06-239

Bottom-up and top-down approaches to the synthesis of 2D gadolinium-doped cerium oxide (CGO) at low temperature

Moraes, L.P.R.(1); Marani, D.(2); Machado, M.F.S.(1); Rodrigues, L.N.(1); Fonseca, F.C.(3); Esposito, V.(4); Sun, Z.(5);
(1) IPEN; (2) UFABC; (3) DTU; (4) QUT; (5) IPEN-CNEN/SP;

In the last decades, 2D nanosheets have been studied for their physicochemical properties, which are different from the bulk of the original material or any other nanostructure, therefore a challenging and exciting area of nanomaterial synthesis. Nanosheets can be used in the production of low cost electro-optics, stable high-performance batteries, high performance catalysts, etc. In general, there are two main approaches in the synthesis of nanomaterials: top-down and bottom-up. A top-down approach starts from a macroscopic material, which undergoes exfoliation or grinding to reduce its size to a nanometric scale. However, this type of process induces defects, compromising its properties. In the bottom-up method the nanostructures are built molecule by molecule, resulting in a more homogenous and controlled material.
In this work, 2D nanostructures of gadolinium-doped cerium oxide (CGO) were synthesized by two simple and reproducible routes; both by aqueous precipitation induced by the hydrolysis of hexamethylenetetramine. The CGO materials synthesized were characterized by their composition, morphology and crystallographic characteristics. The combined experimental results indicated that different morphologies of 2D CGO can be obtained by controlling the synthesis parameters. The temperature of the reaction medium was decisive in the formation of a more homogeneous structure, establishing the optimum temperature to 10 ºC for the synthesis of nanosheets. The method of liquid exfoliation, with a solution of ethanol:water in an ultrasonic bath, was also established to obtain a suspension of nanosheets. Comparing the microscopic images of the materials synthesized by the top-down and bottom-up methods, it can be observed that the latter favours the formation of a more homogeneous nanostructure, leading to the obtention of exfoliated nanosheets with a shorter reaction and ultrasonic exfoliation time.
Lead-based ceramics are widely used piezoelectric materials due to their excellent piezoelectric properties, but they are not environmentally friendly due to lead oxide toxicity. [1] Therefore, a number of studies have been carried out to improve electrical properties of different kind of ABO_3 perovskites. [2] In the $(1-x)K_{0.5}Na_{0.5}NbO_3$-$xBaTiO_3$ system the effect of (K,Na) substitution by Ba decreases the temperature of the maximum dielectric permittivity and improves the dielectric properties. Consequently, this kind of materials can be used as an alternative candidate to replace conventional piezoelectric materials [3]. In this work, we present the synthesis and characterization of $(1-x)K_{0.5}Na_{0.5}NbO_3$–$xBaTiO_3$, (x= 0.03, 0.04, 0.05, 0.06, 0.07) based lead-free piezoelectric ceramics through the solid-state reaction route. Powders were mixed in different compositions with the final propose of obtaining extensive applications.
It was observed that Ba^{2+} ions occupy the A sites of the perovskite structure, while Ti^{4+} ions replace Nb^{5+} ions at the B sites, resulting in the distortion of the perovskite structure. Additionally, for the highest $BaTiO_3$ concentration a practically constant dielectric constant curve was registered from 20 to 500°C, whereas the loss tangent values ??were low.

[1] J. Rödel, W. Jo, K. T. P. Seifert, E. M. Anton, T. Granzow, and D. Damjanovic, J. Am. Ceram. Soc. 92, 1153 (2009).
[2] M. Jiang, X. Liu, C. Liu, Mater. Res. Bull. 45, 220 (2010).
[3] R. Wang, R. Xie, T. Sekiya, and Y. Shimojo, Mater. Res. Bull. 39, 1709 (2004).

Lead-based perovskites are widely used for actuators, sensors and transducers due to their excellent piezoelectric properties. However, the toxicity of lead for the environment and human health led to focus research efforts on finding substitutes for these materials. One candidate is the $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ solid solution, due to its interesting properties attributed to the presence of a morphotropic phase boundary in the composition $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$. It is known, that the synthesis methods of nanopowders, such as the sol-gel process, allow the control of grain size better that other methods. Consequently, this work focuses on the study of processing conditions and final properties of $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$-based ceramics obtained by the sol-gel method.

To obtain the desired phase, the reagents used were sodium acetate (CH_3COONa), potassium acetate (CH_3COOK), bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) and titanium isopropoxide ($Ti(O^iPr)_4$). The acetates and nitrate were dissolved, separately, in glacial acetic acid. Titanium isopropoxide was dissolved in a solution of isopropanol and acetic acid. Acetates and nitrates were added dropwise. The mixture was stirred for one hour. Then, it was dried at 150 °C for 2 hours, and heat-treated at different temperatures (550 to 750 °C). The obtained powders were pressed uniaxially and sintered in the temperature range of 1000