Bull. Mater. Sci., Vol. 27, No. 2, April 2004, pp. 149–153. © Indian Academy of Sciences.

Synthesis and dielectric properties of $MXTi_7O_{16}$ (M = Ba and Sr; X = Mg and Zn) hollandite ceramics

V M MANISHA, K P MURALI, S N POTTY, V PRIYADARSINI and R RATHEESH*

Centre for Materials for Electronics Technology (C-MET), Department of Information Technology, M.G. Kavu, Athani (P.O.), Thrissur 680 771, India

MS received 27 August 2003; revised 7 February 2004

Abstract. **$MXTi_7O_{16}$ (M = Ba and Sr; X = Mg and Zn) ceramics have been synthesized by the conventional solid state ceramic route. The dielectric properties such as dielectric constant (e_r), loss tangent (tan d) and temperature variation of dielectric constant ($t_{\varepsilon r}$) of the sintered ceramic compacts are studied using an impedance analyser up to 13 MHz region. The strontium compounds have relatively high dielectric constant and low loss tangent compared to the barium analogue. The phase purity of these materials has been examined using X-ray diffraction studies and microstructure using SEM method.**

Keywords. **Ceramics; oxides; sintering; titanates.**

1. Introduction

High permittivity dielectric ceramics, which enable the miniaturization of the microwave devices, have received recent attention due to the rapid progress in microwave telecommunications and satellite broadcasting. The most desirable properties of a microwave dielectric resonator are high permittivity ($e_r > 20$), low dielectric loss (tan $d < 10^{-4}$) and low temperature coefficient of resonant frequency ($t_f < 20$ ppm/°C) (Lafez *et al* 1992; Ratheesh *et al* 1997, 1998). So far numerous dielectric materials have been developed for microwave applications including $Ba(Zn_{1/3}Ta_{2/3})O_3$ (Nomura *et al* 1982), $BaO–TiO_2$ compounds (Plourde *et al* 1975), $BaO–TiO_2$-rare earth oxide systems (Kawashima *et al* 1983), $Ba(Mg_{1/3}Ta_{2/3})O_3$ (Wakino *et al* 1986; Ratheesh *et al* 1999), $(Zn, Sn)TiO_4$ (Iddles and Moulson 1992) etc and in general they composed of a single-phase substance, which has excellent microwave characteristics by itself. Although these compositions have very promising dielectric properties, the relatively higher sintering temperatures (> 1400°C) may limit their wide use.

Recently, hollandite type materials have attracted considerable attention owing to their potential use in synthetic mineral assemblage (SYNROC). These synthetic materials are being developed as a host for high-level radioactive waste (Kesson and White 1986). The hollandite group of minerals have the general formula, $Ba_x(M_yTi_{8-y})O_{16}$. The crystal structure of Ba-hollandite materials has been the subject of many investigations. The composition range, lattice parameters and ordering of the Ba ions in the hollandite system, $Ba_x(Mg_xTi_{8-y})O_{16}$, have been investigated using X-ray powder diffraction data by Cheary and Squadrito (1989). Rietveld refinement of high resolution neutron powder diffraction data has been carried out by these authors on the end members, $Ba_{1·14}(Mg_{1·14}Ti_{6·86})O_{16}$ and $Ba_{1·33}(Mg_{1·33}Ti_{6·67})O_{16}$. An increase in monoclinic distortion is noticed in these compounds with respect to an increase in Ba concentration due to the change in shape of the *b*-axis tunnels (Dubeau and Edgar 1985; Fanchon *et al* 1987; Cheary and Squadrito 1989).

Although the crystal structure of hollandite materials has been studied in detail, to the best of our knowledge, no systematic approach has been made so far to study the dielectric properties of these technologically important class of materials. In the present work, we have carried out a detailed study of $MXTi_7O_{16}$ (M = Ba and Sr and X = Mg and Zn) materials in ceramic form to evaluate their dielectric properties.

2. Experimental

The starting materials were reagent grade barium/strontium carbonates (> 99% pure, Merck), MgO/ZnO (Otto Kemi, 99·9%) and TiO_2 (Merck, 99·9%). Stoichiometric proportions of the chemicals were weighed and mixed using distilled water as solvent for 2 h in agate mortar. The slurry was then dried and calcined at 1150°C for 3 h. The calcined powder is ground in an agate mortar for 2 h and 5 wt% polyvinyl alcohol (PVA) is added to it as binder and then dried. The fine powder is then pressed into

*Author for correspondence

disc shaped compacts using a WC die under a pressure of 250 MPa (18·13 T/inch^2). The green compacts were initially fired at a rate of 8°C/min up to 600°C and then at a rate of 10°C/min up to the sintering temperature. An intermediate soaking was given at 600°C for 30 min to expel the binder (PVA). The sintering temperature of the samples was in the range 1240–1350°C for 3 h (table 1). The bulk densities of the sintered and polished samples were measured using Archimedes method. The phase purity of the samples was investigated by powder X-ray diffraction measurement (CuK_a) using a Bruker 5005 model X-ray diffractometer. Well sintered samples were polished and thermally etched at 100°C less than the sintering temperature for 30 min to study the surface morphology using a JEOL Model scanning electron microscope (SEM). The dielectric properties of the sintered samples were studied up to 13 MHz region using an impedance analyser (HP4192A). Very fine silver paste was applied as electrodes to the faces of the well sintered pellets. The temperature variation of dielectric constant of the samples was measured using a Clitech Engineers (India) Pvt. Ltd. make humidity chamber in the 0–100°C region with an accuracy of ± 1°C.

3. Results and discussion

The powder X-ray diffraction pattern recorded using CuK_a radiation of $BaMgTi_7O_{16}$, $BaZnTi_7O_{16}$, $SrMgTi_7O_{16}$ and $SrZnTi_7O_{16}$ (here after referred to as BMT, BZT, SMT and SZT) ceramics are given in figures 1 and 2. These materials fall under the hollandites family. Barium magnesium hollandites {Ba_x(Mg/Ti) hollandites} with $x < 1$ do not form because of pairing of vacant tunnel sites and hence the structure becomes unstable (Cheary 1986). Generally barium magnesium hollandites possess a tetragonal symmetry. However, larger values of x in the Ba-site lead to monoclinic distortion. A detailed crystal structure analysis of these compounds is available in the literature (Cheary and Squadrito 1989). In the present study XRD pattern of the $BaMgTi_7O_{16}$ ceramic is indexed on the basis of a tetragonal symmetry (see figure 1) and the lattice

Table 1. The sintering temperature, sintered density and dielectric properties of $MXTi_7O_{16}$ (M = Ba and Sr; X = Mg and Zn) ceramics at 1 MHz.

Sample name	Optimized sintering temperature (°C)	Sintered density (g/cm^3)	Dielectric constant (e_r)	Loss tangent (tan d)	Temperature coefficient of dielectric constant ($t_{\varepsilon r}$) (ppm/°C)
BMT	1240	3·95	58	0·068	1554
BZT	1240	4·23	55	0·034	618
SMT	1270	3·98	83	0·0016	– 1064
SZT	1260	4·33	75	0·0001	– 690

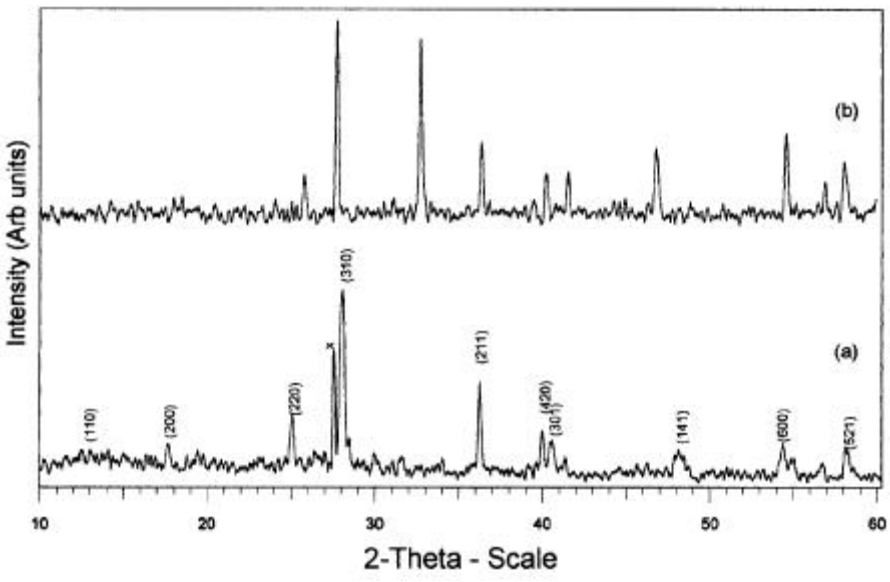

Figure 1. Powder X-ray diffraction patterns of (**a**) $BaMgTi_7O_{16}$ and (**b**) $SrMgTi_7O_{16}$.

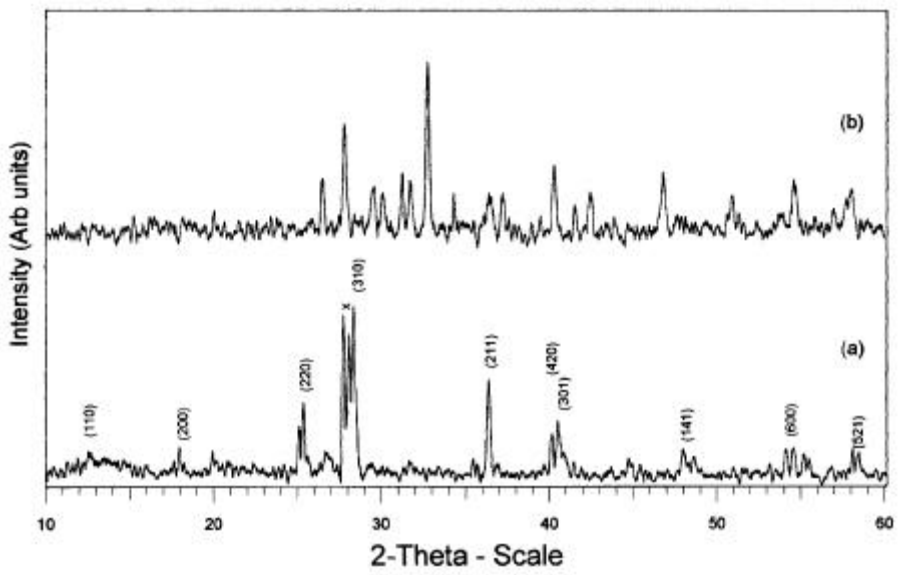

Figure 2. Powder X-ray diffraction patterns of (**a**) $BaZnTi_7O_{16}$ and (**b**) $SrZnTi_7O_{16}$.

parameters are calculated as a = 10·06 Å and c = 2·97 Å. The pattern shows excellent matching with tetragonal barium magnesium oxide (JCPDS card No. 73-0499). However, XRD pattern of $BaZnTi_7O_{16}$ ceramics show additional splitting compared to Mg analogue (figure 2).

In general, hollandites with large A ions and small B ions are tetragonal whereas those with small A ions and large B ions are monoclinic. It is reported that the symmetry of this material could be tetragonal when $R_A/R_B > 2{\cdot}08$ and monoclinic when this ratio is $< 2{\cdot}08$ although this is by no means a general rule for all hollandites (Post *et al* 1982; Cheary 1986). The ratio of the cation radii (R_A/R_B) is 2·33 in the case of BMT and 2·17 in the case of BZT (Shannon 1976). The additional splitting observed in the Zn compound may be due to the deviation of crystal symmetry from tetragonal to monoclinic. This trend is more pronounced in the case of Sr hollandites. XRD patterns of the Sr hollandites are very different from that of barium analogues. When Ba is replaced by a smaller ion in the A site (Sr), one can expect a monoclinic distortion in the lattice. The R_A/R_B ratio is 2·09 for SMT and 1·94 for SZT ceramics (Shannon 1976). It is reported that the distortion in the monoclinic hollandite occurs because the tunnel ions are unable to support the octahedral walls, which collapse onto the tunnel ions (Cheary 1986). However, a detailed structural analysis is required to elucidate the exact crystal symmetry of these compounds, which will be published elsewhere.

The microstructure of BMT and BZT ceramics recorded using a scanning electron microscope is shown in figure 3. The SEM picture of BMT ceramics show two types of grains, one having 10–12 μ in size with polygonal appearance and the other with columnar appearance having 4–5 μ in size. However, BZT ceramics have

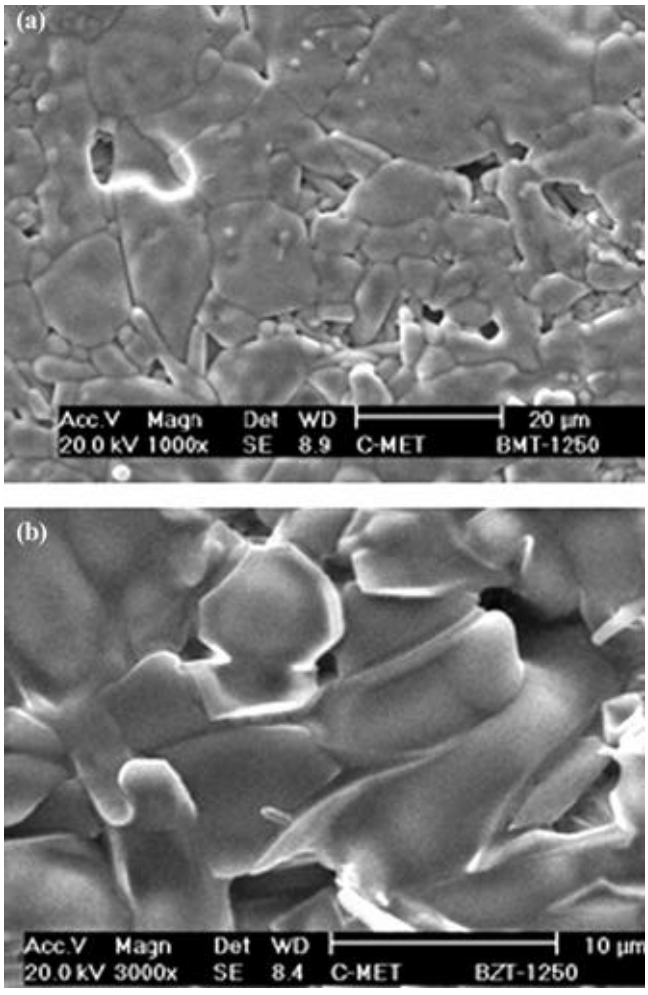

Figure 3. SEM pictures of (**a**) $BaMgTi_7O_{16}$ and (**b**) $BaZnTi_7O_{16}$ ceramics.

large columnar grains (8–10 μ size) and relatively small polygonal grains (~ 3 to 4 μ size).

The fine powders of these compositions are uniaxially pressed using a tungsten carbide (WC) die with a pressure of 250 MPa (18·13 T/in^2) and sintered at different temperatures to obtain optimized densities. A typical temperature vs density plot of BZT ceramics is shown in figure 4. It can be seen that the density of the samples initially increases with temperature and after reaching a maximum value it starts decreasing. The pellets sintered above 1240°C start melting. In the case of BZT ceramics, the maximum density is obtained at 1240°C and hence it is taken as the optimum sintering temperature. The same trend is observed in other analogue compositions as well and hence the temperature at which maximum density is obtained is taken as the optimum sintering temperature in all cases.

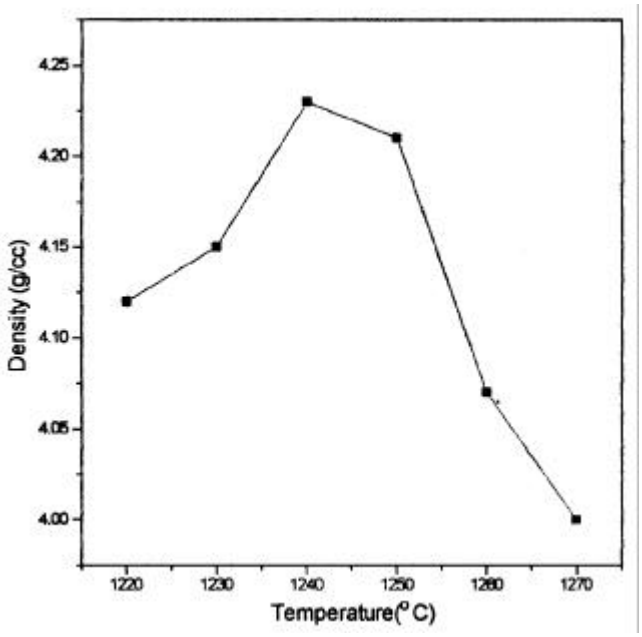

Figure 4. Variation of sintered density with temperature for $BaZnTi_7O_{16}$ ceramics.

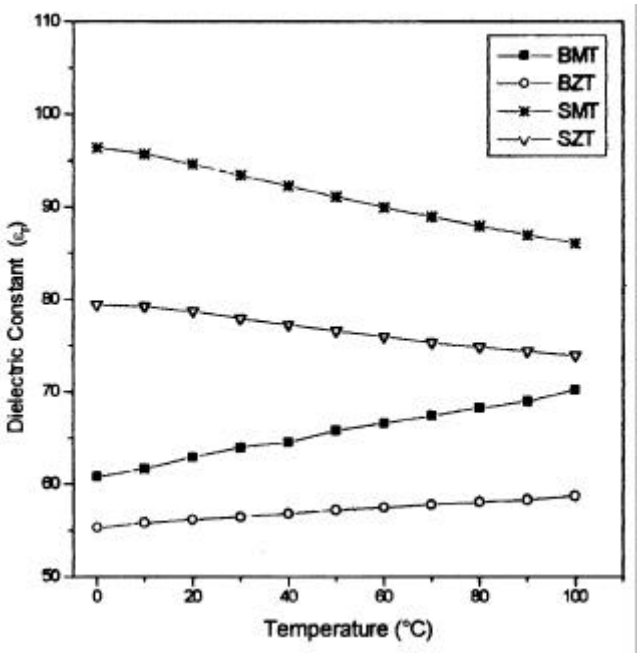

Figure 5. Temperature vs dielectric constant of $MXTi_7O_{16}$ (M = Ba, Sr and X = Mg, Zn) ceramics at 1 MHz.

The dielectric properties of $MXTi_7O_{16}$ (M = Ba and Sr; X = Mg and Zn) ceramics are compiled in table 1. The table presents the dielectric constant (e_r), loss tangent (tan d) and temperature coefficient of resonant frequency ($t_{\varepsilon r}$) of these ceramics at 1 MHz. In general, strontium compounds have slightly higher dielectric constant than that of the barium analogues. BMT and BZT have dielectric constant of 58 and 55, respectively whereas SMT and SZT show a dielectric constant of 83 and 75, respectively. No marginal difference in dielectric constant is observed for the samples under study in the 100 kHz–13 MHz region. Strontium samples show very low loss tangent in the measured frequency range compared to the barium analogue. SZT sample shows a loss tangent of 0·0001 at 1 MHz (table 1).

The temperature variation of dielectric constant ($t_{\varepsilon r}$) of dielectric ceramics is very critical for practical applications. In the present study, the temperature variations of dielectric constant of all the four samples are precisely measured in the 0–100°C region and results are presented in figure 5. It is interesting to note that both BMT and BZT samples show high positive $t_{\varepsilon r}$ in the measured temperature range whereas SMT and SZT show high negative temperature coefficient (table 1).

Low frequency dielectric measurements of $MXTi_7O_{16}$ (M = Ba and Sr; X = Mg and Zn) hollandite show that these materials can be exploited for practical applications, provided temperature compensation can be achieved by tailor making a solid solution of $Ba_{1-x}Sr_xXTi_7O_{16}$ (X = Mg, Zn).

4. Conclusions

$BaMgTi_7O_{16}$, $BaZnTi_7O_{16}$, $SrMgTi_7O_{16}$ and $SrZnTi_7O_{16}$ ceramics have been synthesized by the conventional solid state ceramic route. The phase purity of these materials has been examined using X-ray diffraction studies. The dielectric constant (e_r), loss tangent (tan d) and temperature variation of dielectric constant ($t_{\varepsilon r}$) of well-sintered ceramic compacts have been measured up to 13 MHz region. Strontium compositions show high dielectric constant and low loss tangent compared to barium analogues. Interestingly, barium samples show high positive temperature variation of dielectric constant and strontium samples and high negative temperature variation of dielectric constant. Among the samples studied, $SrZnTi_7O_{16}$ ceramics have relatively high dielectric constant and very low

loss tangent. However, temperature compensation has to be achieved in these compounds through proper tailor making of a solid solution of $Ba_{1-x}Sr_xXTi_7O_{16}$ where X = Mg or Zn.

Acknowledgements

The authors are indebted to Mr I C Rao, Director, C-MET, Thrissur, for extending the facilities to carry out this study.

References

Cheary R W 1986 *Acta Crystallogr*. **42** 229
Cheary R W and Squadrito R 1989 *Acta Crystallogr*. **B45** 205
Dubeau M L and Edgar A D 1985 *Miner. Mag*. **49** 603
Fanchon E, Vicat J, Hodeau J L, Wolfers P, Qui D T and Strobel P 1987 *Acta Crystallogr.* **B43** 440
Iddles D M and Moulson A J 1992 *J. Mater. Sci*. **27** 6303
Kawashima S, Nishida M, Ueda I and Ouchi H 1983 *J. Am. Ceram. Soc*. **66** 421
Kesson S E and White T J 1986 *Proc. R. Soc. London Ser. A* **405** 73
Lafez P, Desgardin G and Raveau B 1992 *J. Mater. Sci*. **27** 5229
Nomura S, Toyama K and Kaneta K 1982 *Jpn J. Appl. Phys*. **21** L621
Plourde J K, Linn D F, O'Bryan H M and Thomson J 1975 *J. Am. Ceram. Soc*. **58** 418
Post J E, Von Dreele R B and Buseck P R 1982 *Acta Crystallogr*. **B38** 1056
Preethi T M and Ratheesh R 2003 *Mater. Lett*. **57** 2545
Ratheesh R, Sreemoolanadhan H, Sebastian M T and Mohanan P 1997 *Ferroelectrics* **21** 1
Ratheesh R, Sreemoolanadhan H, Suma S, Sebastian M T, Jose K A and Mohanan P 1998 *J. Mater. Sci.-Mater. Electron.* **9** 291
Ratheesh R, Sebastian M T, Tobar M E, Harnett J and Blair D G 1999 *J. Phys*. **D32** 2821
Shannon R D 1976 *Acta Crystallogr*. **A32** 751
Wakino K, Murata M and Tamura H 1986 *J. Am. Ceram. Soc.* **69** 34