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Phase analysis and dielectric properties of oxides obtained in the $MgO–(1–x)Nb_2O_5–(x)Ta_2O_5$ system

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Abstract. $MgNb_{2-x}Ta_xO_6$ ($0 \le x \le 2$) phases can be obtained as the major phase (75 to 90%) by solid state reactions starting from oxides. These oxides crystallize in the orthorhombic columbite structure till $x = 1{\cdot}75$ and the tetragonal trirutile structure for $MgTa_2O_6$ ($x = 2{\cdot}0$). For all the compositions there exist secondary phases like Nb_2O_5 or Ta_2O_5 in addition to the major AB_2O_6 phase. Sintered disks (1200°C) show dielectric constants varying between 14·8 and 16·0 for the entire range of composition at a frequency of 500 kHz. The dielectric loss is nearly constant around 0·025 to 0·03 between $0 \le x \le 1$ but increases to 0·17 for the $MgTa_2O_6$ phase ($x = 2{\cdot}0$). Scanning electron micrographs reveal a gradual decrease in grain size with increase in Ta concentration with a size of 3 micron for the $x=0$ composition (sintered at 1200°C) while the $x = 2$ phase shows a grain size of approximately 0·5 microns. The microwave dielectric constant at ~14 GHz is found to be 20·9 for the $x = 0$ composition and 17·7 for the $x = 2$ composition.

Keywords. Ceramics; electronic materials; oxides.

1. Introduction

Niobium- and tantalum-based oxides have been found to be good candidates for novel dielectric applications. Many of these oxides are complex ternary or quaternary niobium/tantalum containing compounds having ordered perovskite-related structures. Among them $Ba_3MgNb_2O_9$, $Ba_3MgTa_2O_9$, $Ba_3ZnTa_2O_9$ show excellent microwave dielectric properties[1–3]. The AB_2O_6 type of oxides where A is an alkaline-earth oxide and B is Nb or Ta have also been investigated recently for their microwave dielectric properties[4–6]. Most of the niobates of this type have the columbite structure while the tantalates have a variety of related structures depending on the A cation. For example $MgTa_2O_6$ has the trirutile structure while $CaTa_2O_6$ has the aeschynite and $ZnTa_2O_6$ has the tri-α-PbO_2 structure. Earlier studies[4–6] on AB_2O_6 type compounds (no solid solutions) have dealt with materials sintered at temperatures between 1300 to 1600°C for short time duration (2 h). However, the X-ray studies of the phases obtained and the secondary phases, if any, have not been reported so far. Here, we report our investigations on the formation of solid solutions between $MgNb_2O_6$ and $MgTa_2O_6$, at sintering temperatures of 1200 to 1300°C. We have analysed the type of phases using powder X-ray diffraction studies after each step. We also discuss the detailed dielectric properties of the sintered disks in the range of 40 Hz to 500 kHz (including the temperature dependence of the dielectric constant and dielectric loss of

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the $MgNb_{2-x}Ta_xO_6$ phases up to 300°C). Some of the compositions have also been studied at microwave frequencies (~14 GHz) at room temperature.

2. Experimental

Compounds belonging to the family $MgNb_{2-x}Ta_xO_6$ were prepared starting from stoichiometric amounts of MgO, Nb_2O_5 and Ta_2O_5. The oxides were thoroughly mixed by hand grinding and then loaded in alumina crucibles in a high temperature furnace for calcination at 1000°C for 30 h. The powder was then pelletized with PVA as binder and sintered in air at 1000°C for 48 h and then at 1200°C for 12 h. Powder X-ray diffraction patterns were obtained after each stage on a Phillips powder X-ray diffractometer at a scan speed of 2 deg/min using CuKα radiation. The lattice parameters were obtained by a least squares fit to the observed *d*-values. Scanning electron micrographs were obtained on a Cambridge Stereoscan 360 electron microscope. The densities measured by the Archimedes method were found to be around 92 to 94% of the theoretical density. The dielectric properties in the frequency range of 40 to 500 kHz were measured on disks coated with aluminium metal using an HP 4284L LCR meter. Temperature-variation was carried out in a cell (connected to the LCR meter) inserted in a small furnace which was controlled by a temperature controller. The high frequency dielectric constant of various samples were measured at ~14 GHz by coupling the dielectric resonator to a microstripline.

3. Results and discussion

We could obtain nearly 80 to 90% of the AB_2O_6 type phase in the $MgNb_{2-x}Ta_xO_6$ system for $x < 1$. For Ta-rich compositions the major AB_2O_6 phase is around 70 to

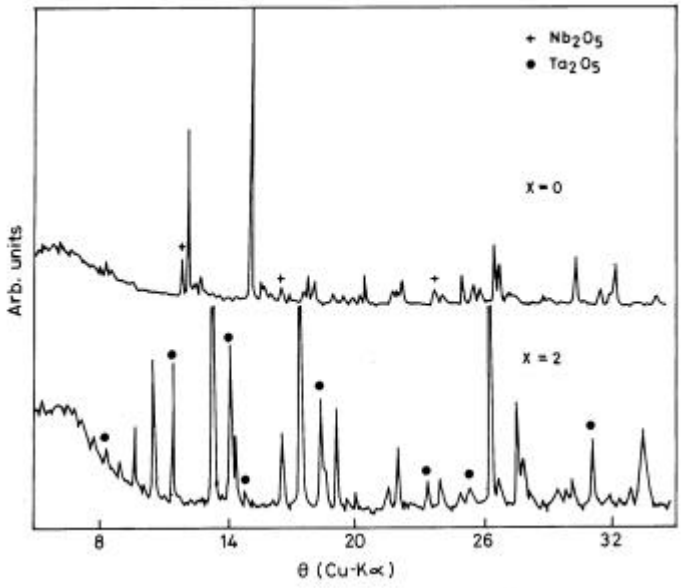

Figure 1. Powder X-ray diffraction patterns of oxides of the $MgNb_{2-x}Ta_xO_6$ system.

Table 1. Lattice parameters and crystal system for 1200°C heated samples belonging to $MgNb_{2-x}Ta_xO_6$ family.

Composition	System	Lattice constant	Impurity phase
$MgNb_2O_6$	Orthorhombic	a = 5·703(5) b = 14·142(6) c = 5·039(2)	Nb_2O_5 (13%)
$MgNb_{1·75}Ta_{0·25}O_6$	Orthorhombic	a = 5·666(5) b = 14·19(1) c = 5·040(3)	Nb_2O_5 (22%)
$MgNb_{1·5}Ta_{0·5}O_6$	Orthorhombic	a = 5·656(3) b = 14·152(6) c = 5·041(2)	Nb_2O_5 (16%)
$MgNb_{1·25}Ta_{0·75}O_6$	Orthorhombic	a = 5·693(6) b = 14·139(6) c = 5·035(3)	Nb_2O_5 (10%) Ta_2O_5 (18%)
$MgNbTaO_6$	Orthorhombic	a = 5·699(7) b = 14·15(1) c = 5·040(3)	Ta_2O_5 (28%)
$MgNb_{0·75}Ta_{1·25}O_6$	Orthorhombic	a = 5·676(6) b = 14·17(2) c = 5·026(4)	Ta_2O_5 (30%) Ta_2O_5 (18%)*
$MgNb_{0·5}Ta_{1·50}O_6$	Orthorhombic	a = 5·682(5) b = 14·16(1) c = 5·019(4)	Ta_2O_5 (29%) Ta_2O_5 (17%)*
$MgNb_{0·25}Ta_{1·75}O_6$	Orthorhombic	a = 5·665(5) b = 14·15(1) c = 5·022(3)	Ta_2O_5 (32%) Ta_2O_5 (20%)*
$MgTa_2O_6$	Tetragonal	a = 4·714(2) c = 9·199(5)	Ta_2O_5 (37%)

*On sintering at 1300°C

75%. Figure 1 shows the powder diffraction patterns of two compositions. The lattice parameters have been listed in table 1. We find that all the compositions till $x = 1·75$ crystallize in the orthorhombic columbite structure while the parent Ta phase ($x = 2$) crystallizes in the tetragonal trirutile structure. The lattice parameters do not show any appreciable change with composition. Presence of the Nb_2O_5 phase was observed in all Nb-rich compositions while Ta_2O_5 was observed for the Ta-rich phases at 1200°C. Some of the Ta-rich compositions when sintered at 1300°C showed a decrease of the secondary Ta_2O_5 phase (table 1).

Scanning electron micrographs of 1200°C sintered samples show grains of around 3 microns diameter for the pure Nb phase which decreases gradually as the concentration of Ta increases, being 0·5 micron for the pure Ta composition (figure 2).

In figure 3 we show the variation of the dielectric constant and dielectric loss with frequency at room temperature for some of the samples. The dielectric constant and dielectric loss both decrease with frequency. The dielectric constant does not vary much with composition (figure 4) lying in the range 14·8 to 16·0 at 500 kHz. The dielectric loss is nearly constant till $x = 1$ and varies between 0·025 and 0·035 at 500 kHz. The loss is somewhat higher for the $x = 2$ composition and has a value of 0·17.

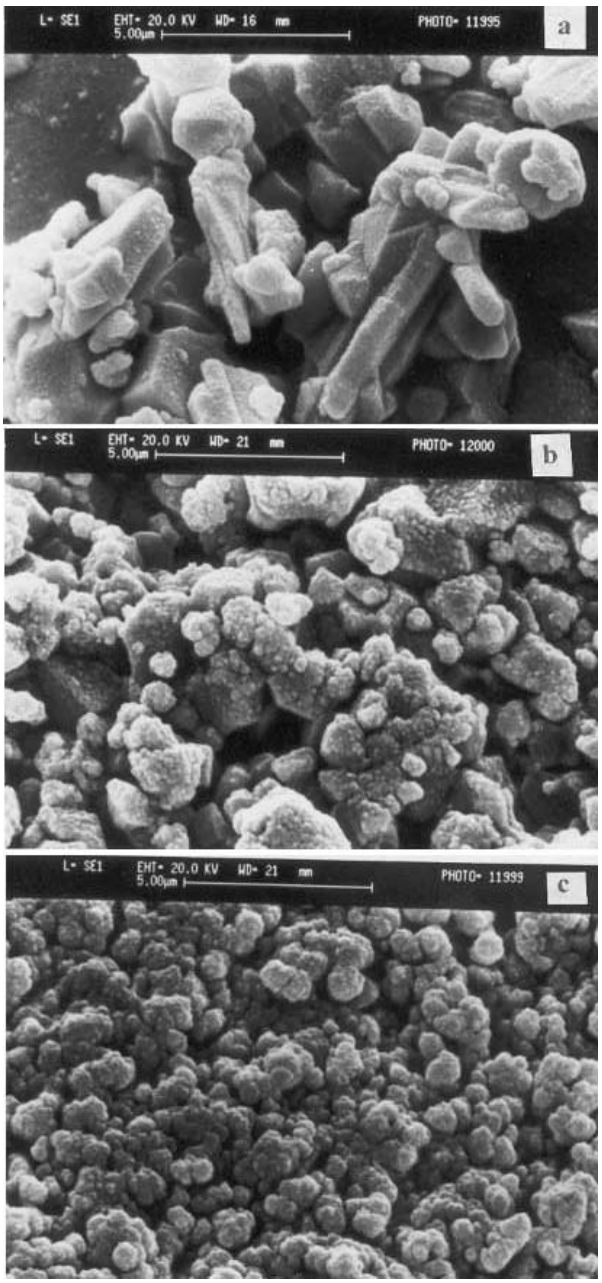

Figure 2. Scanning electron micrographs of samples sintered at 1200°C, (**a**) $MgNb_2O_6$, (**b**) $MgNbTaO_6$, (**c**) $MgTa_2O_6$

Dielectric properties for samples sintered at 1300°C were also obtained for selected samples to determine the effect of sintering temperature on dielectric properties. We find that there is no appreciable change in the dielectric properties of the samples sintered at 1300°C compared to that of materials sintered at 1200°C.

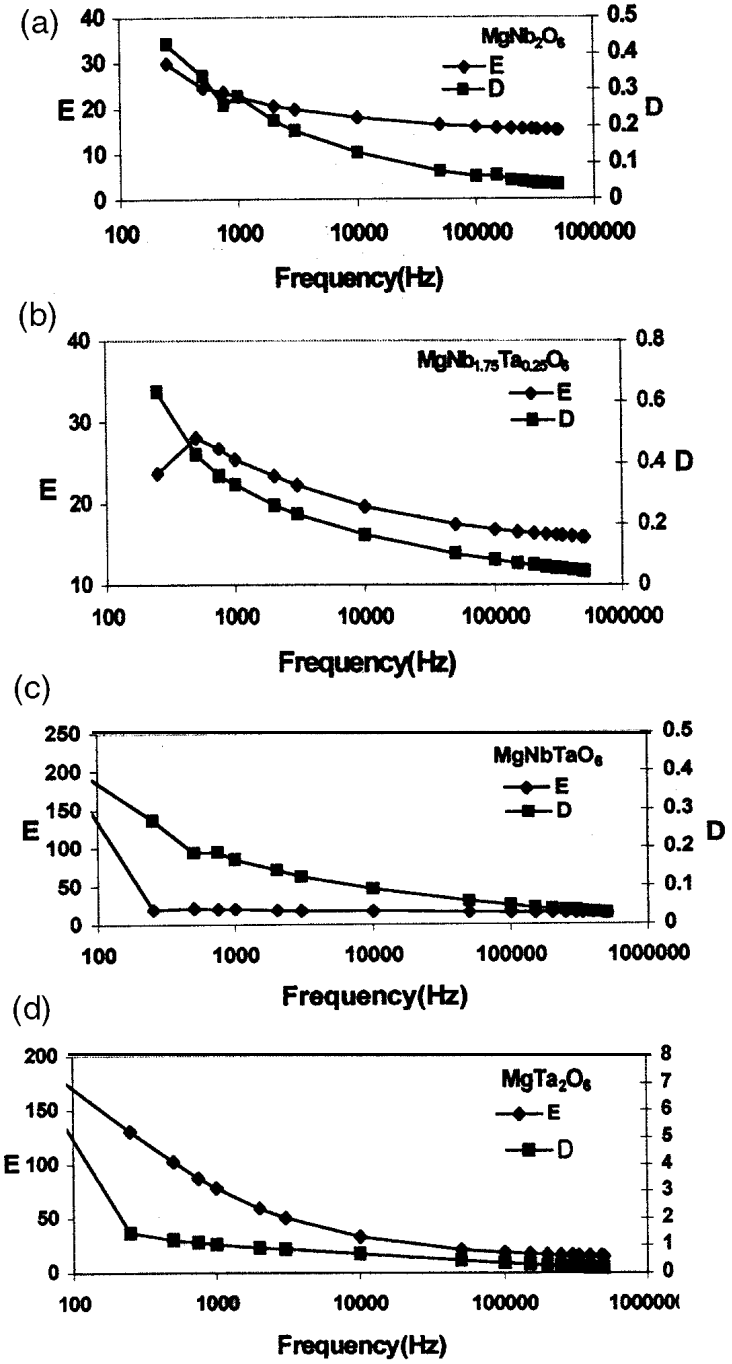

Figure 3. Plot of the variation of dielectric constant (*E*) and loss (*D*) with frequency at room temperature. (**a**) $MgNb_2O_6$, (**b**) $MgNb_{1.75}Ta_{0.25}O_6$, (**c**) $MgNbTaO_6$, (**d**) $MgTa_2O_6$.

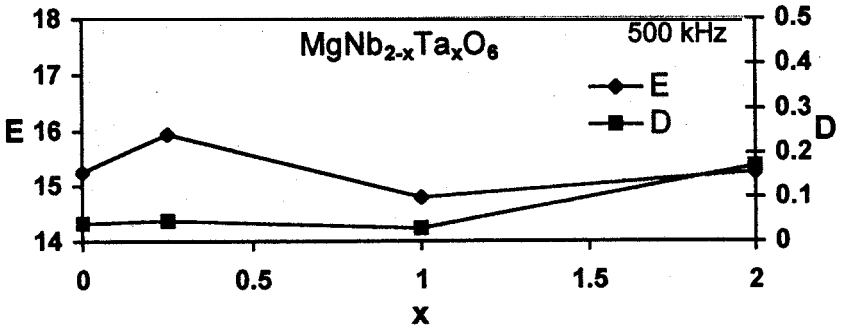

Figure 4. Plot of the variation of dielectric constant (*E*) and loss (*D*) with composition at room temperature and at a frequency of 500 kHz.

Temperature variation studies (over the entire range of frequencies) on some of the compositions (sintered at 1200°C) have been shown in figure 5. We find that the dielectric constant first decreases till 100°C after which it is nearly constant till 300°C. Similar behaviour is also seen with the dielectric loss. In both cases the dielectric loss is at a minimum at 150°C and the increase in dielectric loss beyond this temperature is marginal. Plots of dielectric constant and dielectric loss with temperature (at 500 kHz) for two compositions are shown in figure 6.

Dielectric measurements at gigahertz frequencies have been carried out for few samples of the $MgNb_{2-x}Ta_xO_6$ system at frequencies of 14·3 to 14·6 GHz. The dielectric constant decreases with Ta substitution in $MgNb_2O_6$ (sintered at 1200°C) at gigahertz frequencies (figure 7). The dielectric constants determined are 20·9, 19·4 and 17·7 for the $x = 0$, 0·25 and 2·0 samples respectively. These values can be compared to those known[6] at 10 GHz for the $x = 0$ and $x = 2$ samples and are 21·4 and 30·3 respectively. The smaller value of 17·7 for $MgTa_2O_6$ (in our studies) can be attributed to different density since sintering temperatures were 1200°C in our studies compared to 1550°C in the earlier ones[6]. However the dielectric constant for the $x = 0$ composition, $MgNb_2O_6$ matched quite well with that reported earlier[6]. The earlier study does not give X-ray evidence for the absence of impurity phases.

4. Conclusions

Solid solutions could be obtained for compositions in the $MgNb_{2-x}Ta_xO_6$ system. The $x = 2$ phase crystallizes in the tetragonal trirutile structure while a small amount of Nb stabilizes it in the orthorhombic columbite structure. All the samples have secondary phases. Unreacted Ta_2O_5 (~18%) persists even at 1300°C. The dielectric constant does not change significantly with Ta substitution ($\varepsilon_r \sim 15$) at 500 kHz. The loss shows a nearly constant value of around 0·03 till $x = 1$ but has a much larger value of 0·17 for the $x = 2$ composition. In addition to having the Ta_2O_5 impurity the small grain size of around 0·5 micron for the pure Ta phase compared to 2 to 3 micron for samples $x \leq 1$ may be responsible for the larger loss. Dielectric constant at microwave frequencies (~14 GHz) show a decrease from 20·9 to 17·7 for $x = 0$ to $x = 2$ compositions.

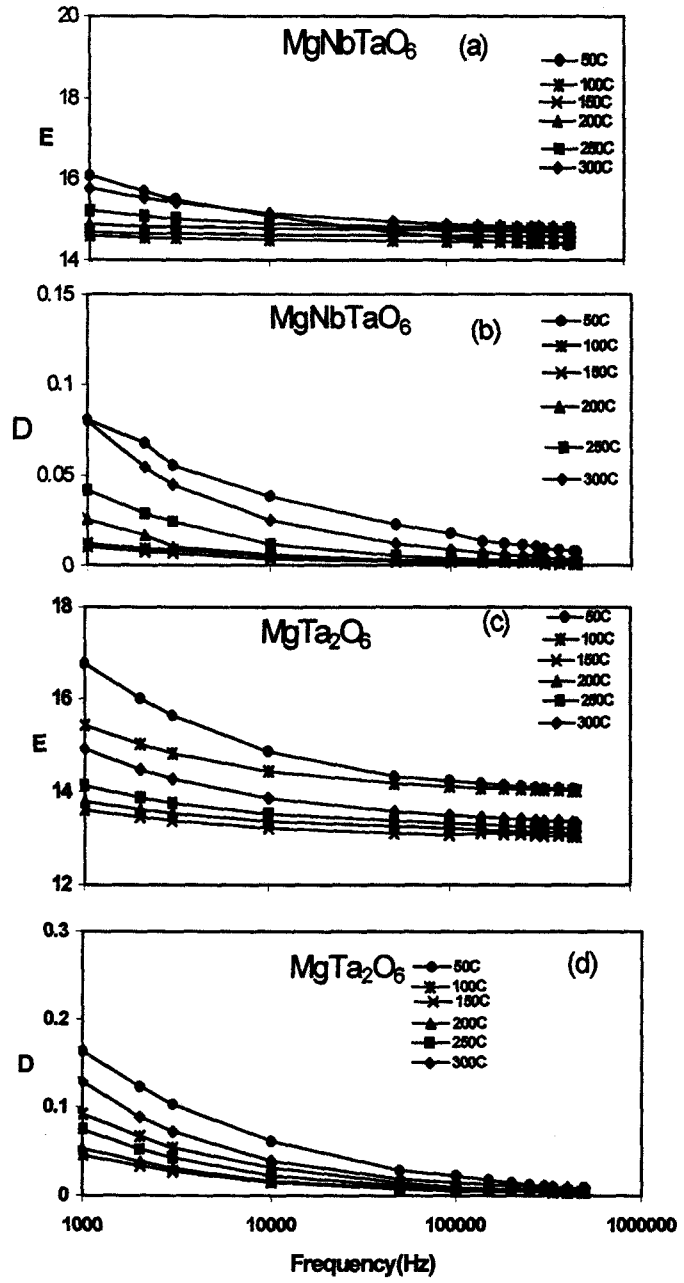

Figure 5. Plot of the variation of the dielectric constant (*E*) and dielectric loss (*D*) with frequency at various temperatures of (**a**) $MgNbTaO_6$ (dielectric constant), (**b**) $MgNbTaO_6$ (dielectric loss), (**c**) $MgTa_2O_6$ (dielectric constant) and (**d**) $MgTa_2O_6$ (dielectric loss).

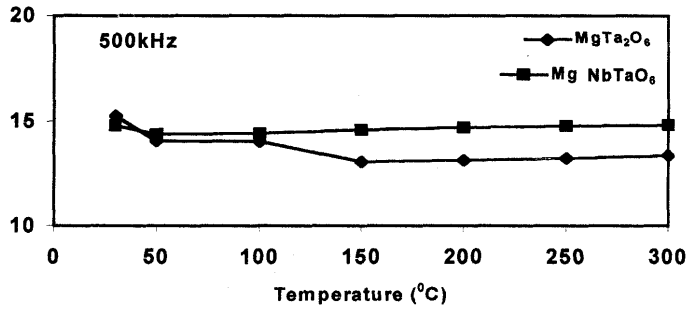

Figure 6. Plot of the variation of dielectric constant with temperature at 500 kHz.

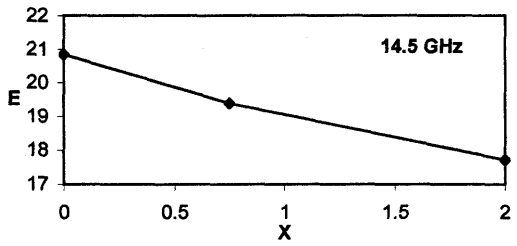

Figure 7. Plot of the variation of the dielectric constant (E) with composition at ~14·5 GHz.

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