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# Structural and microwave dielectric properties of Ba<sub>6-3x</sub>Gd<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> solid-solutions

S.Bindra Narang<sup>a,\*</sup>, Dalveer Kaur<sup>a</sup> and Kulwant Singh Thind<sup>b</sup>

<sup>a</sup>Department of Electronics Technology, Guru Nanak Dev University, Amritsar-143005, Punjab, India <sup>b</sup>Department of Physics, Guru Nanak Dev University, Amritsar-143005, Punjab, India

 $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  (x = 0.0,  $0.2 \le x \le 0.7$ ) composites have been synthesized by employing a solid-state reactive sintering technique and studied from the point of view of microwave dielectric materials. In this series, formation of solid solutions was found, which was deduced from the linear change of the lattice parameters of the unit cells. Unit-cell parameters (Å) have been obtained with the help of the X-Ray powder diffraction (XRD) technique. Multi-phase microstructures have been observed for all the compositions using Scanning electron microscopy (SEM). We found good quality microwave materials which show a high dielectric constant ( $\varepsilon$ ') of 70 and a low loss tangent (tan $\delta$ ) of 0.006336 at 3 GHz. A minimum value of the A.C. dielectric conductivity ( $\sigma_{a.c.}$ ) was 2.32E-12 mho/cm at 0.8 GHz.

Key words: X-Ray Diffraction, Perovskite, Unit-cell parameters, Dielectric properties, Dielectric conductivity.

#### Introduction

For microwave frequency applications, high dielectric constant materials based on BaO- $R_2O_3$ -TiO<sub>2</sub> (R = rare earth) phase systems are widely used in the electronics industry. The solid solubility region with the general molecular formula  $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$  (R = rare earth) is an especially interesting part of these phase systems. Actually, a Ba<sub>6-3x</sub>R<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> solid solution was reported as a ternary compound existing on the tie line between BaTiO<sub>3</sub> and  $R_2Ti_2O_9$  composition in the ternary systems [1-3]. The BaO- $R_2O_3$ -4TiO<sub>2</sub> ternary compound has been known as a microwave resonator material [4, 5], which corresponds exactly to x = 0.5. The crystal structure of compositions from the Ba<sub>6-3x</sub>R<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> solid solubility regions is derived from the perovskite structure [6, 7]. These solid solutions contain two types of large cations which are different in valance, such as divalent  $Ba^{2+}$ and trivalent R<sup>3+</sup>. To maintain electrostatic stability, three Ba<sup>2+</sup> ions should be replaced by two R<sup>3+</sup> ions and one vacancy [2, 3, 6]. The solid solution has a new tungsten bronze type structure with perovskite columns containing  $2 \times 2$  unit cells of perovskite blocks and pentagonal sites occupied by the large cation [1, 2]. The ideal end member of the solid solutions is Ba<sub>6</sub>R<sub>8</sub>Ti<sub>18</sub>O<sub>54</sub> or 3BaO  $-2R_2O_3$ -9TiO<sub>2</sub>, with x = 0.0 in the molecular formula, in which these large cation sites are fully occupied.

Much research has been done on  $Ba_{6\cdot3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) compounds with R = La, Sm, Nd [4, 8, 9]. In this research study, ceramic solid solutions with the formula  $Ba_{6.3x}Gd_{8+2x}Ti_{18}O_{54}$ , where x = 0.0,  $0.2 \le x \le 0.7$ , were synthesized. The structural and microstructural properties of the prepared compacts have been observed, with respect to composition, with the help of XRD (X-Ray powder diffraction) and SEM (scanning electron microscopy) respectively. The dielectric properties have been investigated in the frequency range of 0.3 GHz-3.0 GHz.

#### **Experimental**

The samples in the series  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  were prepared by employing a solid state reactive sintering technique. The initial compounds BaCO<sub>3</sub>, TiO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub> of high purity were mixed in appropriate stoichiometric ratios in an agate mortar for 12 hours. The mixture was pre-sintered at 1100 °C for 2 h followed by grinding. The fine homogeneous powders were then granulated using an organic binder of PVA (poly vinyl alcohol) to provide strength and flowability to the granules. This was followed by shaping. For this, the granulated powders were compacted into pellets of rectangular and cylindrical shapes under a pressure of 75 kN. These pellets were finally sintered at 1300 °C for 2 h in air in a linearly programmable furnace. These sintered pellets were polished with fine emery paper to make the surfaces flat, smooth and parallel for characterization.

Powder diffraction data were taken by a step scan method on an X-ray diffractometer with CuK $\alpha$  radiation filtered by a Ni-filter in order to determine the lattice parameters based on the powder diffraction patterns using diffractions from the range  $20^{\circ} < 20 < 80^{\circ}$ . Microstructural details of the sintered surfaces were studied with the help of SEM. The bulk densities of the sintered specimens

<sup>\*</sup>Corresponding author:

Tel :+91-1832256203

Fax:+91-1832258820

E-mail: sukhleen2@yahoo.com



$$x = 0.3$$

h

$$x = 0.0$$
20 30 40 50 60 70 80
Cu Ka 20 (deg.)

Fig. 1. X-Ray patterns of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics for x = 0.0,  $0.2 \le x \le 0.7$ , sintered at 1300 °C for 2 hours.

were determined by the Archimedes method (liquid displacement method) using deionized water. Dielectric measurements were carried out on an Agilent technologies model 8714ET network analyzer in the frequency range of 0.3 GHz-3.0 GHz at room temperature. The dielectric conductivity ( $\sigma$ ) was obtained from the data of dielectric constant and loss tangent using the relation:

$$\boldsymbol{\sigma} = \boldsymbol{\varepsilon}' \boldsymbol{\varepsilon}_{0} \boldsymbol{\omega} \tan \boldsymbol{\delta} = \boldsymbol{\varepsilon}^{\mathbf{c}} \boldsymbol{\varepsilon}^{0} \boldsymbol{\omega} \tag{1}$$

where, ' $\varepsilon_{o}$ ' is the dielectric constant for free-space and  $\omega = 2_{TT} f$  is the angular frequency.

## **Results and Discussion**

The X-Ray Diffraction (XRD) patterns of  $Ba_{6.3x}Gd_{8+2x}$ Ti<sub>18</sub>O<sub>54</sub> structures with varying values of x are shown in Fig.1. The unit-cell parameters have been calculated employing XRD patterns using least-squares refinement of diffraction data collected with a high angle recording diffractometer using Ni-filtered CuK $\alpha$  radiation. It has been observed that the unit-cell parameters decreased almost linearly with an increasing value of the composition. The response of the parameters with respect to composition is plotted in Fig.2. The linear change in the unit-cell parameters with respect to composition satisfied the Vegard's Law [1, 2] and hence proved the formation of solidsolutions. Basically, Vegard's Law is an approximate empirical rule which holds that a linear relation exists, at constant temperature, between the crystal lattice constant of a compound and the concentration of the constituent elements. Values of the unit-cell parameters decreased as the amount of substitution of Gd for Ba increased,



Fig. 2. Lattice parameters of ceramics sintered at  $1300 \text{ }^{\circ}\text{C}$  as a function of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  (0.0, 0.2-0.7) compositions.

which is attributed basically to the change in ionic radius of the individual components. Data confirmed that the unit-cell had an orthorhombic symmetry and a possible space group of Pbam. The changes of unit-cell parameters were observed to be maximum for the b-axis and minimum for the c-axis. Moreover, with respect to the changes per Å, the minimum change was observed to be 0.24% for the a-axis and a maximum of 0.42% for the c-axis, but 0.34% for the b-axis. These changes in unit-cell dimensions were due to the ionic radii differences of Ba and Gd ions. It was observed that the values of parameters were a maximum for the composition x = 0.0, but decreased gradually as the composition increased to x = 0.7. This was because as the composition increased the Gd content increased and these medium sized valence cations substituted for Ba and Ti ions. Hence the unit cell parameters decreased with this substitution. It was observed from the XRD powder patterns of the crystallized samples that a major peak occurred at a 30° diffraction angle. But the peak height lowered as the angle increased. This was due to a different type of ion substitution for Ba sites of the crystal structure.

SEM micrographs for x = 0.0, 0.2, 0.4 and 0.6 of sintered surfaces are shown in (a), (b), (c) and (d) of Fig. 3 respectively. Microstructural investigations revealed multi-



**Fig. 3.** SEM micrographs of the microstructure of the  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  family of solid solutions with x = 0.0,  $0.2 \le x \le 0.7$  sintered at 1300 °C showing three phase structures :  $A = BaTi_4O_9$ ,  $B = Ba_4Ti_{13}O_{30}$  and  $C = BaGd_2Ti_4O_{12}$  ( $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$ ).



Fig. 4. Response of bulk density (gm/cc) of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics as a function of composition and frequency.

phase microstructures. The micrographs were basically observed to consist of three phase structures:  $A = BaTi_4O_9$ ,  $B = Ba_4Ti_{13}O_{30}$  and  $C = BaGd_2Ti_4O_{12}(Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54})$ solid-solution, marked on the micrographs. Phases A and B were irregular shaped and randomly distributed. Their concentrations were observed to be a maximum for x = 0.0, but decreased with an increase in the concentration of Gd as x increased for Gd and decreased for Ba in the molecular formula. Phase C appeared as crystals of bar-shaped grains with a small amount of block-shaped crystals. The length of the barshaped crystals tended to increase with the amount of x. The growth of grains resulted in an increase in porosity in the microstructure but the density decreased. The long bar-shaped grains grew at the expense of short ones. As the long bar-shaped grains came into contact, continual growth squeezes them away from one another, which results in the formation of new and larger vacant positions where the short grains were originally



Fig. 5. Response of relative density (%) of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics as a function of composition and frequency.

located. This caused expansion of the space between the bar-shaped grains and resulted in an increase of the porosity and a decrease in the bulk density. The values of bulk and relative densities of the sintered samples were also determined and are shown in Figs. 4 and 5. The bulk density of the sintered pellets was measured using Archimedes method. Distilled water was used as the displacement liquid. The relative densities were calculated from the bulk and apparent densities of the sintered samples.

The variation of  $\varepsilon'$  with frequency at room temperature, with x = 0.0, 0.2, 0.4 and 0.6, for the synthesized ceramics is shown in the fig.6. It was observed that  $\varepsilon'$ decreased with frequency. A similar response for various rare earths doped dielectrics has been observed by other researchers [2, 8, 10, 11]. It was also observed that  $\varepsilon'$ decreased with the composition (x). The maximum value of  $\varepsilon'$  was observed to be 70 for x = 0.0 at 0.3 GHz. However, the typical performances of  $\varepsilon' = 48$ 



Fig. 6. Variation in the dielectric constant of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics as a function of composition and frequency.



Fig. 7. Variation in the Loss tangent of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics as a function of composition and frequency.

to 70 were obtained. In normal behavior, the  $\varepsilon$ ' decreases with an increase in the frequency due to the fact that beyond a certain frequency of the applied electric field the particle exchange does not follow the alternating field [12]. The low frequency rise in the dielectric constant is attributable to interfacial effects. These take place at the contacts or in the bulk of the material at grain boundaries. A charge is able to accumulate at these interfacial sites and thereby able to contribute to the total capacity or dielectric permittivity or dielectric constant. As the frequency is raised, eventually the system can no longer follow the time-dependent charge fluctuations and  $\varepsilon$ ' tries to settle down to a value equal to the one without the interfacial charges. Moreover, as the  $Gd^{3+}$  ions substitute for the  $Ba^{2+}$  ions, not only are vacancies created to maintain charge neutrality but the lattice parameters are changed due to the difference in ionic radius between  $Gd^{3+}$  and  $Ba^{2+}$ . The difference of ion radius directly affects the length of the c-axis, which is an important characteristic of the tungsten-bronze type structure. The decrease of the lattice parameters also promotes the shrinkage of the octahedra which decreases the dielectric constant



Fig. 8. Variation in conductivity (mho/cm) of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics as a function of composition and frequency.

indirectly [6].

The Loss tangent for  $Ba_{6\cdot3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics with x = 0.0, 0.2, 0.4 and 0.6 is shown in Fig. 7. The loss tangent was a minimum 0.006336 for x = 0.0 at 3 GHz. It was observed that it decreased with frequency, but increased with composition. Two main factors that are believed to affect the loss tangent: intrinsic loss and extrinsic loss [11]. The intrinsic losses are mainly caused by lattice variation modes while the extrinsic ones are dominated by a multi-phase microstructure, oxygen vacancies, grain sizes and densification or porosity.

A plot for the A.C. dielectric conductivity ( $\sigma_{a,c}$ ) for Ba<sub>6-3x</sub>Gd<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> ceramics is shown in fig.8. Very low conductivities have been observed for the samples prepared. It basically decreased with composition, but increased with frequency. A minimum value of  $\sigma_{A,C}$ was observed to be 2.32E-12 mho/cm for x = 0.6 at 0.8 GHz. Actually, the dielectric conductivity ( $\sigma_{A,C}$ ) sums over all the dissipative effects of the material [12]. It might have originated from migrating charge carriers and it also refers to an energy loss associated with the dispersion of  $\varepsilon'$ , for example, the friction accompanying the orientation of dipoles and also, the defect centers and impurities that could contribute to the conductivity which are generally randomly distributed in dielectrics. Moreover, the excess electrons or excess holes due to their interaction with lattice ions generally distort the surroundings in such a way that a potential well thereby generated is deep enough to introduce localization leading to the existence of conduction. No doubt, its value remains very low in the case of dielectrics but it does exist.

Capacitance, in a real sense, signifies just the dielectric constant of a dielectric material. In many cases  $\varepsilon'$  has been defined simply as the capacity of a condenser having a dielectric between charged plates. Variation in capacitance with respect to frequency and composition for Ba<sub>6-3x</sub>Gd<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> ceramics, with x = 0.0, 0.2, 0.4 and 0.6, is shown in Fig. 9. The capacitance, in picofarads, basically decreased with frequency as well as composition. Its maximum value was observed to be 7.27E-09 pf for



Fig. 9. Variation in capacitance (picofarads) of  $Ba_{6-3x}Gd_{8+2x}Ti_{18}O_{54}$  ceramics as a function of composition and frequency.

x = 0.0 at 0.3 GHz. It was found out from the geometrical dimensions of the pellets and observed that the behavior of capacitance was very similar to that of  $\varepsilon'$ . In the sense that, it also decreased with frequency just like the dielectric constant. The charge storage capability of a capacitor is simply the dielectric permittivity or dielectric constant itself. Moreover, it is proportional to  $\varepsilon'$ .

## Conclusion

In summary, complex ceramics  $Ba_{6.3x}Gd_{8+2x}Ti_{18}O_{54}$  with x = 0.0, 0.2-0.7 were synthesized and characterized in terms of their structural and dielectric properties. It was observed with the help of X-ray powder diffraction data that the lattice parameters decreased linearly with composition. Crystals of the orthorhombic phase were obtained with the possible space group of Pbam. SEM micrographs confirmed the existence of a multi-phase system in the sintered compacts. The microwave dielectric

properties were observed to be quite good. The dielectric constant decreased slightly with an increase in frequency and composition. The typical dielectric performances of  $\varepsilon$ '= 48 to 70 were obtained. A minimum value of loss tangent was observed to be 0.006336 for x = 0.0 at 3 GHz. A minimum value of  $\sigma_{A.C.}$  was observed to be 2.32E-12mho/cm at 0.8 GHz. Ba<sub>6-3x</sub>Gd<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> ceramics in the BaO-Gd<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> ternary system, with high dielectric constant values and low losses could be promising materials for applications in microwave devices.

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