes. There are a number of phenomena associated with mechanical activation, including refinement of crystallite size, amorphization of crystallite phases, creation of point surface and lattice defects, phase transformation and crystallization from an amorphous state and chemical reaction [24]. In addition, the nucleation and subsequent growth of perovskite crystallites were triggered by mechanical activation at room temperature [25].

In this work, PCT powders were successfully synthesized by mechanochemical synthesis in high-energy ball milling. Milling parameters were optimized to reduce milling time. The purpose of this work was to analyze advanced results regarding the effect of milling time on the formation of perovskite structure of PCT material.

2. Experimental procedure

The following reagents were used as starting materials: pure PbO (99.9% purity), CaO (97% purity) and TiO_2 (99.8% purity) supplied by Synth and Vetec, respectively. The composition selected for this study was $[Pb_{0.9}Ca_{0.1}]TiO_3$. According to the chemical formula of the desired PCT ceramics, appropriate amounts of starts oxides were weighed, mixed and further milled in a ball mill (SPEX 8000M-MIXER/MILL). The synthesis was carried at room temperature for high-energy ball milling system up to 30 h in static air. Milling conditions were the following: zirconium oxide jars and zirconium oxide balls ($d = 2$ mm), ball/powder mass ratio was 4:1, air atmosphere, milling time range from 5 to 40 h, respectively.

X-ray diffraction data for milled powders were collected using a Rigaku RINT2000 diffractometer (42 kV × 120 mA) with Cu Kα radiation ($\lambda_{K\alpha1} = 1.5405$ Å, $\lambda_{K\alpha2} = 1.5443$ Å, $I_{K\alpha1}/I_{K\alpha2} = 0.5$), 2θ range between 15 and 110°, step size of 0.02° (2θ), divergence slit = 0.5 mm, receiving slit = 0.3 mm. The data obtained from Rietveld analysis were calculated by using the package General Structure Analysis System program (GSAS) of Larson and Von Dreele [26–28]. The peak profile function was modeled using a convolution of the pseudo-Voigt [27] with the asymmetry function described by Finger et al. [29,30], which accounts for the asymmetry due to axial divergence. Raman measurements of PCT powders were performed using an ISA T 64000 triple monochromator. An optical microscope with 80× objective was used to focus the 514.5-nm radiation from a Coherent Innova 99 Ar^+ laser on the sample. The same microscope was used to collect the back-scattered radiation. The scattering light dispersed was detected by a charge-coupled device (CCD) detection system. Scanning electron microscopy (SEM, model JOEL-5300) was used to evaluate the particle size and the powder morphology. The average grain size of the milled powders were estimated using the Sherrer formula. Specific surface area was determined based on isotherms of nitrogen adsorption using the BET method (Sorptomatic 1990).

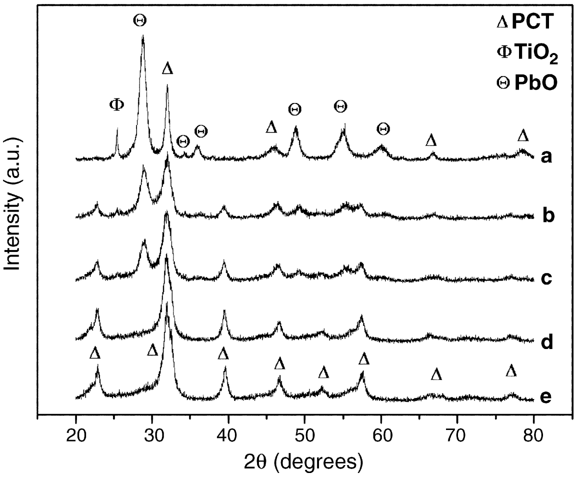

Fig. 1. X-ray diffraction for PCT powders milled at different times: (a) 5 h; (b) 15 h; (c) 25 h; (d) 35 h and (d) 40 h.

3. Results and discussion

XRD patterns of the PCT powders milled for several times are shown in Fig. 1. First traces of perovskite phase have been formed after milling during 5 h. After that, the peaks became broadened indicating a reduction in crystallite size. An increase of perovskite peaks was also evident with the prolongation of milling time. Below 35 h of mechanical activation, the broadened peaks at 2θ at around 22.5, 32, 39, 46 and 57 can be attributed to the formation of lead calcium titanate besides the presence of majority of starting oxides. For 35 h of milling only crystalline peaks of perovskite phase can be observed. The formation of PCT phase indicates the reaction between PbO, CaO and TiO_2 which occurred during the milling process. In this point, the majority of sharp peaks of started oxides were reduced.

Rietveld refinement technique was used to investigate the crystal structure of the PCT powders obtained after a milling time of 35 h. Fig. 2 shows the refinement of the PCT powder which shows tetragonal structure. The quantitative phase analyses were calculated by the Rietveld method and the Hill &

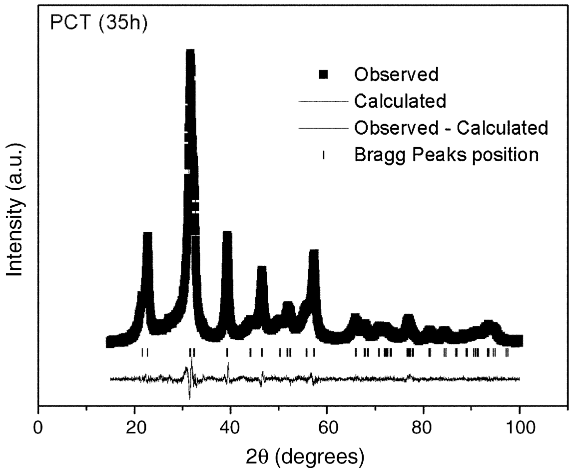

Fig. 2. Rietveld refinement performed for the PCT powder milled for 35 h.

Table 1
Lattice parameters (*a*, *b* and *c*), unit cell volume (*V*) and refinement index for the PCT powder milled for 35 h

Structure: tetragonal			Space group: P4 mm (PDF card no 43–303)			
Composition	Lattice parameters (Å)	Crystallite size (nm)	Volume (Å)^3	Refinement index	Density (g/cm^3)	FWHM
$[Pb_{0.9}Ca_{0.1}]TiO_3$	$a = 3.9065$ $b = 3.9065$ $c = 4.0979$ $(c/a) = 1.049$	≈15	62.536	$R_{wp} = 0.0578$ $R(F)^2 = 0.0151$ $S = 1.3624$	7.087	0.8620

Madsen formalism [28]. The calculated crystallite size was ≈15 nm. The lattice parameters (*a*, *b* and *c*), unit cell volume (*V*) and refinement index are illustrated in Table 1. The space group obtained from the Rietveld analysis was P4mm (PDF Card no 43-303).

Raman spectra were used to determine the vibrational modes for PCT powders milled at 5, 15, 25, 35 and 40 h. The order and disorder degree of the atomic structure at short range was also observed. To compare the bands in the Raman spectra, PT standard spectra was shown (Fig. 3).

Fig. 4 illustrates the Raman spectra of PCT powders milled at 5, 15, 35 and 40 h. It was evident that the increase of milling time leads to a disappearance of the vibrational modes bands. This indicated that for longer milling time the crystalline grains started to be destroyed. Also, it was verified a structural disorder at short range as well as a phase transformation for tetragonal to pseudo-cubic once the tetragonality factor (*c*/*a*) is close to 1 [30]. This is also evident from Rietveld refinement which shows a large FWHM value caused by a structural disorder. The active Raman modes of the PCT powders milled for 35 h was compared to the standard PT spectra (Table 2). At higher frequencies, a displacement of the active vibrational modes was noted, indicating a change in the crystal structure after the calcium addition. Therefore, this indicates that the mechanochemical synthesis leads to a reduction in the particle size and a change in the crystal structure.

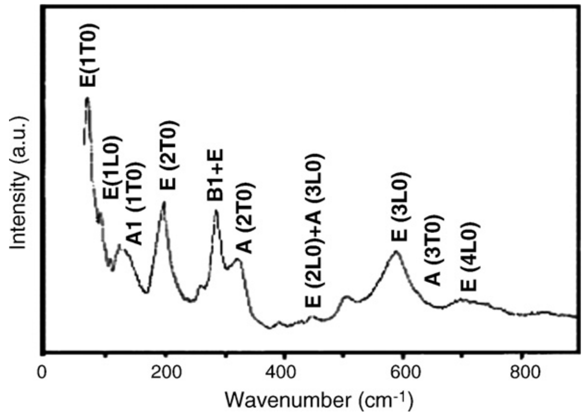

Fig. 3. Standard Raman vibrational modes for the PT system.

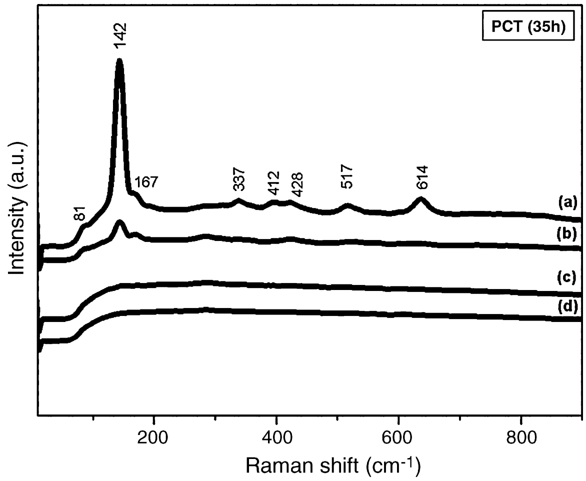

Fig. 4. Raman spectra for the PCT powders milled at different times: (a) 5 h; (b) 15 h; (c) 35 h and (d) 40 h.

Values of the specific surface area of PCT powders were measured from BET analyses. The specific surface area of PCT powders depends on the breaking process of particles and the presence of secondary agglomeration phase. There is a trend to increase the specific surface area from 2.12 m^2/g (0 h) to 5.82 m^2/g (35 h). On the other hand, a decrease of specific surface area value to 5.31 m^2/g (40 h) can be seen as a result of secondary agglomeration process.

SEM analysis of PCT powders milled at different times are shown in Fig. 5. The existence of agglomerates and changes in their size was confirmed. Powders milled for 5 h showed a wide distribution of particle agglomerates, sized 1 μm, while milled for 35 h showed a decrease in agglomerates size probably because during milling the primary agglomerate was destroyed. After that, secondary agglomeration starts and the agglomerates size increased resulting in a decrease of the specific surface area. Further prolongation of milling time resulted in the

Table 2
Raman frequencies for PT Standard and for PCT powders milled for 35 h

Vibrational modes	Raman frequencies (PT standard)	Raman frequencies PCT (mechanochemical)
E1(1TO)	78	80
E1(LO)	100	140
A1(1TO)	141	167
E(2TO)	207	–
B1 + E	288	–
A1(2TO)	330	337
E(2LO)+A(2LO)	449	426
E(3TO)	504	515
A1(3TO)	608	635
E(3LO)	704	–
E(4LO)	717	–

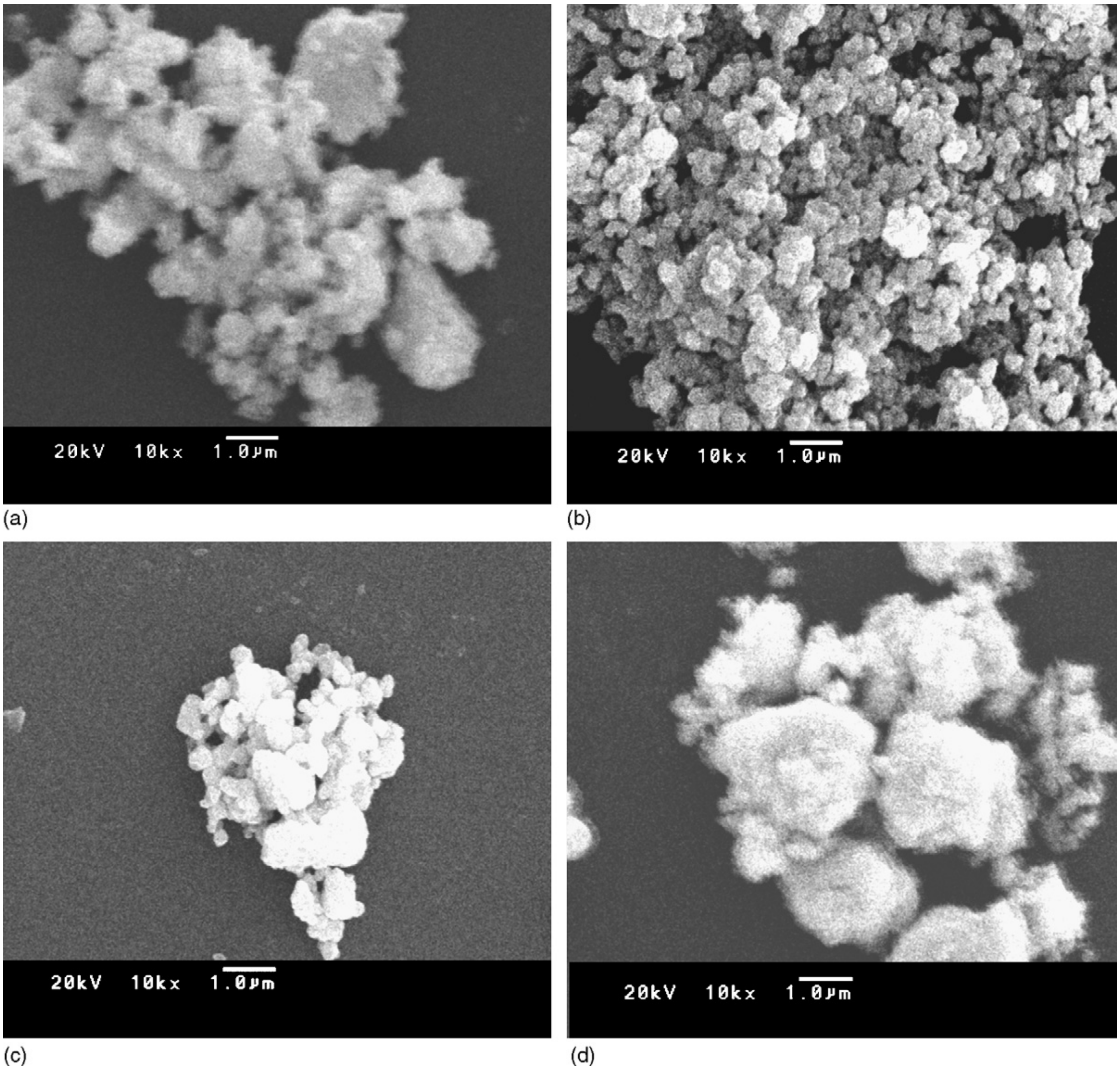

Fig. 5. SEM analysis for PCT powders milled at different times: (a) 5 h; (b) 15 h; (c) 35 h and (d) 40 h.

agglomerates growth. It is accordance with BET analysis that showed a decrease in the specific surface area after milling time of 35 h.

4. Conclusions

The mechanical synthesis can be successfully employed to obtain nanostructure $[Pb_{0.9}Ca_{0.1}]TiO_3$ powders at different milling times. A single phase, nanocrystalline perovskite powder was successfully derived through this method at milling time of 35 h. A prolonged milling time resulted in a change of PCT crystal structure. A tetragonal structure belonging to the point group P4mm was noted after a milling time of 35 h.

Acknowledgements

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