OPEN ACCESS

Morphology and Properties of (Ba, Sr, Ca) Titanates Synthesized by Microwave-Assisted Hydrothermal Method

To cite this article: A E Souza et al 2011 IOP Conf. Ser.: Mater. Sci. Eng. 18 062019

View the article online for updates and enhancements.

You may also like

- Structural relationships and a phase diagram for (Ca,Sr)TiO, perovskites M A Carpenter, C J Howard, K S Knight et al
- A-site vacancy-induced giant strain and the electrical properties in nonstoichiometric ceramics Bi_{0.5+x}(Na_{1y}K_y)_{0.55x}TiO₉ Feng Ni, Laihui Luo, Weiping Li et al.
- Electrical Properties of Yttrium-Doped Strontium Titanate under Reducing Conditions Shiqiang Hui and Anthony Petric





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.142.98.108 on 06/05/2024 at 07:13

Morphology and Properties of (Ba, Sr, Ca) Titanates Synthesized by Microwave-Assisted Hydrothermal Method

A E Souza^{1,2}, G T A Santos^{1,2}, R A Silva^{1,2}, M L Moreira², D P Volante^{2,3}, <u>S R</u> <u>Teixeira^{1,2}</u>, E Longo^{2,3}

¹Universidade Estadual Paulista – Unesp/FCT – Presidente Prudente, SP, Brazil ²Instituto Nacional de Ciência e Tecnologia dos Materiais em Nanotecnologia – INCTMN, Brazil ³Universidade Estadual Paulista – Unesp/IQ – Araraguara SP, Prazil

³Universidade Estadual Paulista – Unesp/IQ – Araraquara, SP, Brazil

E-mail: rainho@fct.unesp.br

Abstract. $Ba_{1-x}Ca_xTiO_3$, $Ba_{1-x}Sr_xTiO_3$ and $Sr_{1-x}Ca_xTiO_3$ (x = 0, 0.25, 0.50, 0.75 and 1) nanoparticles were synthesized using the microwave-assisted hydrothermal method. Samples were prepared for 40 minutes at 140°C under a pressure of 3 MPa using an adapted domestic microwave oven. The samples were characterized by X-Ray diffraction (XRD), scanning electron microscopy (FE-SEM), and Raman, photoluminescence (PL) and ultraviolet-visible (UV-Vis) spectroscopies. XRD data show that ceramic powders have crystalline phases associated with a short-range structural disorder. This structural disorder is confirmed by Raman spectral bands indicating multi-phonon processes and the presence of defects or impurities. Such defects account for a broad band in the photoluminescence spectrum in the green light (460 nm) region for all samples. Gap energy variation, obtained from UV-Vis spectra, suggest a non-uniform band structure of these titanates in accordance with the PL results. The morphology of each sample is changed with doping and varies from a spherical to cubic appearance for energy minimization.

Introduction

The class of compounds with perovskite structure ABO₃, such as SrTiO₃ (ST), CaTiO₃ (CT) and BaTiO₃ (BT) in their crystalline form, show a semiconductor behavior with very interesting properties. Nanocrystalline particles of dust from these types of titanates exhibit the phenomenon of photoluminescence at room temperature, which is explained as a result of quantum confinement or structural defects [1]. Partial substitution of A atoms in titanium compounds, where the other cation is isovalent, modifies the dielectric properties and ferroelectric transition, and also significantly increases the transition phase [2]. Among the perovskite compounds, Ba_{1-x}Ca_xTiO₃ (BCT), Ba_xSr_{1-x}TiO₃ (BST) and Ca_xSr_{1-x}TiO₃ (CST) often draw attention due to their interesting ferroelectric, pyroelectric, and piezoelectric properties and high dielectric constant, along with good thermal stability [3-5]. Several techniques have been used in the preparation of these types of titanates. In this work, Ba_{1-x}Ca_xTiO₃,

¹Silvio Rainho Teixeira

Rua Roberto Simonsen, 305, Presidente Prudente, SP, Brazil, 19060-080

Phone number: +55 18 3229 5355

 $Ba_xSr_{1-x}TiO_3$ and $Ca_xSr_{1-x}TiO_3$ (x = 0, 0.25, 0.50, 0.75 and 1) nanoparticles were directly obtained using the microwave-assisted hydrothermal method. The ceramic powders were characterized by Xray diffraction (XRD), scanning electron microscopy (FE-SEM) and ultraviolet-visible (UV-Vis), Raman, photoluminescence (PL) spectroscopies.

Materials and Method

The compounds $Ba_{1-x}Ca_xTiO_3$, $Ba_xSr_{1-x}TiO_3$ and $Ca_xSr_{1-x}TiO_3$ (x = 0, 25, 50, 75 and 100%) were prepared at a concentration of 0.01 mol, using $BaCl_2.2H_2O$ (99%), $CaCl_2.2H_2O$ (99%), $SrCl_2.6H_2O$ (99%), $C_{12}H_{28}TiO_4$ (97%) and KOH (85%). The solution was synthesized using a heating rate of 140°C/min, maintained at 140°C for 40 minutes and a pressure of 4 MPa in adapted domestic microwave oven. The samples were characterized by XRD (Rigaku, model D/Max-2500/PC) with copper radiation K- α scanning and 4°/min in 0.02° steps. The Raman spectrum was obtained using a Renishaw micro-Raman spectrograph, model Invia equipped with Leica microscope, spatial resolution of ~ 1 μ m² and CCD detector. We conducted a sweep of 100-1400 cm⁻¹ using a wavelength of 633 nm of a He-Ne laser. The photoluminescence spectra were collected using a Jarrell-Ash monochromator and Monospec 27 with a Hamamatsu R446 photomultiplier. The excitation wavelength was 350.7 nm using a Kr laser with an output of 200 mW. UV-Vis spectroscopy was obtained using a Cary 5G UV-Vis Varian equipment in total reflection mode. Two Labsphere certified reflectance standards (SRD SRS 94-010 and 02-010) were used. The FE-SEM images were taken using Zeiss SupraTM 35 Gemini equipment. All measurements were made at room temperature.

Results and Discussion

Figure 1 shows the results of XRD phase ceramic materials. All samples showed a perovskite structure. The phase $BaTiO_3$ (BT) (Figures 1 A-a,B-e) showed tetragonal structure (PDF 83-1878) which denoted by a peak around $2\theta = 45^{\circ}$. Peaks indicating the formation of barium carbonate (PDF 01-0506) were also observed. The results also showed the presence of a phase-pure CaTiO₃ (CT) with an orthorhombic structure (Figures 1 A-e,C-e), also observed by **Marques et al.** [6], using the polymeric precursor method, and by **Moreira et al.** [7], using the microwave-assisted hydrothermal method. Phase SrTiO₃ (ST) (Figures 1 B-a,C-a) showed a cubic structure (PDF 5-0634), and the formation of strontium carbonate (PDF 01-0556).



Figure 1: XRD data of samples: (A) $Ba_{1-x}Ca_xTiO_3$, (B) $Ba_xSr_{1-x}TiO_3$, (C) $Ca_xSr_{1-x}TiO_3$: (a) x = 0, (b) x = 0.25, (c) x = 0.50 (d) x = 0.75, (e) x = 1.

Figure 2 shows the Raman spectra for different compounds. Note that for samples containing Ba (Figures 2 A-a,B-e), the bands at 305 cm⁻¹ indicate that the tetragonal phase of BT is predominant [7]. The nine Raman modes (from 145 to 815 cm⁻¹) observed for the CT phase (Figures 2 A-e,C-e) are assigned to the orthorhombic structure and are consistent with the literature [8]. All vibrational modes found in Figures 2 B-a,C-a), except the band at 1074 cm⁻¹, are first-order Raman modes for the SrTiO₃. The bands shown in the Raman spectra of all samples are associated to local symmetry disorder common in perovskite structures and pronounced here by the cations substituctions.





Figure 2: Raman spectra of samples: (A) $Ba_{1-x}Ca_xTiO_3$, (B) $Ba_xSr_{1-x}TiO_3$, (C) $Ca_xSr_{1-x}TiO_3$: (a) x = 0, (b) x = 0.25, (c) x = 0.50 (d) x = 0.75, (e) x = 1.

Figure 3 shows PL emission. Broad-band luminescent usually observed at low temperatures in perovskite crystals is associated with the presence of imperfections or defects and is typical of a multiphonon and multilevel process. The literature includes many articles that explain the favorable conditions for the PL emission in material showing a degree of order-disorder. In this paper, the authors attributed the process of radiative decay to the distorted octahedron, self-trapped excitons, oxygen vacancies, surface states and charge transfer via intrinsic defects inside oxygen octahedron [9].



Figure 3: Photoluminescence spectra of samples: (A) $Ba_{1-x}Ca_xTiO_3$, (B) $Ba_xSr_{1-x}TiO_3$, (C) $Ca_xSr_{1-x}TiO_3$; (a) x = 0, (b) x = 0.25, (c) x = 0.50 (d) x = 0.75, (e) x = 1.

Table 1 shows the band gap energy values obtained by the Wood and Tauc method using the absorption spectrum in the UV-Vis spectroscopy of all samples [10]. The results show that, in general, band gap energy values vary for intermediate concentrations, suggesting the formation of additional energy levels within the band gap. This behavior influences the photoluminescence emission of the samples, indicating that the broad band spectrum occurs in a characteristic multilevel and multiphonon process [9].

	x = 0	x = 0.25	x = 0.50	x = 0.75	x = 1.0
Ba _{1-x} Ca _x TiO ₃	3,36	3,24	3,44	3,78	3,51
Ba _x Sr _{1-x} TiO ₃	3.41	3.43	3.39	3.50	3.36
Ca _x Sr _{1-x} TiO ₃	3.41	3.41	3.39	3.36	3.51

Table 1: Band gap energy and the average size of crystallites of the samples $Ba_{1-x}Ca_xTiO_3$, $Ba_xSr_{1-x}TiO_3$ and $Ca_xSr_{1-x}TiO_3$

Figure 4 shows the FE-SEM images of all the samples. In these images, the particles display non-homogeneity in size and morphology in agglomerations. Initially, to reduce the surface energy, the particles tend to form clusters (by Van der Waals forces), which are roughly spherical [7]. In general, different crystallographic faces have different surface energies due to differences in bonding or atom density. The equilibrium shape of a crystal corresponds to a minimization of the total surface energy and consequently to different morphologies.



Figure 4: FE-SEM images of samples (A) $Ba_{1-x}Ca_xTiO_3$; (B) $Ba_xSr_{1-x}TiO_3$; (C) $Ca_xSr_{1-x}TiO_3$: (a) x = 0; (b) x = 0.25; (c) x = 0.50; (d) x = 0.75; (e) x = 1.

Conclusion

The results showed that the microwave-assisted hydrothermal method is efficient in obtaining perovskite nanoparticles of BCT, BST and CST. The action of microwaves, combined with certain conditions of pressure and temperature, facilitates the formation of phases in a relatively short time. The ceramic powders obtained display a degree of structural order-disorder that contributes to a photoluminescent behavior in the region of the visible spectrum at room temperature. The morphology of each sample is changed with doping. The mechanism of crystal growth is apparently common for all compounds. First, there is a nucleation process, and then primary growth and aggregation of particles occur, originating the primary nanocrystals. These primary nanocrystals unite to decrease the surface energy and form larger crystallites, called mesocrystals.

Acknowledgments

We thank CMDMC/LIEC for the material support and guidance in the work, FAPESP for their assistance (INCTMN: 2008/57872-1), and CAPES for the doctoral scholarship. Dr. A. Leyva helped with English editing of the manuscript.

References

- [1] W Zhang, H Wang, J Chen, W Zhang, X Xiong and J Zhang, 2008 J. Lumin. **128** 1359
- [2] N C Pramanik, N Anisha, P A Abraham and N Rani Panicker 2009 J. Alloys Compd. 476 524
- [3] Y C Liou and C T Wu, 2008 Ceram. Inter. 34 517
- [4] Z Wang, S Jiang, G Li, M Xi and T Li 2007 Ceram. Inter. 33 1105
- [5] L Wang, H Kang, D Xue and C Liu 2009 J. Crys. Grow. 311 605
- [6] V S Marques, L S Cavalcante, J C Sczancoski, D P Volanti, J W M Espinosa, M R Joya, M R M C Santos, P S Pizani, J A Varela and E Longo 2008 *Solid State Sci.* **10** 1056
- [7] M L Moreira, G P Mambrini, D P Volanti, E R Leite, M O Orlandi, O S Pizani, V R Mastelaro, C O Paiva-Santos, E Longo and J A Varela 2008 *Chem. Mater.***20** 5381
- [8] L S Cavalcante, V S Marques, J C Sczancoski, M T Escote, M R Joya, J A Varela, M R M C Santos, O S Pizani and E Longo 2008 Chem. Eng. J. 143, 299
- [9] W F Zhang, Z Yin, M S Zhang, Z L Du and W C Chen 1999 J. Phys. Condens. Mater. 11 5655
- [10] D L Wood and J Tauc 1972 Phys. Rev. 5 3144