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Swift heavy ion induced modifications in nano-crystalline microwave dielectric $BaTi_4O_9$ ceramics

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ABSTRACT

The pellets of $BaTi_4O_9$ were synthesized via a polymerized complex method and irradiated with 50 MeV Li^{3+} ions for two different fluences. The dielectric constant (ε_r), and dielectric loss ($\tan\delta$) as a function of frequency (1 kHz–2 MHz) and temperature (40–200 °C) were measured for unirradiated and irradiated samples. The values of ε_r for unirradiated and irradiated samples decreased with frequency at room temperature which is explained by Koops′ model. The increase in dielectric constant after the irradiation shows that the damage occurs during irradiation and produces defects due to electronic processes and/or inelastic collisions. Micro-structural properties revealed that the size of pores/holes and their number increased with irradiation fluence giving rise to volume expansion porous defects.

1. Introduction

The development of the telecommunications industry, especially in the satellite and active antennas sector requires the use of radio and microwave frequency substrates. These substrates should essentially exhibit high dielectric constant (ε_r), low dielectric loss ($\tan\delta$) and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stable circuits in the electrical devices [1]. A number of researchers have reported that TiO_2-rich compounds, such as $BaTiO_3$, $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ exhibit suitable radio and microwave dielectric properties for electrical applications [2,3].

Swift heavy ion (SHI) irradiation provides understanding of material structure damage and their modifications. The effect of energetic ion beam on the materials depends on the ion energy, fluence and ion species. The energetic heavy ions loose their energy as they pass through the material. The ions either excite or ionize the atoms by inelastic collisions or displace atoms of the target by elastic collisions. Elastic collisions are dominant in low energy regime, whereas inelastic collisions process dominates at high-energy regime where elastic collisions are insignificant. It is evident from the previous reports that electronic energy loss (S_e) due to inelastic collision can generate point/cluster of defects, if S_e is less than the threshold value of electronic energy loss (S_{eth}) [4,5]. The energetic ions can create columnar amorphization with greater value of S_e than the S_{eth}. The strain/stress developed due to the defects created by the energetic ions and amorphization enables modification in different properties of the materials [6–8]. There have been few attempts to investigate effect of irradiation on ceramic materials particularly derived of BaO–TiO_2 system [6,9,10]. Jiang et al. [6] reported irradiation-induced disorder and amorphization in $BaTiO_3$ wafers using 1 MeV Au^{2+} ions at different fluences and temperature of irradiation. It has been reported that at 170 and 300 K irradiation temperatures, the dependence of disordering was observed to be small. Recovery of disorder was also observed at low damage levels and at room temperature. The experimental investigations to the energy loss of high-energy protons (25 MeV) in $BaTiO_3$ have been reported by Kumar et al. [9]. The observed results in this study were indicative of a new mode of energy loss and can be related to the fluctuations in polarization of cluster of unit cells and the dynamics of their short-range order. The thermal phase transitions and the temperature dependence of the dose for amorphizations in $BaTiO_3$ have been investigated [10].

The dielectric properties of Ba–TiO_2 system depend upon several factors, such as chemical composition, method of preparation and grain size. Study of dielectric characteristics indicates the response of the material to an electric field. Different polarization may result into variations in the dielectric constant and dielectric loss. The purpose of this study is to understand the irradiation-induced changes

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in dielectric properties and damage in micro-structures of $BaTi_4O_9$, as this material exhibit suitable dielectric properties for electrical applications. Ion beam with 50 MeV Li^{3+} was chosen because it enables higher electronic energy loss with low projected ion implantation range in the material. This eventually resulted in the modification of this material, which was investigated by dielectric and micro-structural studies. It is very useful in the study of phase transition taking place in the material before and after irradiation. The dielectric measurements as a function of frequency and temperature can provide understanding of the material modification due to the created defects by the irradiation. Therefore, the present investigation is emphasized on variations in dielectric and micro-structural properties of $BaTi_4O_9$ after irradiation. The dielectric properties were studied as a function of temperature using 50 MeV Li^{3+} ion at different fluences.

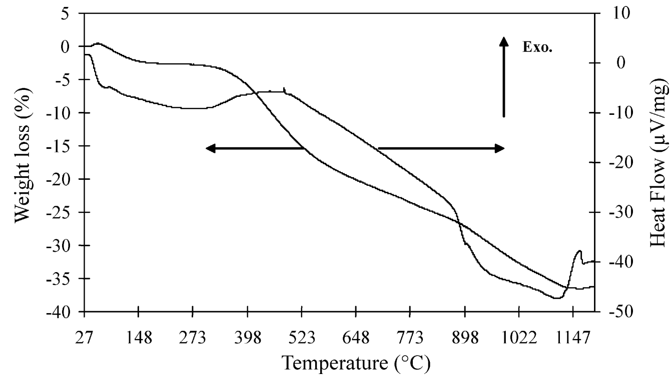

Fig. 1. TG–DTA curve of $BaTi_4O_9$ powder precursor.

2. Experimental details

$BaTi_4O_9$ powders were produced by Pechini method [11]. The starting reagents used were of high-purity and these are: barium carbonate ($BaCO_3$, 99%) and titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$, 98%) supplied from Merck. Ethylene glycol ($C_2H_6O_2$) was heated to 50 °C and then added slowly with $Ti(OCH(CH_3)_2)_4$. After the milk-like solution stirred to become colorless, citric acid ($C_6H_8O_7$) was added to ethylene glycol mixture in the molar ratio of 1:10 and stirred to promote dispersion of the gel. Desired stoichiometry of $BaCO_3$ powder was then added slowly and highly dispersed by mechanical stirring. About 3–4 drops of nitric acid (HNO_3, 65%) was added to the mixture to catalyze the esterification between citric acid and ethylene glycol. The temperature was increased from 50 to 140 °C for 10 h to evaporate the solvent and promote polymerization. The pH value was 3.7 as mixtures became clear and light yellow solution. To prepare $BaTi_4O_9$ powders, the polymeric precursors were further heated at 300 °C for 1–2 h and resulted in the dark colored

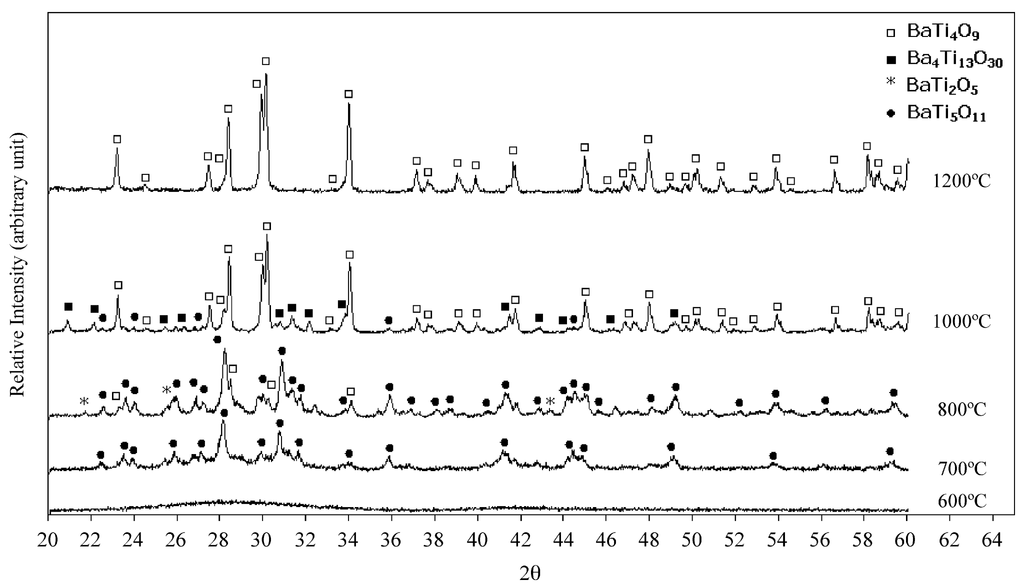

Fig. 2. XRD patterns of $BaTi_4O_9$-precursor calcined at different temperatures.

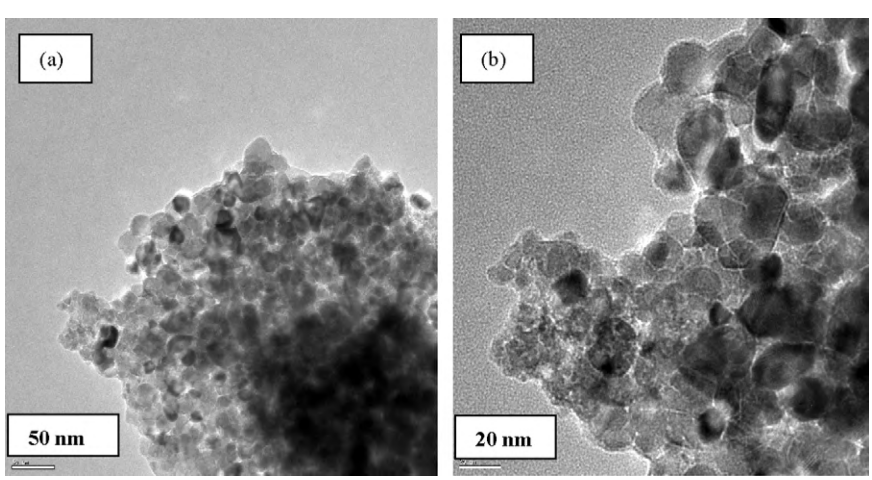

Fig. 3. TEM images of $BaTi_4O_9$ powders calcined at 1100 °C.