ELSEVIER

Materials Science and Engineering B 136 (2007) 50–56

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Microwave dielectric properties of $Sr_2Ce_2Ti_5O_{16}$ ceramics

G. Subodh, M.T. Sebastian*

Materials and Minerals Division, Regional Research Laboratory, Thiruvananthapuram 695 019, India

Received 16 May 2006; received in revised form 28 August 2006; accepted 2 September 2006

Abstract

$Sr_2Ce_2Ti_5O_{16}$ dielectric ceramics were prepared by conventional solid-state ceramic route. The structure and microstructure of the ceramics were investigated by X-ray diffraction and scanning electron microscopic methods. The $Sr_2Ce_2Ti_5O_{16}$ has a psuedocubic structure. It has ε_r of 113, unloaded quality factor ($Q_u \times f$) of 8000 GHz and temperature coefficient of resonant frequency of 306 ppm/°C. The effects of various dopants on the structure, microstructure and microwave dielectric properties of the material have been investigated. It is found that addition of small amount of dopants such as PbO, Al_2O_3, Nd_2O_3, MoO_3, CeO_2, La_2O_3, Fe_2O_3 and NiO improve the microwave dielectric properties of $Sr_2Ce_2Ti_5O_{16}$.

Keywords: $Sr_2Ce_2Ti_5O_{16}$; Dielectrics; Microwave properties; Doping effects

1. Introduction

The recent progress in wireless communication has increased the demand for new microwave dielectric resonator materials with high dielectric constant (ε_r), high-unloaded quality factor (Q_u) and low temperature coefficient of resonant frequency (τ_f) [1–6]. Communication systems operating in the microwave frequency range especially mobile phone systems require low loss and high dielectric constant ($\varepsilon_r > 100$) materials as basic components in oscillators, filters and antennas [4,7]. The applications of such dielectric resonator (DR) materials ensure better performance along with reduction of weight and over all dimensions of the microwave devices [5,6]. In general as the dielectric constant increases, Q_u decreases and τ_f increases [5,6]. The development of microwave ceramics with high dielectric constant and good thermal stability together with small dielectric loss is a challenging problem in the area of dielectric resonator materials research.

Microwave dielectric properties of $SrTiO_3$ and $CaTiO_3$ have been extensively studied [8–11] because of their high ε_r and low loss with the potential to miniaturize the devices. However these materials have relatively high positive τ_f. Recently Santha et al. [12] reported CeO_2 as dielectric resonator material with high $Q_u \times f$ (60,000 GHz), ε_r of 23 and τ_f of −53 ppm/°C. More recently Sremoolanathan et al. [13] reported the microwave dielectric properties of the ceramics in BaO–$2CeO_2$–$n$$TiO_2$ system with reasonably good microwave dielectric properties. However Guha and Kolar [14] reported that ternary compounds did not exist in the BaO–$2CeO_2$–$n$$TiO_2$ system. In 1994 Bamberger et al. [15] reported the existence of a new compound $Sr_2Ce_2Ti_5O_{16}$ with pseudo cubic structure in the SrO–CeO_2–TiO_2 system. They added SrO, $SrCeO_3$, and $SrTiO_3$ to the $Sr_2Ce_2Ti_5O_{16}$ material in different mole percentages and studied its compatibility. The results revealed the existence of a series of compounds $Sr_{6-12x}Ce_{6x}Ti_5O_{16}$ and solid solution $Sr_{2+n}Ce_2Ti_5O_{16+3n}$ ($n \le 6$). $Sr_2Ce_2Ti_5O_{16}$ can be used for the disposal of radioactive elements [16]. $Sr_2Ce_2Ti_5O_{16}$ may be represented as $Sr_{0.4}Ce_{0.4}TiO_{3.2}$ [$(AA')_{1-\delta}BO_{3+\delta}$ A = Sr, A = Ce, B = Ti and $\delta = 0.2$] in the complex perovskite form [17–19]. In the present paper we report the microwave dielectric properties of $Sr_2Ce_2Ti_5O_{16}$ for the first time. Efforts were also made to tailor the microwave dielectric properties of $Sr_2Ce_2Ti_5O_{16}$ by adding dopants of different valence state.

2. Experimental

$Sr_2Ce_2Ti_5O_{16}$ ceramics were prepared by solid-state ceramic route. High purity $SrCO_3$ and TiO_2 (99.9+%, Aldrich Chemical Company, Inc., Milwaukee, WI, USA) and CeO_2 (99.99%, Indian Rare Earth Ltd., Udyogamandal, India) were used as the starting materials. Stoichiometric amount of powder mixtures were ball milled in distilled water medium using yttria

---

* Corresponding author. Fax: +91 471 2491712.
E-mail address: mailadils@yahoo.com (M.T. Sebastian).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.09.015

stabilized zirconia balls in a plastic container for 24 h. The slurry was dried, then ground well, and calcined at 1100 °C/5 h. The calcined material was ground in to fine powder and divided into different batches for optimizing sintering temperature and dopant addition. In order to dope $Sr_2Ce_2Ti_5O_{16}$, different weight percentages (0–0.6) of various dopants like divalent (ZnO, MgO, MnO, BaO, CaO, Co_3O_4, NiO and PbO), trivalent (Bi_2O_3, In_2O_3, Sm_2O_3, Al_2O_3, Nd_2O_3, Cr_2O_3, Fe_2O_3, Gd_2O_3, La_2O_3, Er_2O_3, Eu_2O_3 and Pr_6O_{11}), tetravalent (ZrO_2, CeO_2 and SnO_2), pentavalent (Sb_2O_5, Nb_2O_5 and Ta_2O_5) and hexavalent (WO_3 and MoO_3) were added to the selected weight of the calcined parent material. The $Sr_2Ce_2Ti_5O_{16}$ containing dopants were mixed thoroughly in distilled water medium. It was then dried and mixed with 4 wt% PVA (MW 22,000, BDH Lab Suppliers, England) and again dried and ground well. Cylindrical pucks of about 6–7 mm height and about 14 mm diameter were made by applying a pressure of 100 MPa. These compacts were then fired at 600 °C for 30 min to expel the binder before sintering at temperatures ranging from 1280 to 1400 °C for the $Sr_2Ce_2Ti_5O_{16}$. All the doped material except Bi_2O_3 was sintered at 1300 °C/2 h. The sintering temperature was 1260 °C/2 h for 0.2 wt% Bi_2O_3 doped $Sr_2Ce_2Ti_5O_{16}$ ceramics. The bulk densities of the sintered samples were measured by dimensional method.

$Sr_2Ce_2Ti_5O_{16}$ has a high positive τ_f and hence negative τ_f material were prepared and added to it. High negative τ_f materials like $BaNb_2O_6$, $Bi_2Ti_4O_{11}$, $Li_{1/2}Nd_{1/2}TiO_3$, $Mg_2P_2O_7$ and $PbZrO_3$–CeO_2 were prepared through solid-state ceramic route. High purity $BaCO_3$, Bi_2O_3, TiO_2, $(MgCO_3)_4Mg(OH)_2{\cdot}5H_2O$, Li_2CO_3 and ZrO_2 (99.9+% Aldrich Chemicals), CeO_2 and Nd_2O_3 (99.99% Indian Rare Earth Ltd.) and PbO (CDH, India) were used as the raw materials. As the τ_f of $Sr_2Ce_2Ti_5O_{16}$ is high in the positive side, only higher weight percentage (>1 wt%) of the above negative τ_f materials were added.

The crystal structure and phase purity of the powdered samples were studied by X-ray diffraction technique using Cu Kα radiation (Philips X-ray diffractometer). The sintered samples were thermally etched for 20 min at a temperature of about 25 °C below the sintering temperature and the surface morphology was studied by using a scanning electron microscope (JEOL-JSM 5600 LV, Tokyo, Japan).

The microwave dielectric properties were measured by a Vector Network Analyzer (8753 ET, Agilent Technologies). The unloaded quality factor and dielectric constant of the samples were measured by the resonance method using the $TE_{01\delta}$ mode [20]. The specimen was placed on a low loss quartz spacer inside a copper cavity whose inner side was silver plated. The use of low loss single crystal quartz spacer reduces the effect of losses due to the surface resistivity of the cavity. The diameter of the cavity was about four times larger than that of the sample for better isolation of the excited $TE_{01\delta}$ mode [21]. The τ_f was measured by noting the variations of $TE_{01\delta}$ mode frequency with temperature in the range 25–75 °C. Then τ_f is given by

$$\tau_f = \frac{1}{f}\left(\frac{\Delta f}{\Delta T}\right) \tag{1}$$

where f is the resonant frequency, Δf the variation in resonant frequency from room temperature and ΔT is the difference in temperature.

3. Results and discussion

Fig. 1(a) shows the powder XRD pattern recorded from the pure sample sintered at 1300 °C for 2 h. The diffraction peaks were indexed based on $Sr_2Ce_2Ti_5O_{16}$ [JCPDS File No. 49-1554]. The $Sr_2Ce_2Ti_5O_{16}$ has a cubic structure similar to $SrTiO_3$ [9,10] with lattice parameter 3.8789(9) Å and theoretical density 5.41 g/cm^3. XRD patterns recorded from the most of the doped samples did not show any additional peaks. It may be noted that addition of very small amount of dopants (<0.6 wt%) usually do not give any detectable changes in the XRD pattern. However addition of 0.6 wt% of ZnO (Fig. 1(d)) and 1 wt% of $PbZrO_3$–CeO_2 (Fig. 1(c)) show presence of CeO_2. Hence XRD

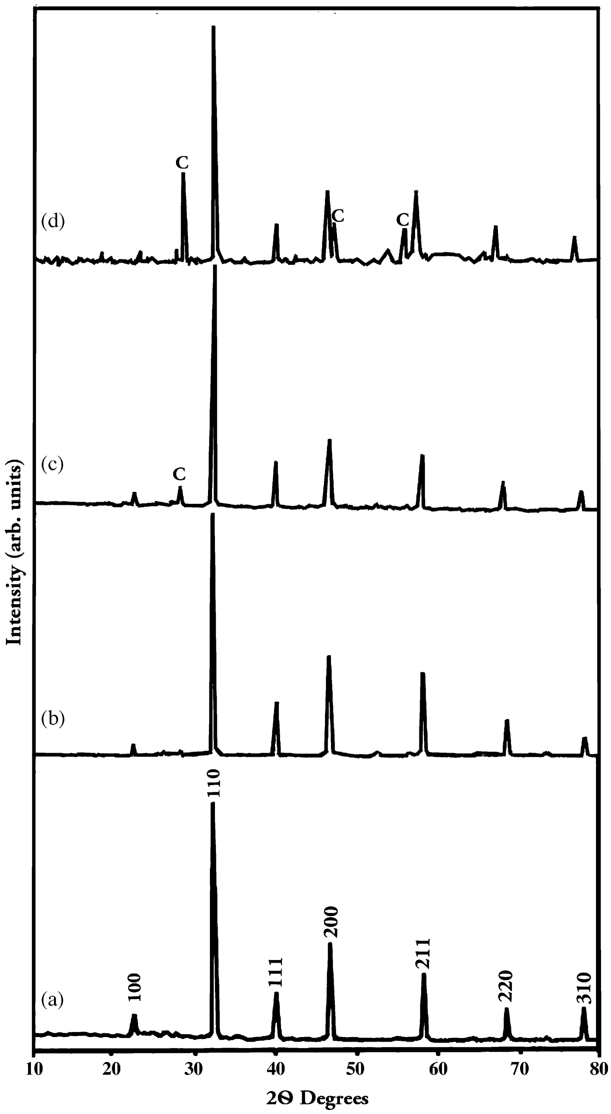

Fig. 1. (a) The XRD pattern of the material $Sr_2Ce_2Ti_5O_{16}$, (b) doped with 0.4 wt% of NiO, (c) doped with 1 wt% of $PbZrO_3 + CeO_2$ and (d) doped with 0.6 wt% of ZnO (the peaks marked C are that of CeO_2).