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Dielectric behaviour of sodium and potassium doped magnesium titanate

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Abstract. Pure phase of magnesium titanate ($MgTiO_3$) was obtained at 1100°C by both the conventional solid-state method as well as by the flux method starting from hexahydrated magnesium nitrate and titanium dioxide as the reactants. $MgTiO_3$ doped with Na or K was also prepared by the solid-state route. Na and K doped compositions led to monophasic $MgTiO_3$ below 5 mol % dopant concentration while biphasic mixture of $MgTiO_3$ (major phase) and $MgTi_2O_5$ (minor phase) were obtained at higher dopant concentration. The dielectric constant and dielectric loss of $MgTiO_3$ were found to be almost the same irrespective of the preparative method. $MgTiO_3$ doped with 5 mol % of Na and K ions displayed optimum dielectric properties.

Keywords. Ceramics; dielectric constant; dielectric loss.

1. Introduction

Magnesium titanate is one of the most widely used materials as resonators at microwave frequencies (Tamura and Katsube 1980). These resonators are widely used in filters and oscillators in microwave communication systems (Kell *et al* 1973; Plourde and Ren 1981; Wakino 1989; Subba Rao *et al* 1990; Wakino *et al* 1990). In earlier reports on synthesis of $MgTiO_3$ by the solid-state method using oxides of magnesium and titanium, a secondary phase of $MgTi_2O_5$ was obtained which was very difficult to remove from the reaction product (Cambier *et al* 1982). Dielectric losses are influenced by the presence of lattice defects (vacancies, dislocations, impurities), secondary phase and porosity (Iddles *et al* 1992; Nomura 1983; Heiao *et al* 1988; Sato *et al* 1981; Ferreira *et al* 1992). To reduce the dielectric loss it is, therefore, important to prepare magnesium titanate without impurity. Several low temperature routes like the Pechini method have been used earlier to prepare pure $MgTiO_3$ (Ferreira and Baptista 1994). The study of various dopants (La, Cr, Fe, Co and Ni) in $MgTiO_3$ has earlier shown that they may affect sintering behaviour and also dielectric loss of the materials (Ferreira *et al* 1992; Ferreira and Baptista 1994; Huang and Weng 2001).

In this paper, nitrate salt of magnesium was chosen as a starting material for the preparation of pure phase of magnesium titanate via the solid-state method and the molten salt (flux) method. In addition, we have also synthesized $MgTiO_3$ doped with 1–10 mol % of Na and K ions. We have also discussed the dielectric properties of undoped and doped (with Na and K) magnesium titanates on sintered disc at much lower sintering temperatures.

2. Experimental

The starting materials, $Mg(NO_3)_2 \cdot 6H_2O$ (Merck 99%), and TiO_2 (Fluka 99%), Na_2CO_3 (Merck 99%) and K_2CO_3 (Merck 99%) were taken in their stoichiometric ratio for the synthesis of undoped and (Na, K)-doped $MgTiO_3$. Pure phase of $MgTiO_3$ was prepared by both flux and solid-state methods. For (Na, K)-doped compositions, only the solid-state method was used. In the preparation of $MgTiO_3$ by flux method, stoichiometric amount of $Mg(NO_3)_2 \cdot 6H_2O$ and TiO_2 were taken along with a eutectic mixture (1:1) of NaCl and KCl in the ratio of 2:1. The mixture of reactants and flux was homogenized in an agate mortar and then loaded in alumina crucibles for heating at 900°C for 6 h. The precursor was then washed several times with chloride-free hot double distilled water to remove the flux. The dried powder (at 110°C) was further heated at 1000°C for 20 h and 1100°C for 24 h with intermittent grinding. Stoichiometric ratio of $Mg(NO_3)_2 \cdot 6H_2O$ and TiO_2 were taken for the preparation of magnesium titanate by solid-state method. The mixture was properly homogenized in an agate mortar. The homogenized mixture was loaded in an alumina crucible and kept in the programmable furnace for heating at 900°C for 12 h. The sample was further heated at 1025°C for 19 h and at 1100°C for 10 h. Magnesium titanate doped with sodium and potassium was also synthesized by the solid-state method by using Na_2CO_3 and K_2CO_3 as the source of dopants. Powdered samples of undoped and doped magnesium titanate were treated with a 5% polyvinyl alcohol (PVA) solution and then compacted into disks by applying uniaxial pressure of 8 tonnes. The compacted disks were sintered at 1100°C for 12 h. Powder X-ray diffraction (PXRD) studies

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of the compounds were carried out after every stage of heating on a Bruker D8 Advance X-ray diffractometer with a step size of 0·05° and a scan speed of 1 s per step in the 2 theta range of 10° to 70°. The refined lattice parameters were obtained by a least-square fit to the observed *d*-values. Scanning electron micrographs (SEM) were obtained on the sintered disks (at 1100°C) using a Cambridge Stereoscan 360 electron microscope in order to study grain size and morphology of the sample. The dielectric properties were measured on sintered pellets (coated on both sides with Ag-paste to act as electrodes) using an HP 4284L LCR meter in the frequency range 50–500 kHz with varying temperatures from room temperature to 200°C. The density of sintered pellets of undoped and doped magnesium titanate was measured using the Archimedes method and found in the range of 92–94% of theoretical density.

3. Results and discussion

Magnesium titanate was prepared by using hexahydrated magnesium nitrate by both solid-state and flux methods. The sodium and potassium doped compositions of magnesium titanate were prepared by the solid-state method. In the synthesis using flux, a minor impurity phase was present along with the major phase of $MgTiO_3$ after the initial reaction at 900°C. Further heating at 1000°C for 20 h and 1100°C for 12 h led to pure phase of $MgTiO_3$ (figure 1a). The solid-state method led to the formation of a biphasic mixture containing $MgTi_2O_5$ (15%) along with the major phase ($MgTiO_3$) after heating the homogenized sample at 900°C for 12 h. On further heating at 1025°C for 20 h a pure phase of $MgTiO_3$ was obtained. The oxides were sintered at 1100°C for 12 h and were found to be monophasic (figure 1b). It may be
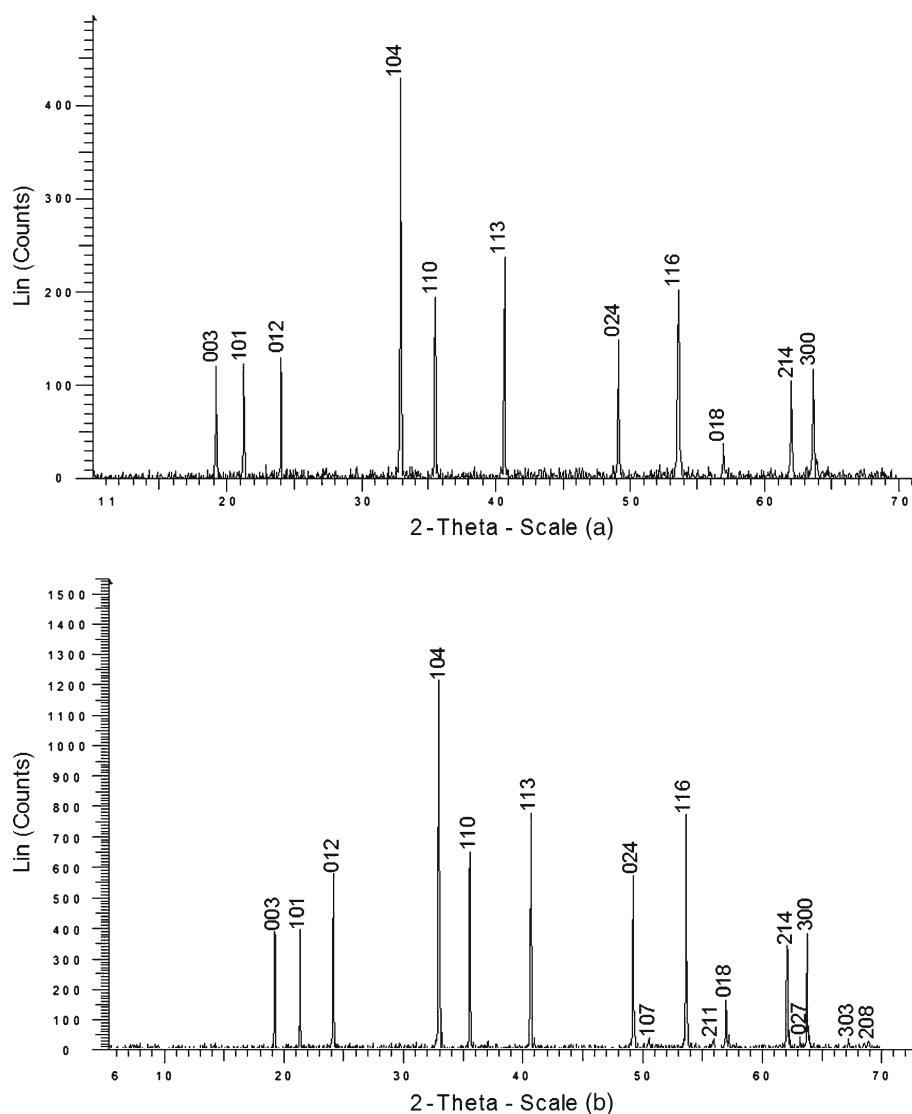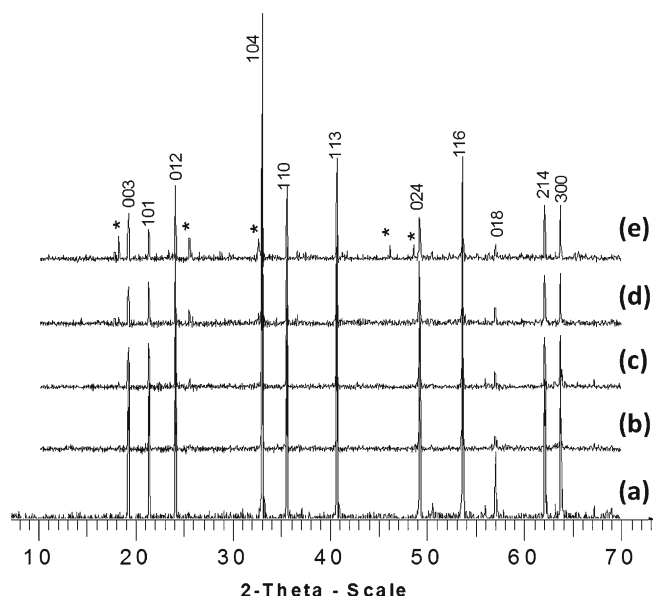

Figure 1. Powder X-ray diffraction pattern of $MgTiO_3$ prepared by (**a**) flux method and (**b**) solid-state method after 1100°C heating.

noted that the solid-state route to $MgTiO_3$ (from MgO and TiO_2) always yields a small percentage of $MgTi_2O_5$ as secondary phase even at elevated temperatures. However, we have avoided formation of the $MgTi_2O_5$ using $Mg(NO_3)_2 \cdot 6H_2O$ rather than MgO. In case of doped magnesium titanate compositions prepared by solid-state method

Figure 2. Powder X-ray diffraction pattern of (**a**) undoped $MgTiO_3$, (**b**) 1% Na, (**c**) 2 % Na, (**d**) 5 % Na and (**e**) 10 % Na prepared by solid-state method at 1100°C.
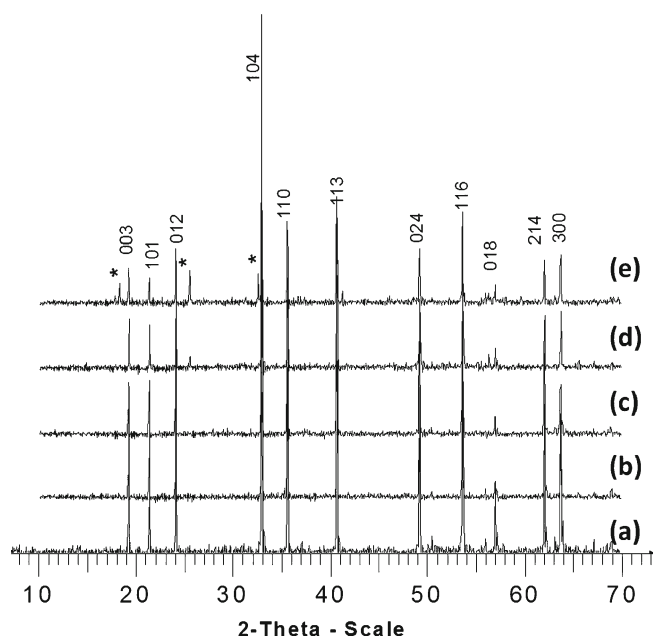
Figure 3. Powder X-ray diffraction pattern of (**a**) undoped $MgTiO_3$, (**b**) 1% K, (**c**) 2 % K, (**d**) 5 % K and (**e**) 10 % K prepared by solid-state method at 1100°C.

at 1100°C, pure phase of $MgTiO_3$ was observed for 1 mol % Na dopant whereas in K doped composition it was observed at 1 and 2 mol % dopants. The secondary phase of $MgTi_2O_5$ appeared at higher dopant concentration (5 mol %) and the secondary phase was increasing with increased dopant concentration (figures 2 and 3). PXRD pattern for pure $MgTiO_3$ could be indexed satisfactorily in the hexagonal cell as is known for the ilmenite structure of $MgTiO_3$ (**a** ~ 5·05 Å and **c** ~ 13·86 Å).

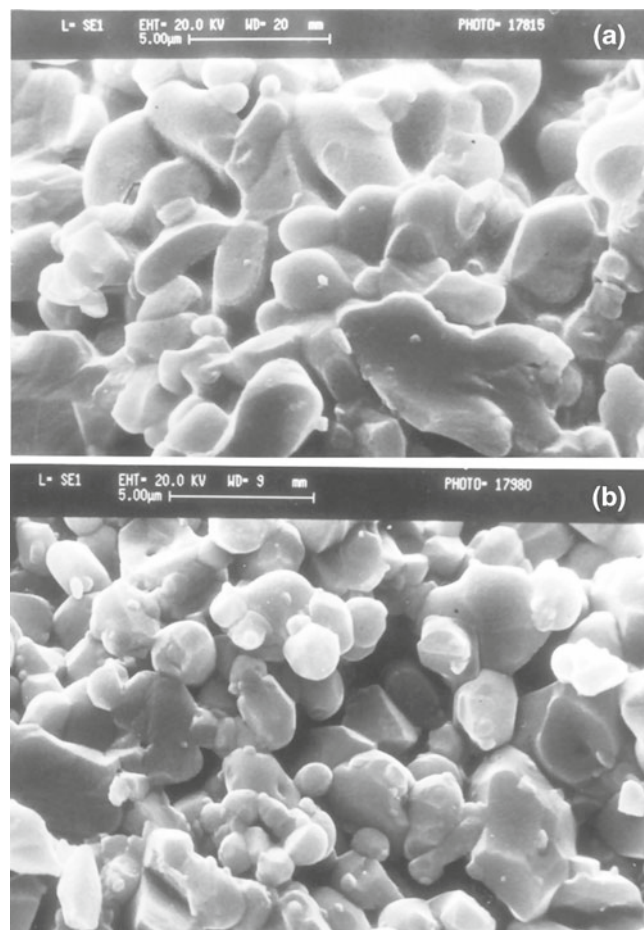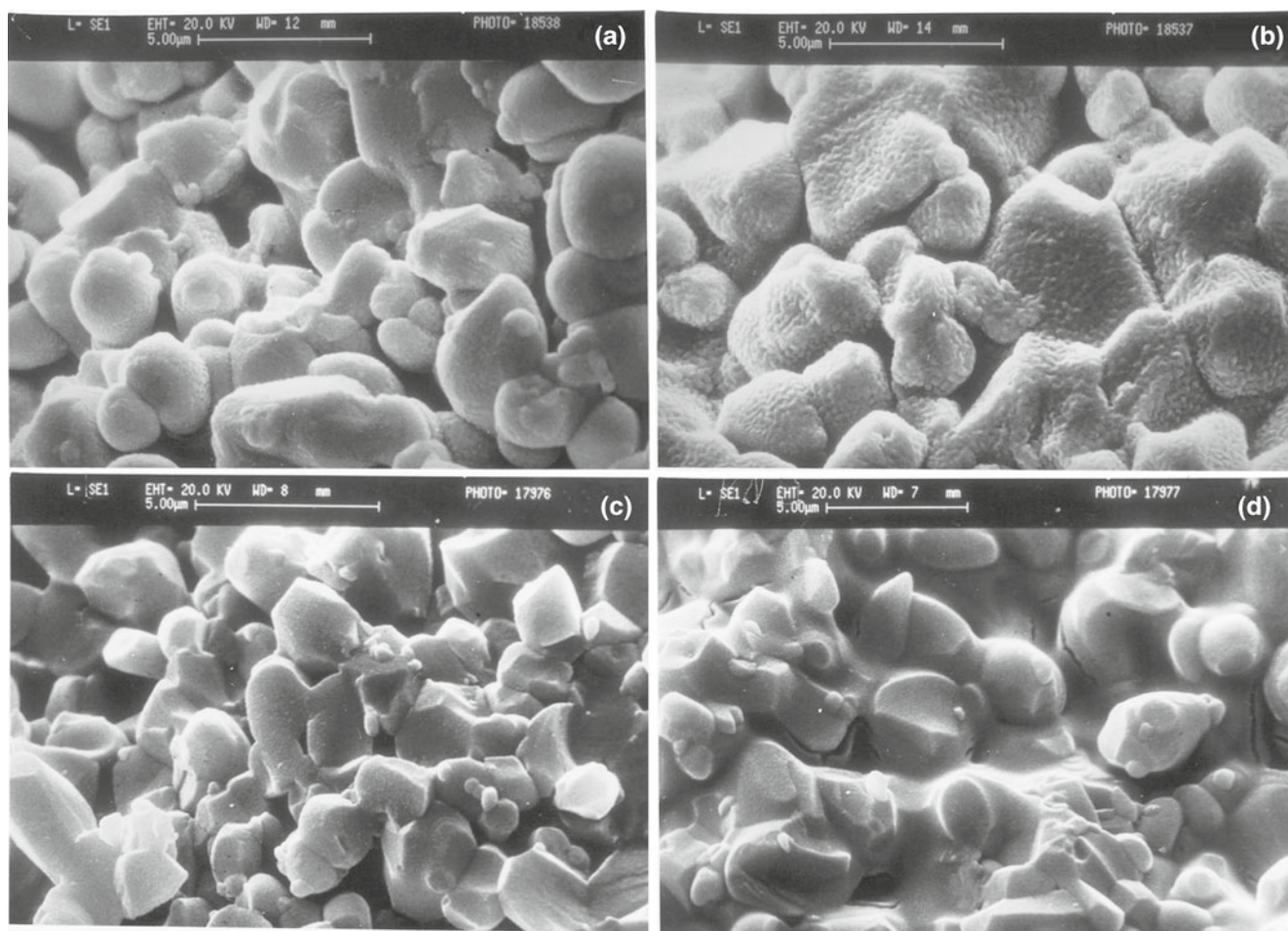Scanning electron micrographs (SEM) of $MgTiO_3$ prepared by the flux method and solid-state method were recorded of sintered sample at 1100°C. The micrographs show that the grain boundaries are better defined in the oxide obtained by the solid-state route (figure 4b). The grain size was found to be 2–4 μm (figures 4a and b). SEM studies on sintered (at 1100°C) sample of doped (Na, K)–$MgTiO_3$ shows that grain size increases (~ 5 μm) as concentration of dopant increases up to 2 mol % (figures 5b and 6b). However, further increasing the dopant concentration (5 mol %) leads to smaller grains (~ 2–3 μm). However, these grains are dense and have well developed facets (figures 5c and 6c). The secondary phase ($MgTi_2O_5$), which is clear from PXRD

Figure 4. Scanning electron micrograph of $MgTiO_3$ sintered at 1100°C synthesized by (**a**) flux method and (**b**) solid-state method.
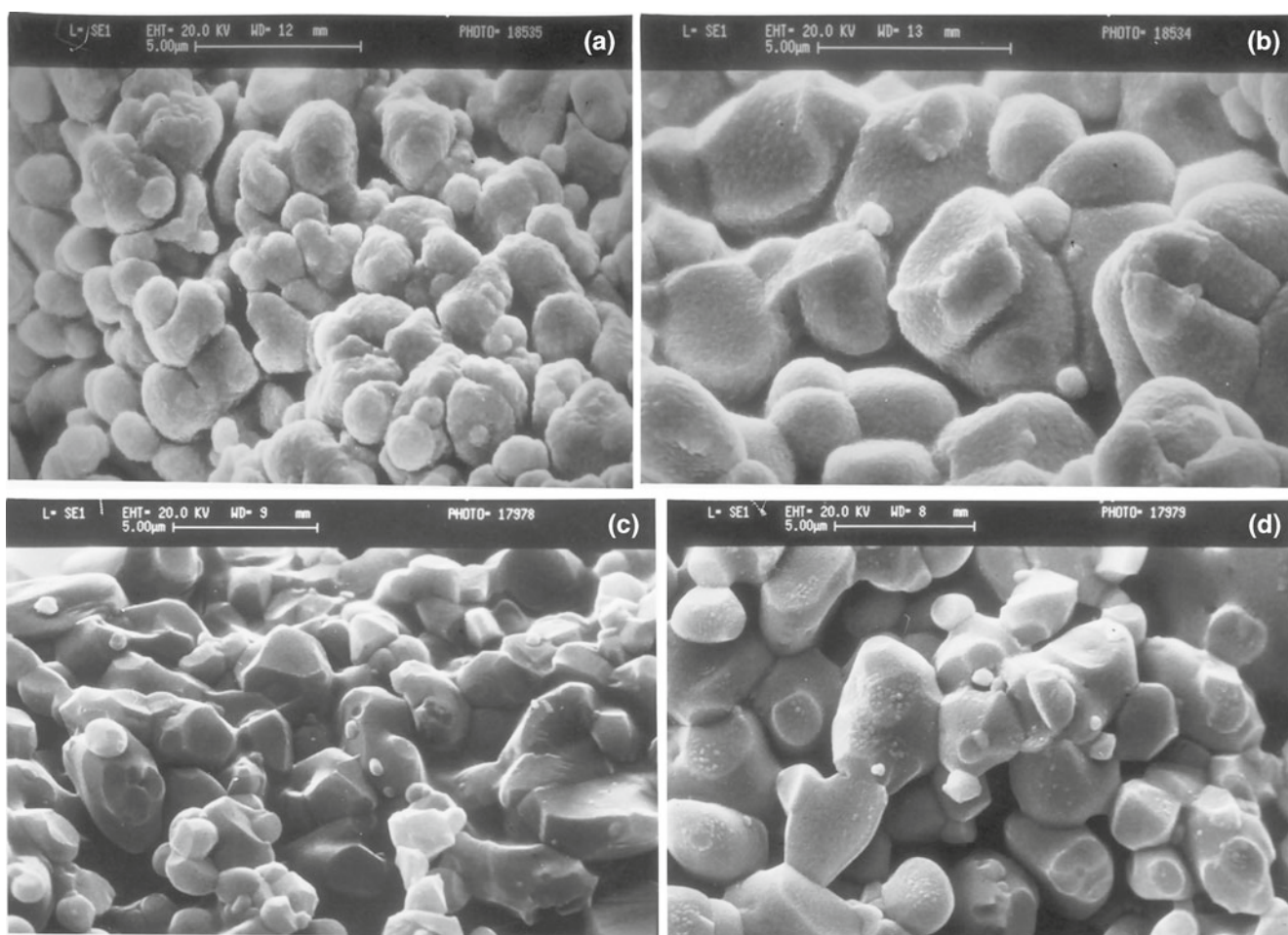
Figure 5. Scanning electron micrograph of sintered disk of (**a**) 1 mol %, (**b**) 2 mol %, (**c**) 5 mol % and (**d**) 10 mol % Na doped MgTiO$_3$ at 1100°C.

pattern, seems to appear at higher (10 mol %) dopant concentrations (figures 5d and 6d). These studies clearly show that the grain size increased as the percentage of Na and K dopants increased. The grain boundaries were also well defined in the doped magnesium titanate. The grain sizes of all the compounds have been given in table 1.

Measurement of dielectric properties of all the compounds, pure and doped MgTiO$_3$, was carried out on disks sintered at 1100°C in the temperature range from room temperature to 200°C. The variation of dielectric constant and dielectric loss with frequency in the range of 50 Hz to 500 kHz at room temperature are shown in figures 7a and b. The dielectric constant (ε) obtained was 14·8 and dielectric loss (D) was 0·0004 at 100 kHz for MgTiO$_3$ synthesized by the flux route and was quite similar to MgTiO$_3$ obtained by the solid-state method. The dielectric constant (ε) was stable in the entire range of frequencies irrespective of the preparative method. The dielectric loss (D) shows stability in the frequency range of 10–200 kHz. However, there is an increase in the dielectric loss beyond 300 kHz till 500 kHz, which may suggest a well-defined loss peak at higher frequencies (figures 7a and b). The dielectric constant was highly

stable in the entire temperature range from room temperature to 200°C, for MgTiO$_3$ prepared by either method (flux and solid-state) and is shown in figures 8a and b. The behaviour of dielectric properties of doped magnesium titanate with increase in the percentage of Na and K as dopants are shown in figures 9a and b. The dielectric constant was found to be maximum for 5 mol % of dopant. However, dielectric loss was higher for 1 mol % of Na doped magnesium tiatnate whereas in K dopant it was higher at 2 mol % composition. It is interesting to note that the variation of the dielectric constant with mol % of either 'Na' or 'K' is nearly identical. The initial decrease (minimum ε at 2 mol %) and then increase (maximum ε at 5 mol %) occurs for both the dopants (figure 9a). It may be noted that at higher concentration of dopant (5–10 %), the secondary phase MgTi$_2$O$_5$ starts forming. MgTi$_2$O$_5$ synthesized by the solid-state route under similar conditions as the other oxides discussed above, shows a dielectric constant of ~16 and loss of 0·04 at 100 kHz. The observed ε values at 5 mol % of Na and K dopants are much higher (18–21) than that observed for pure MgTiO$_3$ (~15) and that of MgTi$_2$O$_5$ (16). It appears that the grains are very densely packed at 5 mol % of dopant

Figure 6. Scanning electron micrograph of sintered disk of (**a**) 1 mol %, (**b**) 2 mol %, (**c**) 5 mol % and (**d**) 10 mol % K doped MgTiO$_3$ at 1100°C.

Table 1. Details of doped MgTiO$_3$ synthesized by solid-state route.

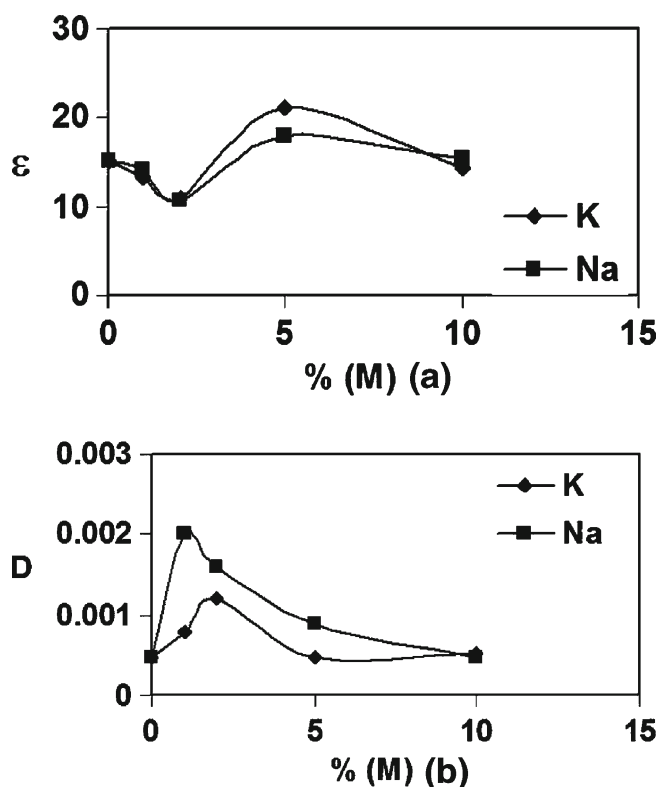| Dopant concentration	Secondary phase	ε (100 kHz)	D (100 kHz)	Grain size (μm)
None*	–	14·8	0·0004	2·5–3·5
None	–	15·0	0·00048	2–4
1 mol % Na$^+$	–	14·0	0·002	2–4
2 mol % Na$^+$	7% MgTi$_2$O$_5$	10·8	0·0016	3–6
5 mol % Na$^+$	7% MgTi$_2$O$_5$	18·1	0·0009	2–3·5
10 mol % Na$^+$	26% MgTi$_2$O$_5$	15·4	0·00046	4–5
1 mol % K$^+$	–	13·2	0·00078	1·5–3
2 mol % K$^+$	–	10·9	0·0012	3–6
5 mol % K$^+$	9% MgTi$_2$O$_5$	21·2	0·00047	1·5–3·5
10 mol % K$^+$	21% MgTi$_2$O$_5$	14·2	0·00052	3–5

* Prepared by flux method.

concentration as observed in SEM (figures 5c and 6c) and are well faceted. It may also be seen that the loss is quite low for this dopant concentration. Both the high dielectric constant and low loss may be rationalized by the well-sintered nature of the grains of this material containing 5 mol % of
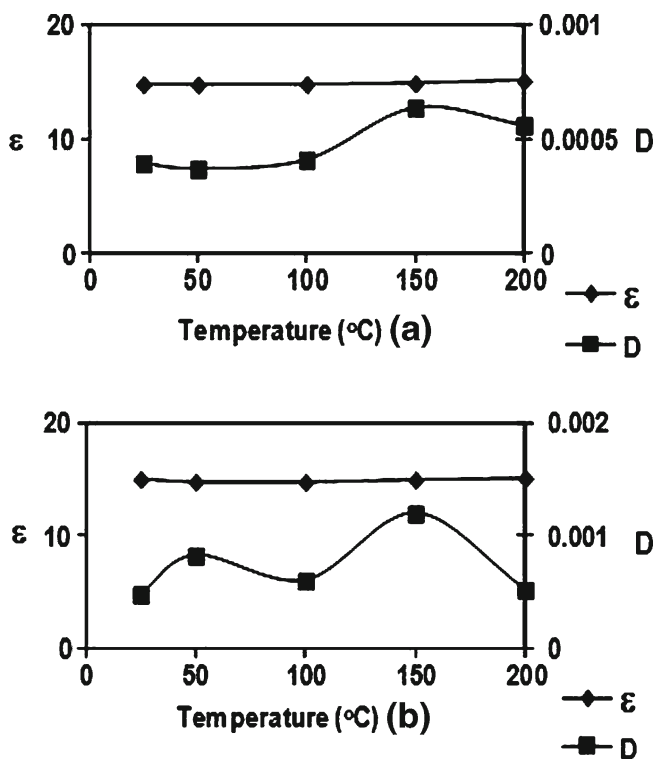
dopant. The minimum ε found at 2 mol % doping may also be correlated with the microstructure. SEM images of 2 mol % doping (figures 5b and 6b) show large grains where the surface morphology is very different from the well faceted grain obtained at 5 mol % of dopant (figures 5c and 6c). This
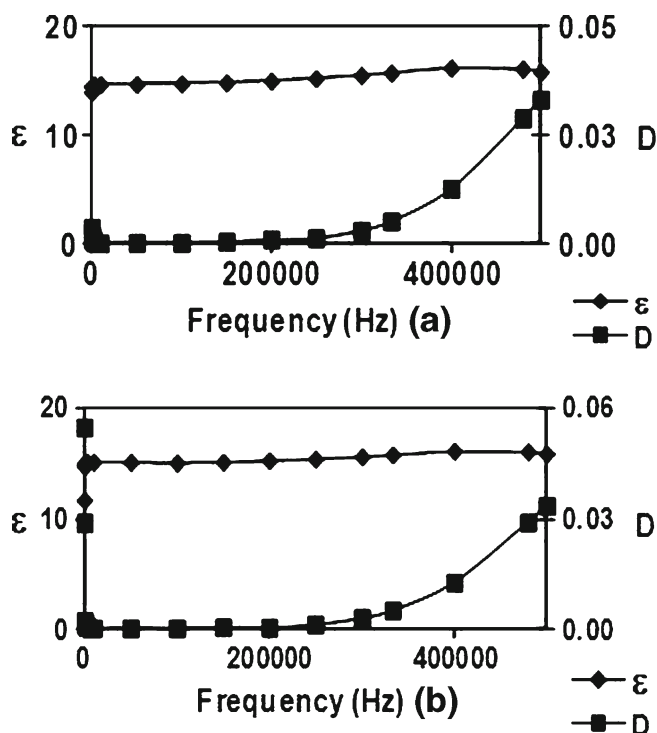
Figure 7. Variation of dielectric constant (ε) and dielectric loss (D) with frequency at room temperature for MgTiO$_3$ prepared by (**a**) flux method and (**b**) solid-state method.

Figure 8. Variation of dielectric constant (ε) and dielectric loss (D) at 100 kHz with temperature for MgTiO$_3$ prepared by (**a**) flux method and (**b**) solid-state method.

Figure 9. Variation of (**a**) dielectric constant (ε) and (**b**) dielectric loss (D) with mol % of dopant concentration (M) at 100 kHz.

may be due to small grains covering surface of the large grains. The different microstructures obtained may be due to difference in liquid phase wetting at the higher dopant concentrations.

4. Conclusions

We could obtain pure phase of MgTiO$_3$ using Mg(NO$_3$)$\cdot$6H$_2$O by both the flux and solid-state methods with the absence of MgTi$_2$O$_5$, an inevitable secondary phase in the solid-state synthesis of MgTiO$_3$. The dielectric loss was found to be almost the same in undoped MgTiO$_3$ irrespective of the preparative method. However, a small increase in the dielectric constant was observed in undoped MgTiO$_3$ obtained by solid-state method. The optimal dopant concentration (5 mol %) leads to higher dielectric constant and lower loss irrespective of the doped metal ion (Na or K). This is probably due to the increased sinterability of materials obtained at such dopant levels.

References

Cambier F, Leblud C and Anseau M R 1982 *Ceram. Int.* **8** 77

Ferreira V M and Baptista J L 1994 *Mater. Res. Bull.* **29** 1017

Ferreira V M, Azough F, Baptista J L and Freer R 1992 *Ferroelectrics* **133** 127

Heiao Y C, Wu L and Wei C C 1988 *Mater. Res. Bull.* **23** 687

Huang C L and Weng M H 2001 *Mater. Res. Bull.* **36** 2741

Iddles D M, Bell A J and Moulson A J 1992 *J. Mater. Sci.* **27** 1603

Kell R C, Greenham A C and Olds G C E 1973 *J. Am. Ceram. Soc.* **56** 352

Nomura S 1983 *Ferroelectrics* **49** 61

Plourde J K and Ren C L 1981 *IEEE Trans. Microwave Theory and Techniques* **29** 754

Sato T, Miyamoto R and Fukasawa A 1981 *Jap. J. Appl. Phys.* **20** 60

Subba Rao T, Murthy V R K and Viswanathan B 1990 *Ferroelectrics* **102** 155

Tamura H and Katsube M 1980 U. S. Patent 4224213

Wakino K 1989 *Ferroelectrics* **91** 66

Wakino K, Nishikawa T, Nishikawa Y and Tamura H 1990 *Br. Ceram. Trans. J.* **89** 39