Journal of the European Ceramic Society 36 (2016) 1939–1944

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Structural, thermal and dielectric properties of rare earth substituted eulytite for LTCC applications

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ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 26 January 2016
Accepted 7 February 2016
Available online 18 February 2016

Keywords:
Crystal structure
LTCC
Microwave ceramics
Sintering
Rare earth

ABSTRACT

A new series of LTCC compositions having the general formula $Bi_{3.9}RE_{0.1}(SiO_4)_3$ where, (RE = Yb, Tm, Er, Gd, Sm, Nd, Pr) were developed. The crystal structure analysis using Rietveld refinement of the powder diffraction data of all compositions confirmed partial substitution of rare earth at bismuth site. The microwave dielectric and thermal properties of these new LTCC compositions were studied. Some of the rare earth substituted compound namely, $Bi_{3.9}Tm_{0.1}(SiO_4)_3$, $Bi_{3.9}Sm_{0.1}(SiO_4)_3$, show improvement in $Q_u \times f$ value (22,600 GHz and 24,100 GHz respectively at 8.2 GHz) as compared to the parent $Bi_4(SiO_4)_3$ (20,500 GHz, at 8.2 GHz).

1. Introduction

With the advent of 'mobile phone revolution', the miniaturization of the microwave devices is one of the major challenges in electronic industry. Due to their low-manufacturing cost, excellent performance, and high level of integration the low temperature co-fired ceramic (LTCC) technology has emerged as a crucial step towards the fabrication of 3D integrated circuits [1–7]. In typical LTCC techniques, highly conducting silver (Ag) metal is commonly used as the electrode material, despite its high cost constraints [8]. The approach of multilayer fabrication helps to integrate the passive components like resistors, capacitors and insulators within individual layers, that helps to reduce the size and cost of the multi-chip module [9,10]. The LTCC technology get a wide variety of application including microsystem, multilayer capacitors, sensors and actuators, chip antennas, Filters, automobiles, RF applications, aerospace, SOFC components etc. [11–15]. The primary requirements of an LTCC material are low dielectric constant, low dielectric loss or high quality factor, high thermal conductivity, low coefficient of thermal expansion, temperature stability of dielectric properties and most importantly the sintering temperature should be less than the melting point of silver (961 °C) [16–20]. Apart from developing novel materials and methods, considerable efforts have been made, in establishing structure-property correlation of the reported dielectric materials [1]. Furthermore, several reports were recently published describing the effect of various dopants including rare earth ions on the physical properties of the ceramic solid solutions [21–25].

Among several of dielectric materials developed, bismuth silicate, [$Bi_4(SiO_4)_3$, BSO] has received a resurged interest by the ceramic industries due to its multifunctionality possessing interesting dielectric, thermoluminescent and photocatalytic characteristics. The crystal structure features of $Bi_4(SiO_4)_3$ were elucidated by Liu and Kuo in 1997 [26]. Of late in 2014, Xiong et al. reported the UV excited fluorescence and thermoluminescence spectra of pure and rare-earth-doped bismuth silicate crystals grown by the modified Bridgman method [27]. Batool et al. recently investigated the photocatalytic activity of bismuth modified silica nano fibres (based on $Bi_4(SiO_4)_3$) and reported enhancement in photocatalytic activity as compared with pure silica [28]. As hinted before, the bismuth silicate is also an interesting dielectric material as well. Though Sirdeshmukh and Reddy in 1980 reported

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.02.019
0955-2219/

the dielectric properties of $Bi_4(SiO_4)_3$ single crystal [29], their microwave dielectric properties were largely unknown until 2008 when Kim et al. [30,31] suggested it as a suitable material for LTCC substrate for microelectronic applications. More recently, Abhilash et al. developed glass-free $Bi_4(SiO_4)_3$ LTCC tapes [2] with excellent microwave dielectric properties. With an objective of improving the dielectric properties, in the present paper, we explore the effect of rare earth substitution on the structural and dielectric properties of $Bi_{3.9}RE_{0.1}(SiO_4)_3$, (RE = Yb, Tm, Er, Gd, Sm, Nd, Pr) ceramics.

2. Experimental

2.1. Methodology

The $Bi_{3.9}RE_{0.1}(SiO_4)_3$ (BRESO) ceramic were prepared through conventional solid state ceramic route. The required amount of the precursors, Bi_2O_3 (<10 μm, 99.9%, Sigma–Aldrich, St. Louis, MO, USA) and SiO_2 (325 mesh, 99.6% metal basis, Sigma–Aldrich) and rare earth oxides: Yb_2O_3, Tm_2O_3, Er_2O_3, Gd_2O_3, Sm_2O_3, Nd_2O_3 and Pr_6O_{11} (IRE, Kerala, India) were weighed accurately and mixed in an agate mortar. The resultant mixture was dried overnight at 70 °C in a hot air oven. The dried powder was calcined at 850 °C for 4 h and was subsequently ground into fine powder by ball milling for 48 h using yttria stabilized zirconia balls and ethanol as the grinding media. The ground powder was mixed with 5 wt.% polyvinyl alcohol solution (PVA, molecular weight 22,000, BDH Poole, U.K.), dried and pressed into cylindrical pellets of different dimensions for different property measurements such as microwave dielectric, coefficient of linear thermal expansion and thermal conductivity using uniaxial hydraulic press by applying a pressure of 100 MPa. The pellets were then sintered at 900 °C for 8–12 h in air.

2.2. Characterizations

The phase formation of the calcined powder was identified by X-ray diffraction analysis (PANalytical X'Pert PRO diffractometer having Nickel filtered Cu Kα, Netherlands). Detailed structural investigation of the samples was carried out by Rietveld refinement using commercial X'Pert High Score Plus software. The crystal structure of the BRESO was interpreted using Crystal Maker software. The thermal conductivity (TC) of the sintered ceramic pellets was measured using laser flash thermal property analyzer (Flash Line 2000, Anter Corporation, Pittsburgh, USA). The coefficient of thermal expansion (CTE) was measured using thermomechanical analyzer (TMA/SS7300, SII Nano Technology Inc.). The bulk density of sintered samples was estimated using Archimedes method. The SEM analysis of samples was done using a scanning electron microscope (JEOL JSM 5600LV, Tokyo, Japan). For SEM analysis, the surface of sintered samples was mirror polished and then thermally etched below 20 °C of the sintering temperature at very fast heating and cooling rates. The microwave dielectric properties were measured using a vector network analyzer (Model No. E5071C ENA series; Agilent Technologies, Santa Clara, CA). The relative permittivity (ε_r) of the samples was measured by the Hakki–Coleman method modified by Courtney [32] in the frequency range of 8–12 GHz. The unloaded quality factor was measured by the resonant cavity method [32].The temperature variation of resonant frequency (τ_f) and temperature variation of dielectric constant (τ_ε) of the samples were measured in the temperature range of 25 °C–70 °C in Hakki–Coleman method [32].

3. Results and discussions

In order to examine the solid solubility of rare earth at the bismuth site, we have chosen Sm^{3+} as the typical rare earth cation

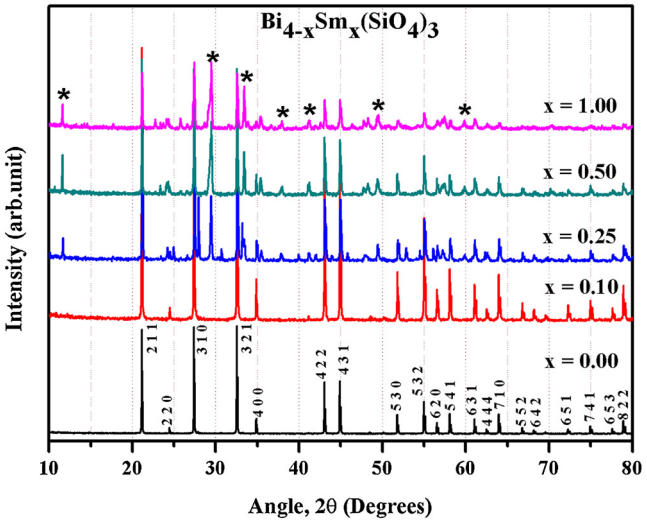

Fig. 1. XRD patterns of $Bi_{4-x}Sm_x(SiO_4)_3$ calcined at 850 °C for 4 h (the secondary phase of Sm_2O_3 is represented by asterisk).

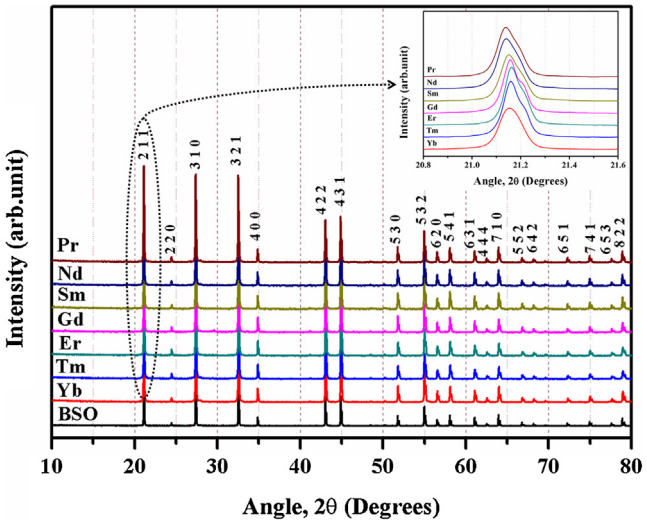

Fig. 2. XRD patterns of BSO and BRESO (RE = Yb, Tm, Er, Gd, Sm, Nd, and Pr) calcined at 850 °C for 4 h. The inset shows the magnified image of [2 1 1] peak.

to be substituted for Bi^{3+} due to their similarity in ionic radius. A series of samarium substituted samples having a general formula $Bi_{4-x}Sm_x(SiO_4)_3$ were prepared, [x = 0.00, 0.10, 0.25, 0.50 and 1.00 respectively]. The XRD patterns of the $Bi_{4-x}Sm_x(SiO_4)_3$ powders calcined at 850 °C for 4 h are shown in Fig. 1.

From the Figure, one could clearly observe that for compositions up to x = 0.10 only form a solid solution, where all the relevant peaks in this XRD pattern can be well indexed using standard JCPDS file of parent bismuth silicate (JCPDS file 35–1007) having cubic structure with $I\bar{4}3d$ space group. As the substitution concentration increases from 0.10, additional peaks could be observed in the XRD patterns (represented by asterisk) which correspond to Sm_2O_3. Hence, the optimum rare earth ion concentration to form complete solid solution was restricted up to x = 0.10, and all other rare earth substitution in bismuth silicate used in this study was carried out with x = 0.10 only.

Fig. 2 represents the XRD patterns of pure BSO and BRESO powder calcined at 850 °C for 4 h. It is evident from the Figure that all the rare earth substituted compound form complete solid solution, and all peaks in the XRD pattern could be indexed using standard JCPDS file (JCPDS file 35–1007). The inset of the Figure shows the