

# Effect of Heat Treatment on the Formation of Calcium Titanate Hollow-Crystals Nanostructures Prepared by Hydrothermal Method

S. Manafi\* and S. Jougehdoost

\*ali\_manafi2005@yahoo.com

Received: January 2019 Revised: June 2019 Accepted: September 2019

Department of Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran.

DOI: 10.22068/ijmse.17.2.51

**Abstract:** In this research, calcium titanate ( $\text{CaTiO}_3$ ) hollow crystals have been successfully prepared via hydrothermal method. Titanium tetrachloride, calcium chloride dehydrate, and potassium hydroxide were used as Ti, Ca, and precipitating agents, respectively. The hydrothermal synthesis was performed at different temperatures and time durations. The negative amount of the Gibbs free energy shows the reactivity of the reaction at room temperature. Characterization of  $\text{CaTiO}_3$  was carried out using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD). The optimum condition to prepare  $\text{CaTiO}_3$  is when the sample kept in an autoclave at 300 °C for 3 h that requires less energy and time which consists of a high degree of crystallinity. In this research, tetragonal  $\text{CaTiO}_3$  hollow crystals have been successfully prepared via hydrothermal method.  $\text{TiCl}_4$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and KOH were used as Ti, Ca, and precipitating agents, respectively. The hydrothermal synthesis was performed at different temperatures and time durations. Characterization of  $\text{CaTiO}_3$  was carried out using SEM, HRTEM, and XRD. The sample kept in the autoclave at 300 °C for 3 h well crystallized and required less energy and time for synthesis. The powder has a homogenous dispersity of crystals with the range of nanometer to micrometer sizes which makes it a good candidate as a photocatalyst material.

**Keywords:** Hydrothermal, Crystal growth, Morphology, Nanostructure.

## 1. INTRODUCTION

The perovskite oxides (such as  $\text{PbTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{GdFeO}_3$ , and  $\text{CaTiO}_3$ ) are a proper candidate to be used as a Ferro/antiferroelectrics, superconductors, insulating dielectrics and thermoelectrics [1-5]. Especially, calcium titanate ( $\text{CaTiO}_3$ ) is considered to be used as a capacitor, PTC thermistor, catalysis, and biomaterials [6-9]. because of its ferroelectric properties, visible photoluminescence, air-sensitivity, conductivity, piezoelectricity, photoelectricity, and so on [6-8]. It has a high dielectric constant ( $\epsilon_r$ ), low dielectric loss ( $\tan\delta$ ) and large temperature coefficient of resonant frequency ( $\tau_p$ ), which makes it a promising component in the production of communication equipment operating at microwave frequencies (UHF and SHF), which in turn are used in microwave dielectric applications (as resonators and filters) [10, 11].

$\text{CaTiO}_3$  with the structures of cubes, prisms, dendrites, and nanoparticles has been synthesized by different methods such as microwave [3,12], sol-gel [13], hydrothermal [14], solvothermal [15], solid-state reaction [16], co-precipitation

[12], polymeric precursor [17], organic-inorganic solution [18] and combustion [19].

Many kinds of ceramic materials can be synthesized by the hydrothermal method [1, 5, 20-22]. The advantage of this method is producing of phase-pure products from low-cost and easily accessible precursors in a single experimental step. Moreover, the hydrothermal process can be completed in mild temperatures and pressures and optimized by varying chemical process variables such as reagent concentrations, temperature, pressure, pH, etc [20].

In this research, the synthesis of calcium titanate by the hydrothermal method was investigated. The effect of experimental parameters, including hydrothermal temperature, and time were studied in detail. The relation of crystallite sizes and the temperature of calcination beside of the morphology and the degree of crystallinity were evaluated.

## 2. MATERIALS AND METHODS

To synthesize the calcium titanate by hydrothermal method, titanium tetrachloride ( $\text{TiCl}_4$ ) and calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) with

the molar ratio of 1:1 were used. First, 5.5 cc tetra chloride titanium was added to 125 cc distilled water while was cooling in an ice-water bath and stirred for 1 h. Then, 7.35 g calcium chloride was added to 125 cc distilled water and stirred for 1 h. The Ti-based solution was added dropwise to Ca-based solution till a white precipitate with a pH=1 was obtained. Hydroxide concentration (i.e., pH) is significant to promoting the hydrothermal formation of perovskite oxides, as the reaction consumes OH<sup>-</sup>. 22.. 10 M potassium hydroxide (KOH) was mixed into the solution and pH was raised to 13 and stirred for 2 h. Afterward, the solution was placed in a 100 mL Teflon-lined autoclave for various time durations and temperatures. The autoclave was sealed and calcined to increase the crystallinity of the sample. After the hydrothermal reaction, the system was naturally cooled to room temperature. The powder was rinsed in water and ethanol several times and dried in an oven at 90 °C for 5 h. The hydrothermal condition for the whole process was summarized in Table 1.

The samples were characterized using an X-ray diffractometer with CuK<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ ) (XRD, XMD 300), scanning electron microscope (SEM, VEGA//TESCAN-LMU) and transmission electron microscope (TEM, FEG Philips CM 200).

X-ray diffraction is a proper method for determining the mean size of nanocrystallites in nanocrystalline materials. The size of the crystallites was estimated by the Scherrer equation [23]:

$$D = \frac{K\lambda}{B_{1/2} \cos\theta} \quad (1)$$

with D, the size of the crystallite in Å, K, the shape factor of the average crystallite (approximately equals 0.9),  $\lambda$ , the wavelength of the X-ray i.e. 1.54056 Å,  $\theta$ , the Bragg angle of the diffracted peak and  $\beta_{1/2}$ , the parameter calculated in radians as the below:

$$B_{1/2} = (B_m^2 - B_s^2)^{1/2} \quad (2)$$

where  $B_m$ , is the peak width at half-maximum of the sample, and  $B_s$  is the peak width at half-maximum of the standard sample.

The Origin software was used for measuring the crystallinity degree of the powders. Savitsky-Golay filter was utilized for the smoothing of the noises of XRD peaks. The percent of crystallinity was calculated by the areas under the peaks of XRD ( $A_{\text{crystalline}}$  and  $A_{\text{amorphous}}$  are the areas under the XRD pattern of crystalline and amorphous parts), according to the formula [24]:

**Table 1.** The hydrothermal condition for the synthesis of CaTiO<sub>3</sub>

Specimen	Temperature of autoclave (°C)	Holding time in autoclave before calcination (h)	Calcination temperature (°C)	Calcination time duration (h)
1	200	20	-	-
2	200	20	1000	2
3	200	20	900	2
4	200	20	800	2
5	200	20	600	2
6	200	20	400	2
7	250	50	-	-
8	250	40	-	-
9	250	30	-	-
10	250	20	-	-
11	250	10	-	-
12	300	5	-	-
13	300	3	-	-

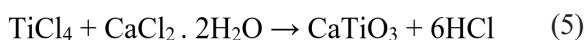
$$\text{Percent of crystallinity} = \frac{A_{\text{crystalline}}}{(A_{\text{crystalline}} + A_{\text{amorphous}})} \times 100 \quad (3)$$

This is not a precise method for measuring areas of crystalline and amorphous phases, however, it can give valuable information about the crystallinity.

### 3. RESULTS AND DISCUSSION

To find the thermodynamic possibility for the formation mechanism of the calcium titanate, the Gibbs energy ( $\Delta G^\circ$ ) of formation has to be calculated. The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy ( $\Delta H^\circ$ ) of the system minus the change in the product of the temperature times the entropy ( $\Delta S^\circ$ ) of the system.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (4)$$



The amounts of enthalpy and entropy of the precursors and the calcium titanate are written in Table 2.

**Table 2.** The amounts of enthalpy and entropy of the precursors and calcium titanate.

Materials	$\Delta S^\circ_{298}$ (J/mol K)	$-\Delta H^\circ_{298}$ (kJ/mol)
TiCl <sub>4</sub>	252.4	804.2
CaCl <sub>2</sub>	108.4	795
HCl	186	92.3
H <sub>2</sub> O	69.9	285.8
CaTiO <sub>3</sub>	93.7	1660.6

The calculation was carried out according to the values of Table 2 and equations 1, 2, as below:

$$\Delta H^\circ_{298} = -329.4 \text{ kJ/mol}$$

$$\Delta S^\circ_{298} = 779 \text{ J/mol.K}$$

$$\Delta G^\circ_{298} = -561.542 \text{ kJ/mol}$$

The negative amount of the Gibbs free energy shows the reactivity of the reaction at room temperature.

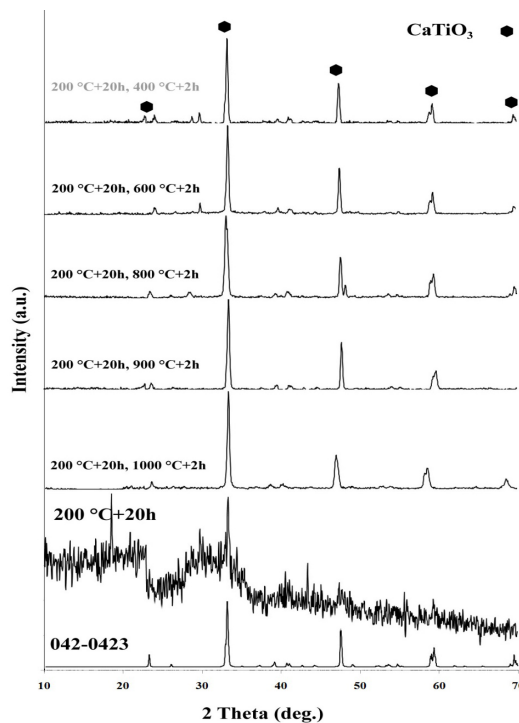
The phase development of the samples was investigated with X-ray diffraction (XRD) analysis. Fig. 1 shows the XRD peaks of the samples were kept in the autoclave at 200 °C for 20 h, before and

after the calcination. The intensity of the sample's peaks before the calcination was weak indicating the low crystallinity of the powder. To increase the crystallization degree, the samples were heat-treated at different temperatures (400-1000 °C).

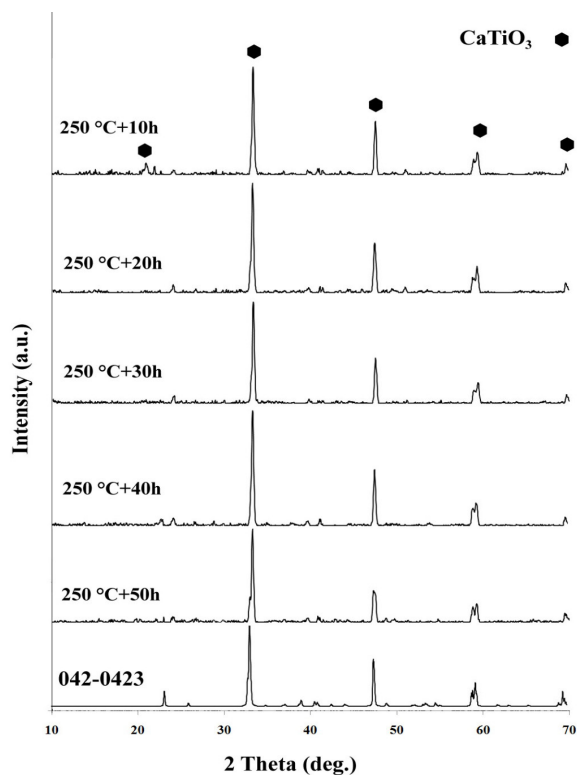
Fig 1 shows the XRD patterns of the samples prepared in the autoclave at 200 °C for 20 h. At the initial stage, before the calcination, the sample has a more amorphous phase. When the samples heat-treated at different temperatures, all the diffraction peaks can be indexed to the orthorhombic CaTiO<sub>3</sub> (JCPDS card No. 42-0423, unit cell a=5.43, b=7.65, and c=5.39 Å).

When the calcination temperature rose from 400 °C to 1000 °C, the intensity of the diffraction peaks was enhanced and the amorphous part started to be disappeared while no diffraction peaks were presented from other crystalline phases.

The aim of this research is the synthesis of CaTiO<sub>3</sub> by the hydrothermal method. Therefore, the samples were placed in the autoclave for longer times at a higher temperature. Fig. 2 shows the XRD patterns of the samples prepared in the autoclave at 250 °C for different times from 10 h to 50 h.

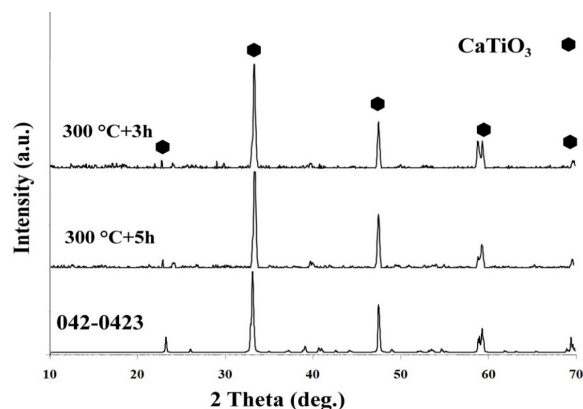


**Fig. 1.** XRD patterns for CaTiO<sub>3</sub> samples were kept in the autoclave at 200 °C for 20 h; before the calcination, and after the calcination at 400 -1000 °C (042-0423 (JCPDS standard card number) is the XRD pattern related to the standard peak of the calcium titanate).



**Fig. 2.** XRD patterns for  $\text{CaTiO}_3$  samples were kept in the autoclave at 250 °C for different times (10 -50 h) without the calcination (042-0423 (JCPDS standard card number) is the XRD pattern related to the standard peak of the calcium titanate).

The autoclave process was carried out in a long period time, so the samples were kept in the autoclave at a higher temperature (300 °C) for shorter times (3 and 5 h). The obtained  $\text{CaTiO}_3$  powders were orthorhombic structure because of all the XRD patterns of calcium titanate phase (JCPDS card: 42-0423). Thus, it can be concluded that the optimum condition to prepare the  $\text{CaTiO}_3$  was when the sample kept in the autoclave at 300 °C for 3 h that requires less energy and time.



**Fig. 3.** XRD patterns for  $\text{CaTiO}_3$  samples were kept in the autoclave at 300 °C for 3 h and 5 h (042-0423 (JCPDS standard card number) is the XRD pattern related to the standard peak of the calcium titanate).

It can be observed that all peaks of XRD patterns in Figs. 1-3 are calcium titanate phase. The polycrystalline nature of the synthesized  $\text{CaTiO}_3$  was confirmed by these patterns which were identified as an orthorhombic phase with the Pbnm space group.

The crystallite sizes increase with rising of the temperature from 25 nm to 60 nm, due to nucleation and growth mechanism (Table 3). The Scherrer formula is not an accurate method to calculate the crystallite sizes [25, 26]. Therefore, these numbers are not precise but prove that the crystallites are growing with increasing the temperature. The degrees of crystallinity was calculated according to the formula (3) and the results are displayed in table 4. The results show a very high degree of the crystallinity of both samples, but a bit of improvement in the crystallinity of the sample kept for a longer time in the autoclave is clear.

**Table 3.** Crystallite sizes of the powders after the calcination in different temperatures.

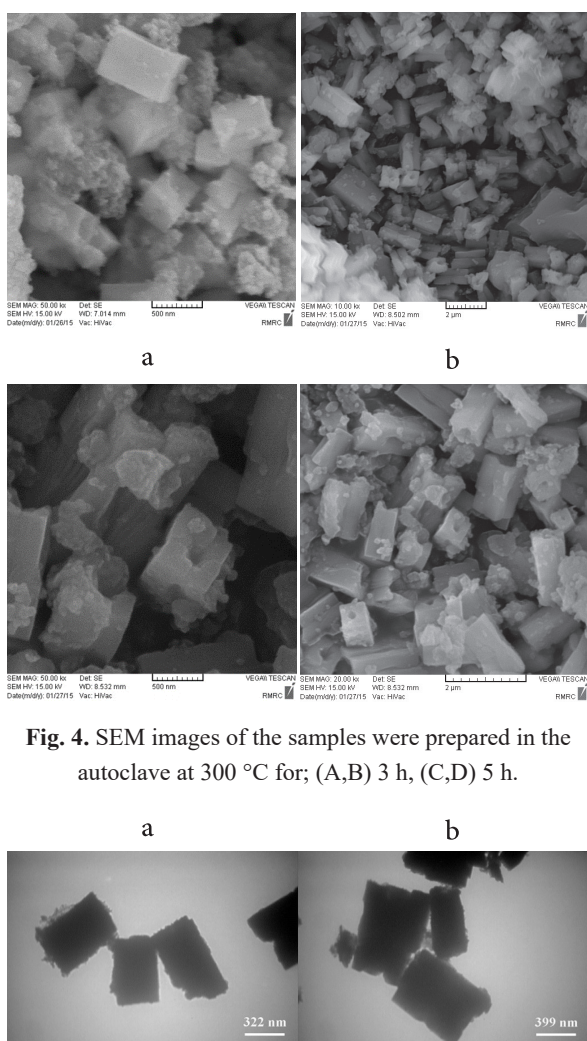
Specimen	Temperature of autoclave (°C)	Holding time in autoclave before calcination (h)	Calcination temperature (°C)	Calcination time duration (h)	Crystallite size (nm)
2	200	20	1000	2	60
3	200	20	900	2	56
4	200	20	800	2	47
5	200	20	600	2	39
6	200	20	400	2	25
13	300	3	-	-	38



**Table 4.** The degree of crystallinity of the sample which kept in the autoclave at 300 °C for 3 h and 5 h.

Time (h)	The crystalline area	The area under the curves of XRD	Crystallinity (%)
3	21854.46	23506.22	93
5	22558.23	23417.45	96.33

Figs. 4 and 5, respectively, show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the samples which kept in the autoclave at 300 °C. The powder with the tetragonal morphology has a homogeneous dispersity.



**Fig. 4.** SEM images of the samples were prepared in the autoclave at 300 °C for; (A,B) 3 h, (C,D) 5 h.

**Fig. 5.** TEM images of the samples were prepared in the autoclave at 300 °C for; (A)3 h, (B)5 h.

Synthesis of CaTiO<sub>3</sub> with different kinds of morphology was studied in different researches. Singh synthesized calcium titanate nanopowder

by microwave method [25]. The prepared powder was formed of agglomerated irregular grain shapes and sizes. Numerous nano-dimensional particles agglomerated and constructed bigger irregular grains of different shapes. Shi et al. [6] synthesized the aligned CaTiO<sub>3</sub> nanotubes by the hydrothermal method. Moreira et al., [26], obtained calcium titanate by microwave-assisted hydrothermal method and the particles had a monodispersed micro-cubes shape. Dong et al. [27], prepared microspheres of CaTiO<sub>3</sub> by solvothermal method. Palaniandy and Jamil synthesized calcium titanate nanopowder with a rhombohedron structure by the mechanochemical method [28]. Durrani et al. [29], investigated the hydrothermal growth of calcium titanate nanowires from titania. They observed powders with different morphologies (large twinned crystals, cubic, rectangular and nanowire shape) for different hydrothermally grown specimens that prepared at various pHs.

Hydroxide concentration (i.e., pH) is significant to promote the hydrothermal formation of perovskite oxides, as the reaction consumes OH<sup>-</sup>. Moreover, the heat treatment and the temperature can especially influence the mechanisms of nucleation and crystal growth in the synthesis of ceramic structures [30]. In this study, KOH was used for adjusting the pH. Calcium titanate powders with a high degree of crystallinity and tetragonal crystals were synthesized in hydrothermal conditions. The powder has a homogenous dispersity of crystals with the range of nanometer to micrometer sizes which makes it a good candidate as a photocatalyst material.

There are some hollows inside the crystals. The orthorhombic unit cell, corresponding to the orientations of 121. unit cell. Ostwald ripening process led to spherical hollow crystals which grow in the c-axis direction [31]. Ostwald ripening is the process in which small crystals, driven by surface tension, dissolve in a supersaturated solution, while larger crystals, whose surface

tension is not sufficient to counteract the effect of supersaturation, grow [32].

The crystals were observed in TEM bright-field images are dark and the hollows cannot be detected. Depending on the orientation of the crystal, scattered electrons may pass through the objective lens aperture and produce a bright area, or most commonly, the electrons may be blocked by the aperture, thereby producing a dark area [33]. Also, the perovskite materials can absorb the light and transport the electron [34,35]. which can influence the transmission of the TEM electron beam through the sample and show a dark view of the sample.

#### 4. CONCLUSION

A hydrothermal method has been successfully carried out to prepare  $\text{CaTiO}_3$  powders. Well-crystallized, pure  $\text{CaTiO}_3$  particles with tetragonal hollow crystal structures with the range of nanometer to micrometer have been obtained at 300 °C for 3 h. The degree of crystallinity of the powders synthesized at this temperature was high, therefore extra calcination could be overlooked. The Ostwald ripening process led to spherical hollow crystals which grow in the c-axis direction inside of the tetragonal crystals.

#### REFERENCES

1. Moon, J., Li, T., Randall, C. A. and Adair, J. H., "Low temperature synthesis of lead titanate by a hydrothermal method". *J. Mater. Res.*, 2011, 12, 189-197.
2. Potdar, H., Deshpande, S., Godbole P. and Gunjkar, V., "Low temperature synthesis of ultra-fine strontium titanate ( $\text{SrTiO}_3$ ) powders". *J. Mater. Res.*, 1992, 7, 429-434.
3. Muhammad, R. and Iqbal, Y., "Microwave dielectric properties of  $\text{Ga}^{3+}$  and  $\text{Ta}^{5+}$  co-doped  $\text{CaTiO}_3$ ." *J. Mater. Sci.*, 2016, 51, 2958-63.
4. Soderlind, M., Fortin, Y., Petoral, R., Klasson, A., Veres, T., Engstrom, M., Uvdal, K. and Kall, P., "Colloidal synthesis and characterization of ultrasmall perovskite  $\text{GdFeO}_3$  nanocrystals", *Nanotechnology*, 2008, 19, 395501-395508.
5. Tang, H., Zhou, Z. and Bowland, C. S. H., "Growth of highly textured  $\text{PbTiO}_3$  films on conductive substrate under hydrothermal conditions", *Nanotechnology*, 2015, 26, 345602-345607.
6. Shi, X. Y. H., Liang, Z., Tian A. and Xue, X., "Synthesis of vertically aligned  $\text{CaTiO}_3$  nanotubes with simple hydrothermal method and its photoelectrochemical property", *Nanotechnology*, 2018, 29, 385605-385615.
7. Lei, X., Xu, B., Yang B. and Xu, B. G. X., "A novel method of synthesis and microstructural investigation of calcium titanate powders", *J. Alloy. Compd.*, 2017, 690, 916-22.
8. Bagchi, A., S. Meka, Rao, B.N. and Chatterjee, K., "Perovskite ceramic nanoparticles in polymer composites for augmenting bone tissue regeneration", *Nanotechnology*, 2014, 25, 485101-485101.
9. Zhang, Q., Li, Y., Ren, Z., Ahmad, Z., Lia X. and Han, G., "Synthesis of porous  $\text{CaTiO}_3$  nanotubes with tunable hollow structures via single-nozzle electrospinning", *Materials Letters*, 2015, 152, 82-85.
10. Samayamutthirian Palaniandy, N. H. J., "Influence of milling conditions on the mechanochemical synthesis of  $\text{CaTiO}_3$  nanoparticles", *J. Alloy. Compd.*, 2009, 476, 894-902.
11. Evans, I., Howard J. and Sreckovic, T. R. M., "Variable temperature in situ X-ray diffraction study of mechanically activated synthesis of calcium titanate", *CaTiO<sub>3</sub>, Mater. Res. Bull.*, 2003, 38, 1203-1213.
12. Gopalakrishnamurthy, H., Rao M. and Kutty, T., *Thermochim. Acta*, 1975, 13, 109-252.
13. Y. Huo, H. Yang, T. Xian, J. Jiang, Z. Wei, R. Li and W. Feng, "A polyacrylamide gel route to different-sized  $\text{CaTiO}_3$  nanoparticles and their photocatalytic activity for dye degradation," *Journal of Sol-Gel Science and Technology*, vol. 71, p. 254-259, 2014.
14. Kimijima, T., Kanie, K., Nakaya M. and Muramatsu, A., "Hydrothermal synthesis of size- and shape-controlled  $\text{CaTiO}_3$  fine particles and their photocatalytic activity", *CrystEngComm*, 2014, 16, 5591-5597.
15. Yu, D., Zhang, J., Wang, F., Zhao, M., Du, K. Shu, S., Zou J. and Wang, Y., "High-Symmetry Epitaxial Growth under Solvothermal Conditions: A Strategy for Architectural Growth of Tubular and Nontubular  $\text{CaTiO}_3$  Microstructures with Regular Geometrical Morphologies and Tunable Dimensions", *Cryst. Growth*, 2013, 13, 3138-3143.
16. Wiczorek-Ciurowa, K., Dulian, P., Nosal A. and Domagała, J., "Effects of reagents' nature on mechanochemical synthesis of calcium titanate", *J. Therm. Anal. Calorim.*, 2010, 101,

- 471–477.
17. Cavalcante, L., Marques, V., Sczancoski, J., Escote, M., Joya, M., Varela, J., Santos, M., Pizani P. and Longo, “Synthesis, structural refinement and optical behavior of  $\text{CaTiO}_3$  powders: A comparative study of processing in different furnaces”, *E., Chem. Eng. J.*, 2008, 143, 299-307.
  18. Lee, S. J., Kim Y. C. and Hwang, J. H., “An organic-inorganic solution technique for fabrication of nanosized  $\text{CaTiO}_3$  Powder”, *J. Ceram. Process. Res.*, 2004, 5, 223-226.
  19. Muthuraman, M., Patil, K., Senbagaraman S. and Umarji, A., “Sintering, microstructural and dilatometric Sintering, microstructural and dilatometric studies of combustion synthesized synroc phases studies of combustion synthesized synroc phases”, *Mater. Res. Bull.*, 1996, 31, 1375-1381.
  20. Lencka, M. M. and Riman, R. E., “Hydrothermal synthesis of perovskite materials: Thermodynamic modeling and experimental verification”, *Ferroelectrics*, 1994, 151, 159-164.
  21. Manafi, S. and Joughedoust, S., “Synthesis of Hydroxyapatite Nanostructure by Hydrothermal Condition for Biomedical Application”, *IJPS*, 2009, 5, 89-94.
  22. Canua, G. and Buscaglia, V., “Hydrothermal synthesis of strontium titanate: thermodynamic considerations, morphology control and crystallisation mechanisms”, *CrystEngComm*, 2017, 19, 3867-3891.
  23. Cullity, B., “Elements of X-ray diffraction”, ed. M. Cohen, San Diego, Addison- Wesley, 1977.
  24. Manafi, S. and Joughedoust, S., “Determination of Microstructural Parameters of Nanocrystalline Hydroxyapatite Prepared by Mechanical Alloying Method”, *AIP. Conf. Proc. Antalia*, 2011.
  25. Monshi, A., Foroughi, M. R., Monshi, M. R., “Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD”, *WJNSE*, 2012, 2, 154-160.
  26. Vorokh, A. S., “Scherrer formula: estimation of error in determining small nanoparticle size Nanosystems: Phys”. *Chem. Math.*, 2018, 9, 364–369.
  27. Singh, R. P., “Conventional and microwave synthesis of mesoporous calcium titanate nanoparticles: a comparative study”, *J. Solgel Sci. Technol.*, 2018, 88, 1-10.
  28. Moreira, M. L., Paris, E. C., do Nascimento, G. S., Longo, V. M., Sambrano, J. R., Mastelaro, V. R., Bernardi, M. I., Andres, J., Varela J. A. and Longo, E., “Structural and optical properties of  $\text{CaTiO}_3$  perovskite-based materials obtained by microwave-assisted hydrothermal synthesis: An experimental and theoretical insight”, *Acta Mater.*, 2009, 57, 5174–5185.
  29. Dong, W., Song, B., Meng, W., Zhao G. and Han, G., “A simple solvothermal process to synthesize  $\text{CaTiO}_3$  microspheres and its photocatalytic properties”, *Appl. Surf. Sci.*, 2015, 349, 272-278.
  30. Palaniandy S. and Hidayu Jamil, N., “Influence of milling conditions on the mechanochemical synthesis of  $\text{CaTiO}_3$  nanoparticles”, *J. Alloys Compd.*, 2009, 476, 894–902.
  31. Durrani, S., Khan, Y., Ahmed, N., Ahmad M. and Hussain, M., “Hydrothermal Growth of Calcium Titanate Nanowires from Titania”, *J. Iran. Chem. Soc.*, 2011, 8, 562-569.
  32. Houllberghs, M., Breynaert, E., Asselman, K., Vaneeckhaute, E., Radhakrishnan, S., Anderson, M. V., Taulelle, F., Haouas, M., Martens J. A. and Kirschhock, C. E., “Evolution of the crystal growth mechanism of zeolite W (MER) with temperature”, *Microporous and Mesoporous Mater.*, 2019, 274, 379-384.
  33. Yang, X., Fu, J., Liang, C., Wu, M. and Zhou, W., “Formation Mechanism of  $\text{CaTiO}_3$  Hollow Crystals with Different Microstructures”, *J. Am. Chem. Soc.*, 2010, 132, 14279–1428.
  34. Friedman A. and Ross, D. S., “Crystal Growth — Ostwald Ripening, in *Mathematical Models in Photographic Science*”, Springer, 2003, Berlin, Heidelberg, 12-26.
  35. Ramanathaswamy, P., “Phase-change thin films: resistance switching and isothermal crystallization studies”, University of Groningen, Netherlands, 2008, 148.
  36. Zhou, D., Zhou, T., Tian, Y., Zhu, X. and Tu, Y., “Perovskite-Based Solar Cells: Materials, Methods, and Future Perspectives”, *J. Nanomater.*, 2018, 11, 729-762.
  37. Yan, X., Huang, X., Fang, Y., Min, Y., Wu, Z., Li, W., Yuan, J., Tan, L., “Synthesis of Rodlike  $\text{CaTiO}_3$  with Enhanced Charge Separation Efficiency and High Photocatalytic Activity”, *Int. J. Electrochem. Sci.*, 2014, 9, 5155-5163.