Domestic microwave oven adapted for fast heat treatment of Ba$_{0.5}$Sr$_{0.5}$(Ti$_{0.8}$Sn$_{0.2}$)O$_3$ powders

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Received 3 February 2006; received in revised form 30 January 2007; accepted 1 February 2007

Abstract

In this work, BSTSn powders prepared by the polymeric precursor method were heat treated in a domestic microwave oven (MW) using a SiC susceptor to absorb the microwave energy and transfer the heat to the powder. The main advantage of MW is to reduce the thermal treatment time for phase crystallization. The powders were heat treated at 300 °C for 20 h in conventional oven, 300 °C for 10 min, 20 min, and 30 min in MW and at 500 °C for 1 min in MW. After thermal treatment, the photoluminescent properties of powders at room temperature were analyzed.

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Keywords: Microwave processing; Fast heat treatment; BSTSn; Photoluminescence

1. Introduction

Microwaves (MW) are electromagnetic waves, whose spectral frequency ranges from 300 to 300,000 MHz. Such a wide range confers to those oscillators great application versatility, as a function of the selected frequency. Civil aircraft radars, cellular telephones and domestic microwave ovens are examples of devices widely used by more than one billion people, operating at different frequencies using MW region. In several field of chemistry and materials science, the application of microwave technology have been arisen special interest for the synthesis of organic and inorganic compounds, as well for thermal treatment of many materials at laboratorial and industrial scales [1–5]. Thus, the microwave oven (MW) is becoming a powerful tool in the laboratory level being much used in scientific research [6].

Several experiments involving the preparation and treatment of compounds by MW annealing have been growing. Recently, all materials obtained by this technique were reported in the literature as non-transparent materials. In other words, it was required that at least one of the components directly involved in the process was susceptible to the MW.

Barium strontium titanate (Ba,Sr)TiO$_3$ is of great interest for the most promising capacitor material in DRAM applications because of its low leakage current at operating voltage as well as high dielectric constant [11,12] and photoluminescence at room temperature in Ba$_{0.45}$Sr$_{0.55}$TiO$_3$ powders [13]. Thus, Ba(Sn$_x$Ti$_{1-x}$)O$_3$ solid solutions show an influence of Sn concentration on the character of dielectric phase transformation. With increase of Sn concentration, the temperature of ferroelectric-paraelectric phase transformation decreases and becomes more diffused [14]. Recently, ferroelectric, dielectric and photoluminescent properties of Ba$_{0.5}$Sr$_{0.5}$(Ti$_{0.8}$Sn$_{0.2}$)O$_3$(BSTSn) thin films have been investigated on platinum-coated silicon substrates and prepared by the polymeric precursor method (PPM).
with excellent structural, microstructural, electrical properties and photoluminescents [15,16].

In this work, BSTSn powders were prepared by the polymeric precursor method, heat treated in a domestic microwave oven adapted, using a SiC susceptor to absorb the microwave energy and transfer the heat to the powder. The crystallization temperature is reached with the main advantage of reducing the time of the thermal treatment. The susceptor was placed below of the powders. The powders were heat treated at 300 °C for 20 h in conventional oven, 300 °C for 10 min, 20 min, and 30 min in MW and at 500 °C for 1 min in MW for crystallization. After the thermal treatment, the photoluminescent properties at room temperature of powders were analyzed.

2. Experimental

2.1. Domestic Microwave adaptation

The device consists in a series of adaptations performed in a domestic microwave oven, coupled to a simple apparatus called susceptor cell, according to schematic representation in Fig. 1. The microwave oven employed was a simple domestic model (M-301, LG®, 2.45 GHz frequency and 900 W).

The system consists of: (a) drilling of a 3 mm diameter opening in the upper part of the oven cavity for the passage of a thermocouple, (b) magnetron control by an external temperature controller, and, (c) addition of the microwave cell (apparatus developed for this purpose) within the cavity of the oven. The thermocouple is connected to an external controller, which receives the information of oven temperature from the thermocouple and controls the activity of the oven magnetron.

The microwave-sensitive cell is constituted of two main pieces: the refractory body and the microwave susceptor. The material used for the manufacture of the cell refractory body was a mixture of aluminum oxide and silica at the approximate proportion of 7:3, commercially known as KAOWOOL® 1600 [17]. This material presents refractory properties and it transparent to the MW applied, and it is adequate to the high temperatures (up to 1600 °C) and high MW irradiation to which the apparatus will be submitted.

The MW susceptor is a dense SiC pellet working as converter MW energy into heat. Due to the high dielectric loss and an excitation/relaxation time according to the changes of MW dipole directions (2.450.000 times a second), it works efficiently as a converter of microwaves into heat.

The SiC pellet, placed in the lower internal part of the cavity of the microwave cell, is the point from which the thermal energy is irradiated on crucible for the powders that will be thermally treated.

When the cell which is susceptible to MW is introduced within the cavity of a MW (Fig. 1), the apparatus works as small programmable oven for heating at a programmed temperature profile, like a conventional electric oven. The SiC susceptor acts similarly to an electric resistance, from which heat is irradiated and the inner part of the refractory body of the cell is similar to the cavity of the small oven.

Once inserted within the cavity of the susceptor cell, the BSTSn powders inside of crucible can be processed with a good thermal stability owed to the good refractoriness of cell body material. Usually, powders prepared by the polymeric precursor method and heat treated in conventional oven are obtained in crystalline form at temperatures superior 600 °C.

2.2. Synthesis of Ba0.5Sr0.5(Ti0.80Sn0.20)O3 powders

BSTSn powders were prepared by the PPM, which is based on the chelation of the metallic cations by citric acid in a water solution and ethylene glycol. BSTSn precursor solution was prepared from a titanium and tin citrates formed by dissolving titanium isopropoxide (99.9% purity-Aldrich) and tin cloret (99.9% purity- Merck) in aqueous solution of citric acid heated to about 70 °C. A stoichiometric amount of BaCO3 (99.9% purity-Aldrich) was added to the titanium citrate solution, which was slowly stirred until the reactional mixture became clear. SrCO3 (99.9% purity-Aldrich) was then added slowly. Tin citrate was posterior added to the final solution. To completely dissolve the BaCO3 and SrCO3, ammonium hydroxide was added until pH reached 7. The complete dissolution of the salts resulted in a transparent solution. After the solution containing Ba and Sr cations was homogenized, ethylene glycol was added to promote the polyesterication reaction. The solution became viscous as the heat reach 90 °C, without any visible precipitation. The molar ratio of strontium-barium and titanium cations was 1:1. The citric acid/metal molar ratio was mixed at 3:1, and the mass ratio of the citric acid/ethylene glycol was set at 60:40. This resin was then placed in a furnace and heated to 350 °C for 4 h, causing it to pulverize into powder. The crystalline phase was obtained by heating the powder at 500 °C for 1 min. X-ray diffraction data for milled powders were collected using a Rigaku RINT2000 diffractometer (42 kV × 120 mA) with Cu-Kα (λ=1.5405 Å, I=1.5443 Å, 2θ range between 20° and 60°, step size of 0.02°(2θ), divergence slit = 0.5 mm, receiving slit. The PL spectra of the BSTSn powders were taken with a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelength of an argon ion laser was used, with the laser’s maximum output power kept at 20 mW. A cylindrical lens was used to prevent the sample from overheating. The slit width used...
was 100 μm. All measurements were taken at room temperature.

3. Results and discussion

Microwave energy is being developed as a new tool for high-temperature processing of materials. This technology has received great attention due to the advantages observed with microwave processing, which include: reduced processing costs, better production quality, new materials and product, among others. With proper understanding and control, many technically important materials can be heated rapidly, uniformly, selectively, less expansively and with greater control than is possible with conventional methods [18]. With the microwave energy is possible the fast attainment of niobates, tantalates and titanates thin films such as LiNbO₃ [19], SrBi₂Ta₂O₉ [20], Bi₃.25La₀.75Ti₃O₁₂ [21], and BSTSn powders, studied in this article.

Among the results obtained in the synthesis of powders, it should be emphasized a new type of doped aluminum oxide, which was called black alumina due to the presence of carbon, as a dopant, inserted within the crystalline network [22]. In the case of the films, the most expressive results were the epitaxial growth of LiNbO₃ thin films [7], and effect of the heat flow direction on the electrical properties of SrBi₂Nb₂O₉ thin films crystallized using a microwave oven, showed in Fig. 1 of following paper [8]. It was observed a better lattice orientation of the substrate/film when it is placed over the SiC susceptor and the very large dielectric constant of highly oriented (Pb₁₋ₓBaₓ)TiO₃ thin films prepared by chemical deposition [23].

Fig. 2 illustrates the X-ray patterns of BSTSn powders heat treated in a conventional furnace and in a domestic microwave oven. As can be seen, BSTSn powders heat treated in a conventional furnace and microwave oven at temperatures as low as 500 °C are not crystalline. Meanwhile, BSTSn powders heat treated at 500 °C for 1 min showed diffraction peaks, indicating periodicity at long-range order.

In general powders prepared by the polymeric precursor method and heat treated in conventional oven are obtained in crystalline form, in temperatures higher (above 600 °C). According to this hypothesis, although the starting material is not susceptible and the effect of the heat flow is disregarded, can occur a higher mobility within the material under processing, due to the more and more pronounced interaction between the electric dipoles of the material and the MW.

Fig. 3 shows photoluminescence (PL) spectra of BSTSn powders processed in the microwaves and conventional treatment and the necessary order-disordered behaviour to explain the photoluminescent properties. The broad PL peak of the BSTSn in its disordered state is shown in the visible range with a maximum at around 562 nm. The PL is strongly dependent on the heat treatment conditions, revealing the influence of temperature or thermal exposure time on the organization of the disordered material. This disordered material is initially composed of the polymeric precursor, which already presents a slight photoluminescence. The PL intensity decreases with the increase of structural order, as indicated in Fig. 3(b)–(e). Fig. 3(a) depicts the maximum PL intensity observed in this experiment. This intensity is likely associated with the structural order-disorder. Fig. 3(c) and (d) shows the PL spectra of the disordered material in an organized phase, being its intensity decreases progressively to zero, characterizing the crystalline phase, as shown in Fig. 3(e).

When the temperature of many materials surpasses the ordinary levels, there is an increase in the susceptibility of those materials to MW. In this way, the heated material itself, now behave as a susceptor, contributing to an additional heat fraction to be used during the synthesis process.

Regarding the building aspect of the apparatus, the choice of the KAOWOOL® refractory blanket was due its joint properties of transparency to the microwaves, thermal isolation and high melting point. Obviously, any other material that displays those characteristics could be conveniently used for the construction of similar cells. However, it is possible to foresee susceptor cells
that are neither necessarily refractory nor transparent, bearing in mind the convenience of their application.

4. Conclusions

An adapted domestic microwave oven was used for crystallization of BSTSn powders prepared by the polymeric precursor method. A crystalline structure was obtained when the powders were heat treated at 500 °C for 1 min. This method allows to obtain BSTSn powders with photoluminescent properties in a reduced time when compared with the powders heat treated at 300 °C for 20 h in conventional furnace. The time required to crystallize BSTSn powders is drastically reduced (heat treated at 500 °C for 1 min) compared with the conventional way (normally heat treated at 700 °C for 4 h [18]). This is of great advantage to obtain BSTSn powders crystallized faster, photoluminescence at room temperature and minimize the electric energy costs.

Acknowledgements

The authors thank the financial support of the Brazilian funding agencies: CAPES, FAPESP and CNPq. The authors gratefully acknowledge the Dra. Miryam R. Joya and Paulo S. Pizani, of Universidade Federal de São Carlos Physics Department for collaboration in the PL measurements.

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