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# Synthesis of perovskite $CaTiO_3$ nanopowders with different morphologies by mechanical alloying without heat treatment

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**Mechanical alloying (MA) method is one of the methods used for large scale production of different nanopowders. In this study, calcium titanate ($CaTiO_3$: CTO) nanoparticles have been synthesized via mechanical alloying (MA) without using heat treatment. The milled powders and CTO were characterized by XRD, SEM, and zetasizer. It is found that the CTO has a diameter of 30 - 70 nm with different morphologies. The results showed the minimum time of calcium titanate synthesis via mechanical alloying without heat treatment is 70 h that formed and the range of grain size (apparent size) using Williamson-Hall equation is 69 nm.**

**Key words:** Mechanical alloying/activation, morphology, perovskite, $CaTiO_3$.

## INTRODUCTION

Calcium titanate ($CaTiO_3$: CTO) 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 (Evans et al., 2003). 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 (Kim, 2000; Ganesh and Goo, 1997). 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 mechano-chemical synthesis from different precursors, such as $CaCO_3$, $Ca(OH)_2$ or CaO, with $TiO_2$ (Vukotic et al., 2004; Mi et al., 1998). Up until now, various methods have been reported in the literatures for the syntheses of $CaTiO_3$. These methods included: (a) conventional solid state reaction between $TiO_2$ and $CaCO_3$ or CaO at a high temperature (Redfern, 1996; Chen et al., 2009), (b) mechanochemical methods (Mi et al., 2009; Brankovic et al., 2007; Palaniandy and Jamil, 2009), (c) chemical co-precipitation method (Gopalakrishna et al., 1975), (d) hydrothermal method (Wang et al., 2007; Li et al., 2009), (e) sol–gel route (Holliday and Stanishevsky, 2004; Zhang et al., 2008), and (f) polymeric precursor method (Pan et al., 2003). Among these methods, mechanical alloying (MA) is a solid-state powder process at ambient temperature and has been applied to synthesize different kinds of materials, such as crystalline, nanocrystalline, quasicrystalline and amorphous materials (Zoz, 1995; Suryanarayana, 2001).

Mechanical alloying, high-energy ball milling, has been used for many years now in producing ultra fine powders in the range of a sub-micron to a nanometer. Aside from size reduction, this process causes severe and intense mechanical action on the solid surfaces, which was

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known to lead to physical and chemical changes in the near surface region where the solids come into contact under mechanical forces (Venkataraman and Narayanan, 1998). These mechanically initiated chemical and physicochemical effects in solids were generally termed as the mechanochemical effect. In this work, Calcium titanate (CTO) is mostly prepared by a mechanical alloying between $CaCO_3$ and $TiO_2$ without heat treatment. The mechanical synthesis process is carried out in high intensity grinding mills such as vibro mills, planetary mills, and oscillating mills. It has been noticed that the size reduction process and the microstructural evolution of the $CaTiO_3$ during milling process were mainly influenced by the type of impulsive stress applied by the grinding media, which can either be an impact or shear type. Moreover, other parameters such as milling time, mill rotational speed and ball to powder at 3 different ratios affect the mechanical process. In fact, when the mechanical synthesis of the $CaCO_3$ and $TiO_2$ was carried out in planetary mills at higher ball to powder (70 : 1) ratio to produce $CaTiO_3$, the impact stress was dominant, and not much attention was given on the mechanochemical mechanism itself. The aim of this work, therefore, is to give additional contribution in understanding the influence of milling conditions on the mechanical synthesis of $CaTiO_3$ nanoparticles without any the deleterious phase and heat treatment.

## EXPERIMENTAL

Oxide powders of $TiO_2$ (99% < 1 µm, 99% purity) and $CaCO_3$ (99%<1 µm, 99% purity) were used as raw materials which were mechanically ground in a purified air atmosphere. The ball-to-powder weight ratio was used at different ratios (20 : 1, 30 : 1 and 70 : 1). Mechanical alloying (MA) was carried out at ambient temperature and at a rotational speed (cup speed) of 350 rpm in a planetary ball mill. The mechanical alloying process was interrupted at regular intervals with a small amount of the MAed powder taken out from the vial to study changes in the microstructures at selected milling duration. The crystal phase was determined with powder X-ray diffraction. For these experiments, a Siemens diffractometer (30 kV and 25 mA) with the $K_{\alpha 1}$, radiation of copper (λ = 1.5406 Å), was used. The structural and compositional information of the product materials was obtained with scanning election microscopy (SEM). The crystalline size (D) and lattice strain were estimated by Williamson-Hall (Williamson and Hall, 1953):

$$\beta \cos\theta = 2\varepsilon \sin\theta + 0.9\frac{\lambda}{D}$$

Where λ is the wavelength of the X-ray, ß the full width at half-maximum (FWHM), θ the Bragg angle, and ε is the microstrain. Finally, the particle size distribution of the powders was measured by zetasizer instrument (Malvern Co, HS C1330-3000, England).

## RESULTS AND DISCUSSION

The XRD patterns of the samples consisting of $TiO_2$ and $CaCO_3$ that had been ball milled for 0, 15, 20, 25, 40, 50, 60 and 70 h are illustrated in Figure 1. In the time of zero, only the $TiO_2$ and $CaCO_3$ peaks are observed. As shown in Figure 1, at 25 h, nothing significant takes place and only starting materials peaks are observed but in 40 h, all the peaks disappear because the material has become amorphous. In 40 and 50 h, we see the same situation. Because of the decrease of the particle size in milling the diffusion paths are shortened. Additionally, high energy is stored in the particles due to the cold work. Thus, the amorphous phase begins to grow around the crystals until all the material become amorphous. Due to the above, it seems that the mechanism of changing crystalline to amorphous in MA is diffusion controlled. There are reports showing that in some cases after amorphization, the crystalline phase has engendered again. As a result of the fact, that with the increase of milling time the kinetic energy of the systems intensifies, hence, the temperature increases which provides the needed energy for the reappearance of the stable state, i.e. crystallization (Koch, 1991). While rising the milling time, after 15 h, $TiO_2$ peaks disappear and $CaTiO_3$ peaks emerge. In this situation, the only distinguishable phase is $CaTiO_3$. It seems that like an SHS reaction that needs a critical amount of energy to start and perform, in this case also, all $TiO_2$ and $CaCO_3$ have been transformed into $CaTiO_3$ due to the energy gained from milling. The thermal analysis of the 70 h milled sample showed no $TiO_2$ or $CaCO_3$ in the final composition of the synthesized powder to participate in reaction and therefore it seems that all reactants have changed to $CaTiO_3$. Using the XRD patterns, the grain sizes were calculated. Figure 2 shows Williamson–Hall diagram of the system for 70 h and the mean size of the grains and the strain percentages are shown in Figure 2. In Figure 2, y represents bcosθ and x represents 2sinθ in Williamson–Hall equation. Hence, a as the slope represents the strain (η) and b as the y-intercept identifies 0.9λ/d from which the grain sizes (d) can be calculated. The grain size of $CaTiO_3$ were 69 nm for the milling time of 70 h. It is predicted that if the milling process continues, the grains become finer until they reach a critical value for the reason that MA process is the result of the competition of cold fusion and breaking of the components that causes the fineness and activation of the particles (Wang et al., 2001). At the critical point, the speeds of fusion and breaking balance out and the particles will no longer be fined (Ko et al., 2002).

According to SEM micrographs of the powders mechanically milleded for 70 h in air atmosphere are shown in Figure 3a to h, that MAed powders are an ultra-agglomeration powder with approximately 100 ± 20 nanometers in size. Because, highly chemically active particles, these are strongly agglomerated. Interestingly, Figure 4a to d show that the product obtained after heat-treatment at 2 different temperatures (500 and 600°C) for 1 h is are mainly uniform special structures with suitable

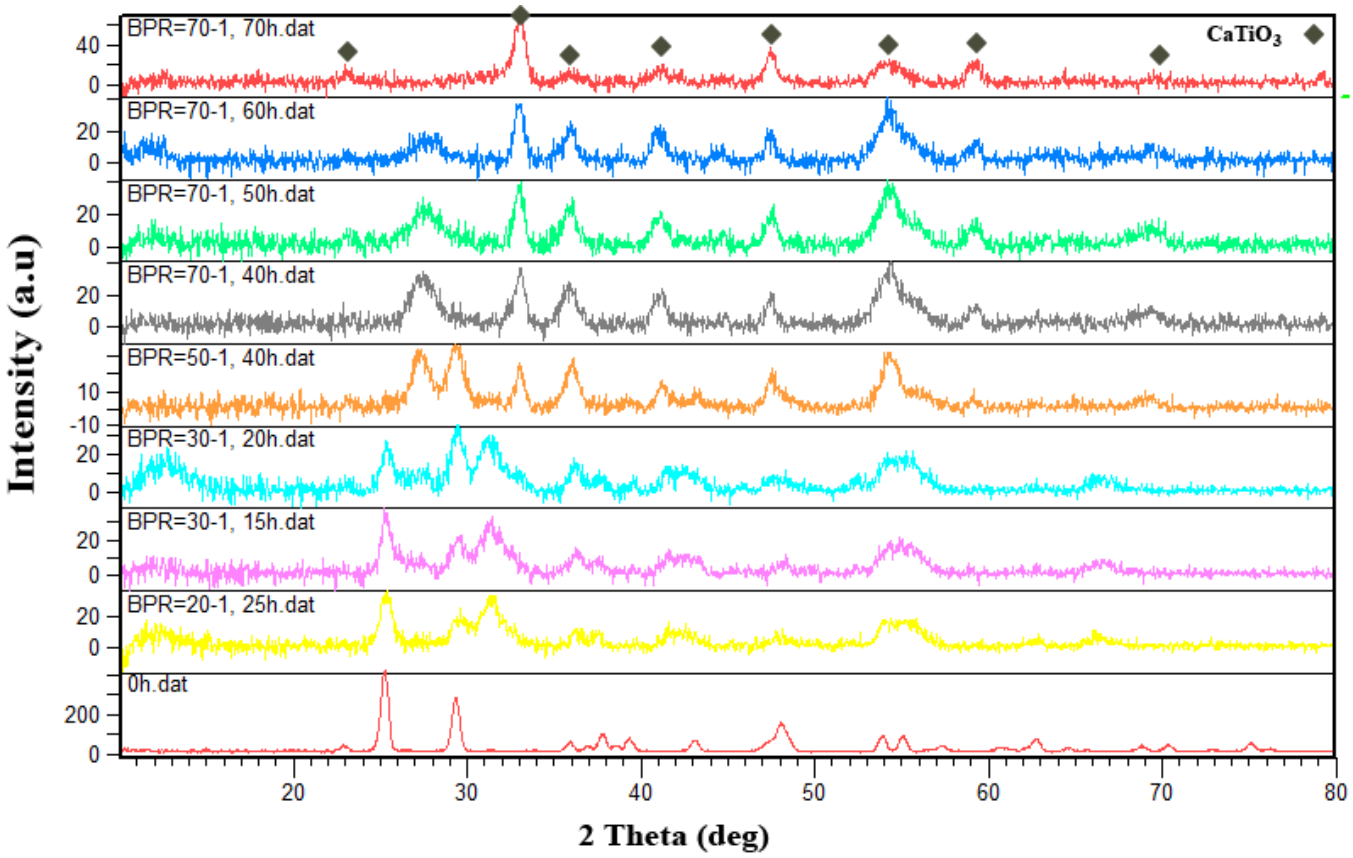


**Figure 1.** The X-ray diffraction spectra of mechanically alloyed $CaCO_3/TiO_2$ powders at different milling times.

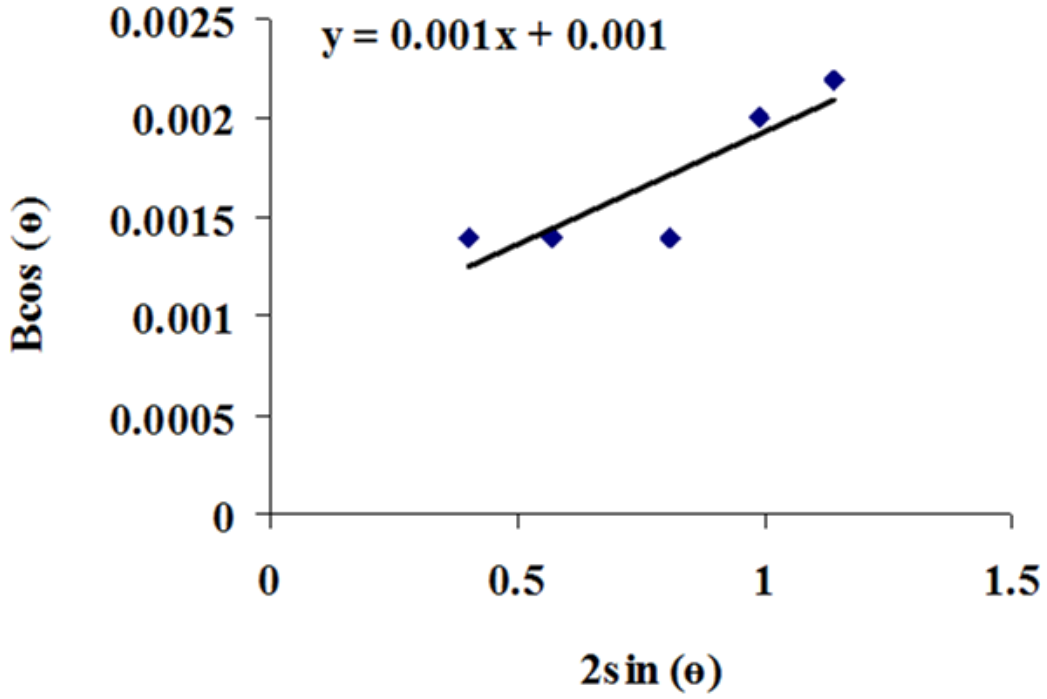


**Figure 2.** Calculation of strain and particle size in accordance to Williamson–Hall equation for CTO after 70 h of ball milling.

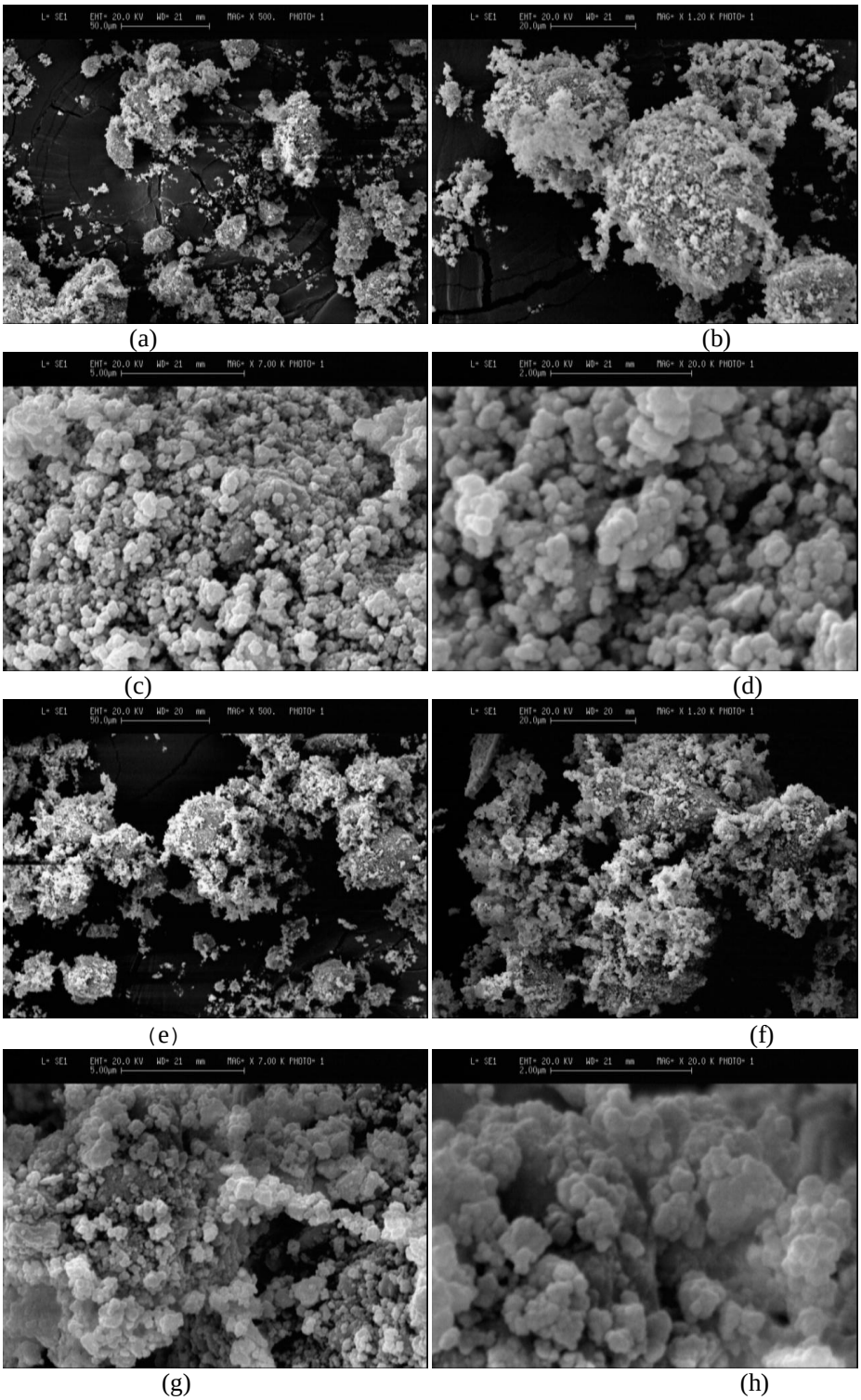


**Figure 3.** SEM images of milled samples in 70 h at different magnifications.

crystallinity grades with a diameter of 60 to 90 nm, which is of very extraordinary uniform morphologies. Finally, in this investigation, an effective method was developed for the formation of ultra-crystallinity with uniform morphologies. As the matter of fact, this method (MA) guarantees its production in the synthesis of CTO for different applications.

The nanoparticle size of CTO milled (70 h) product was

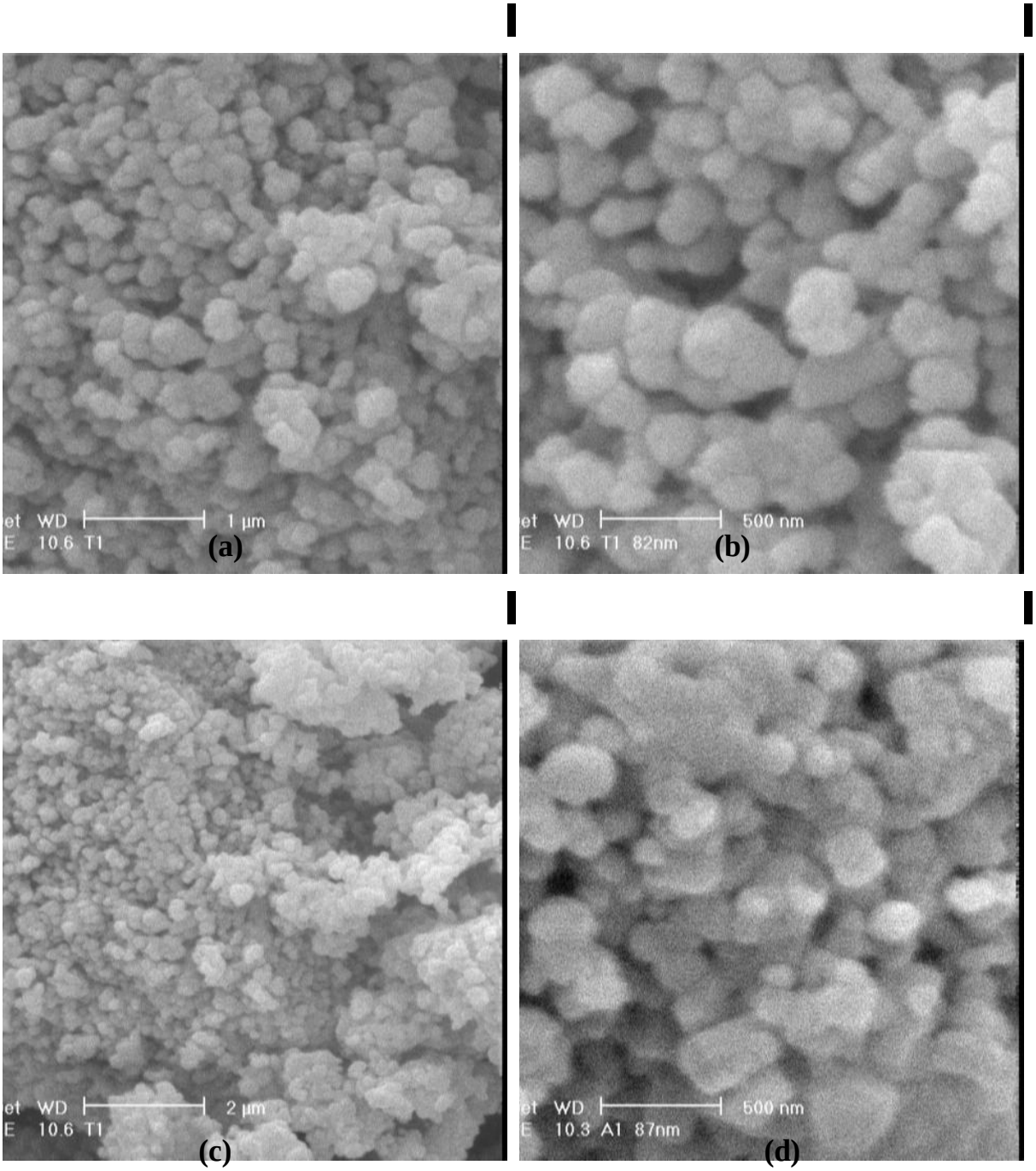


**Figure 4.** SEM different images after heat-treatment at different annealing temperatures with different magnifications a-b) 500°C, c-d) 600°C.

analyzed using a zetasizer method. These measurements reveal the particles to be highly wide distribution (Figure 5a). The milled CTO powders were particles with diameters 2 ranging from 55 to 100 nm and 300 to 550 nm. Figure 5b shows the zetasizer curves of the CTO powders obtained from the heat treatment for 2 h and 500°C. As can be observed in these images, the particle sizes grow up with increasing the aging time. The average particle sizes of powders aged for 2 were regular and uniform.

## Conclusion

CTO with different morphologies was synthesized by a MA method. The purity and good quality of CTO obtained

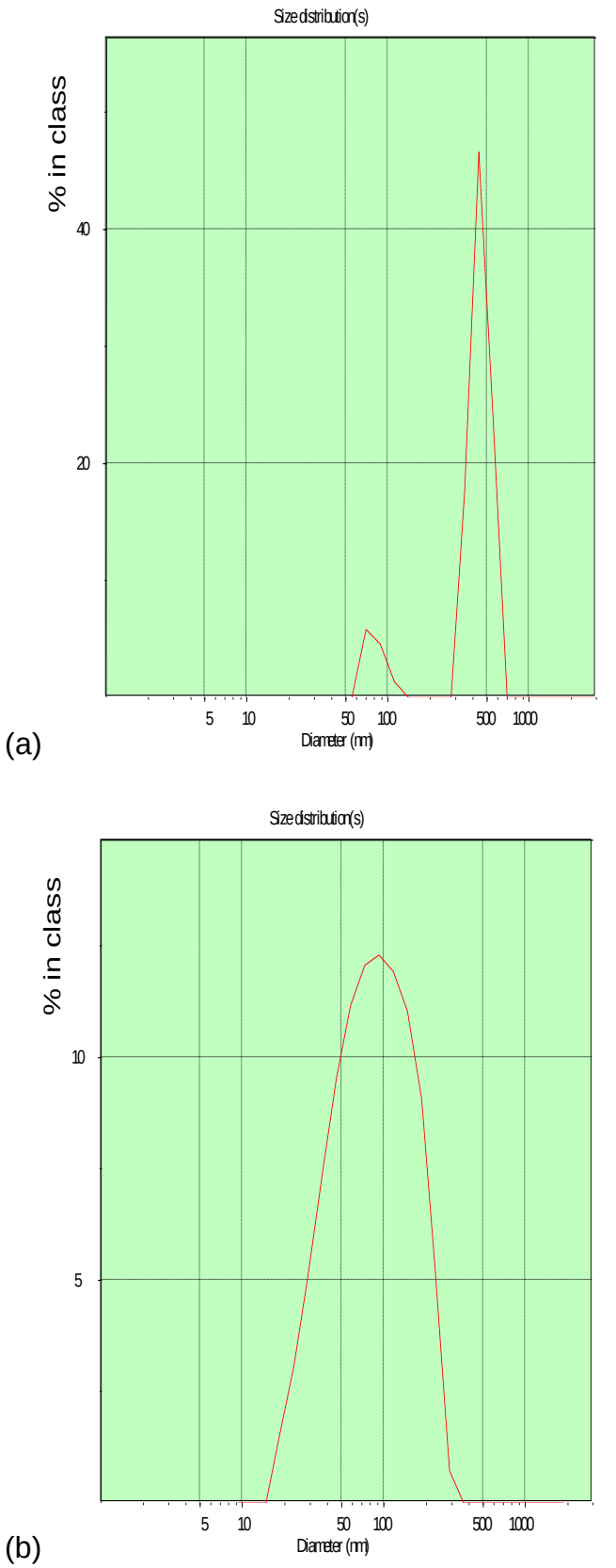


**Figure 5a and b.** Zetasizer images of the CTO powders obtained from the MA a) only 70 h of ball milling, b) 70 h of ball milling with heat treatment in 500°C.

by MA make it a promising method for the production of CTO. The synthesis of CTO was strongly dependant on the experimental parameters such as milling time and ball to powder ratio. Optimal conditions of CTO synthesis were selected as 70 : 1 ratio and 70 h of milling time. This simple approach should promise us a future large-scale synthesis of this nanostructured materials for many important applications in nanotechnology in a controlled manner.

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