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Dielectric Properties of (x) MgO-(1-y) Nb_2O_5-(5y/2) TiO_2 Ceramics [for x = 1-6 and y = 0-1] in the Microwave Frequency

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Abstract:
The precursors of $_{MgxNb2}O_{x+5}$ for x = 1-6 ceramics were prepared by conventional solid state reaction method. X-ray diffraction and scanning electron microscopic techniques were used for the characterization. Microwave dielectric properties of the samples were measured using an Agilent network analyzer. Better dielectric properties were observed for the series of $Mg_xNb_2O_{x+5}$ ceramics. Dielectric properties were tuned by the substitution of Nb_2O_5 with TiO_2 in the chemical formula (x) MgO-(1-y) Nb_2O_5-(5y/2) TiO_2 for x = 2, 3, 5 & 6 and y = 0-1.

Keywords: *Microwave dielectrics, perovskites, Fergusonite, Magnesium rare earth Niobate.*

1. Introduction

Dielectric ceramic is a fundamental component of filters, Global Positioning System devices, satellites and cellular phones. Cheap and nonetheless high performance dielectric ceramic resonators are needed for the development of microwave communication technologies. High relative permittivity (>10), high quality factor (>5000) [i,ii,iii,iv] and low temperature coefficient of resonant frequency (≤±10 ppm/°C) [v] are the requirements for a Dielectric resonator material in the microwave frequency field. Small dielectric constant is needed for reducing time delay (TPD) by the relation [vi] $\sqrt{\varepsilon_r}/c$. Mg based dielectric ceramics have low ε_r and high Q-factor compared to other ceramics. $Mg_4Nb_2O_9$ has attracted attention due to its low loss at microwave frequencies [vii,viii]. It has a potential corundum-type hexagonal structure. $MgNb_2O_6$ was reported [ix,x,xi,xii]with high quality factor with orthorhombic structure (space group = pnca). Y.C. You et.al. [xiii] reported that only $MgNb_2O_6$, $Mg_4Nb_2O_9$, $Mg_5Nb_4O_{15}$ and $Mg_2Nb_{11}O_{29}$[xiv]are the only stable phases at room temperature among the presently identified magnesium niobates. In the present study, we are reporting an interesting series of Magnesium-Niobium-Oxide system. Since titanium and niobium have same ionic radii, they play an interesting role in the magnesium-niobate precursor.

2. Experimental

Conventional solid state reaction method is used for the preparation of chemical formulae $Mg_xNb_2O_{x+5}$ for$x$ = 1-6 and (x)MgO-(1-y) Nb_2O_5-(5y/2) TiO_2 for x = 2, 3, 5 & 6 and y = 0-1. Magnesium carbonate hydroxide pentahydrate [$(MgCO_3)_4Mg(OH)_25H_2O$; Aldrich; 99% purity]; Niobium pentoxide [Nb_2O_5; Nuclear Fuel Complex, Hyderabad, India; 99.9%], and Titanium dioxide [TiO_2; Aldrich; 99.9%;] were used for synthesis of the ceramics. Ball milling for 24 hours and hand grinding were adopted for uniform stoichiometric mixing and powdering. The powders calcined at 1200°C/4h were ground well and shaped into cylindrical discs at a pressure of 150 MPa. Poly Vinyl Alcohol (3 wt%; BDH laboratory, Poole, England, molecular weight ≈ 22000, degree of hydrolysis ≥ 98%) solution was added to the ground powder as a binder. The compacts were densified at the temperature of 1350°C for 4 h.

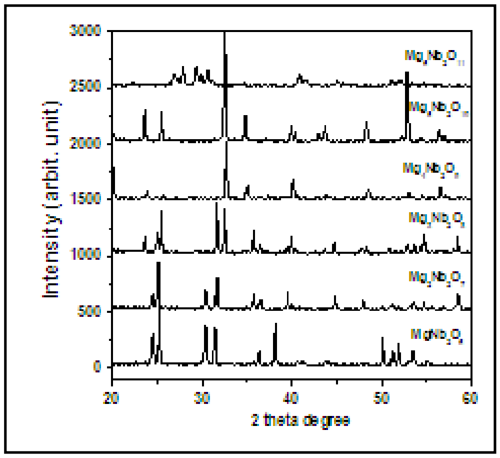

Figure1: X-ray diffraction patterns of $Mg_xNb_2O_{x+\delta}$ ceramics for x = 1-6

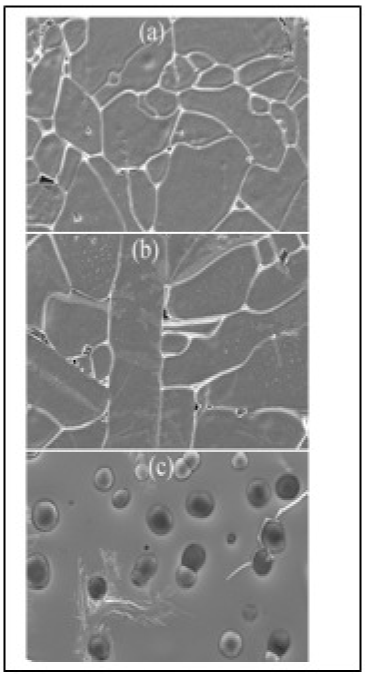

Figure 2: Micrographs of $MgNb_2O_6$, $Mg_4Nb_2O_9$ and$Mg_5Nb_2O_{10}$ ceramics

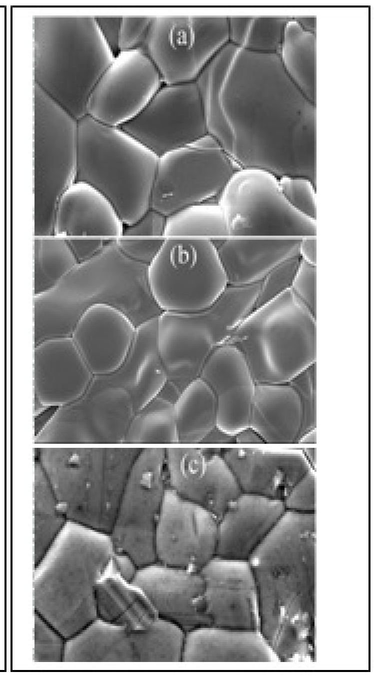

Figure 3: Micrographs of $Mg_2Nb_2O_7$, $Mg_3Nb_2O_8$ and $Mg_6Nb_2O_{11}$ ceramics

The bulk densities of the sintered samples were measured using Archimede's method. The phase purity and structure of the sintered and powdered samples were analyzed by X-ray diffraction method using Cuk$_\alpha$ radiation (Philips X'pert PRO MPD X- ray diffract meter; Philips, Eindhoven, The Netherlands). The surface morphology of the sintered, polished and thermally etched samples was examined using Scanning Electron Microscopy (JEOL-SEM 560LV, Tokyo, Japan) and the formed phases were analyzed by EDAX. Sintered and polished samples were used for microwave dielectric property measurements using an Agilent Network Analyzer (Agilent Technologies, Model No. 8753 ET, Inc., Palo Alto, California). The dielectric constant (ε_r) was measured by the post resonator method of Hakki and Coleman [xv] using $TE_{01\delta}$ mode of resonance coupled through E-field probes as described by Courtney [xvi]. The unloaded quality factor (Q_u) of resonance was determined using a resonance cavity method proposed by Krupka et al. [xvii]. The coefficient of temperature variation of resonant frequency (τ_f) was measured by noting the variation of resonant frequency of $TE_{01\delta}$ mode in the reflection configuration over a temperature range of 25-75^{o}C.

3. Results and Discussion

The $Mg_xNb_2O_{x+5}$ ceramics for x = 1-6 and y=0 in the composition (x) MgO-(1-y) Nb_2O_5-(5y/2) TiO_2were sintered in to a dense form on sintering at 1350^{o}C with relative density ≥95%. The X-ray diffraction pattern of $Mg_xNb_2O_{x+5}$ ceramics are shown in Figure 1.

The crystal structure of columbite type $MgNb_2O_6$was reported as orthorhombic [ix-xii] structure and corundum type $Mg_4Nb_2O_9$ was reported as hexagonal [vi]structure with space group pnca. A mixture phase of $MgNb_2O_6$ and $Mg_4Nb_2O_9$ was reported [xviii] in the synthesis of $Mg_4Nb_2O_9$. Such a mixture phase is not observed in this study. These two ceramics are attracted with their low loss at microwave frequencies. From Figure 1 it is observed that $Mg_2Nb_2O_7$ and $Mg_3Nb_2O_8$ have similar XRD patterns and more comparable to $MgNb_2O_6$. $Mg_5Nb_2O_{10}$ has a similar pattern as that of $Mg_4Nb_2O_9$ with some additional peaks of $MgTiO_3$. Among the series, $Mg_6Nb_2O_{11}$show an entirely different pattern, which has to be indexed. The surface morphology of this group of materials is shown in Figures 2&3. Micrograph of $MgNb_2O_6$ and $Mg_4Nb_2O_9$ are shown in Figs. 2a &2b in agreement with the previous reports [xviii].$Mg_2Nb_2O_7$ and $Mg_3Nb_2O_8$ have similar XRD patterns (Figs. 1b and 1c) and have similar micrographs (Figs. 3a & 3b). $Mg_2Nb_2O_7$ and $Mg_3Nb_2O_8$ ceramics show single phase grains with grain size nearly equal to 10-20 µm. Surface morphology of $Mg_5Nb_2O_{10}$ ceramic (Figure 2c) shows a mixture phase of $MgTiO_3$ and $Mg_4Nb_2O_9$. X-ray diffraction pattern of $Mg_5Nb_2O_{10}$ ceramic shows its main peak as that of $Mg_4Nb_2O_9$. It is evidenced by SEM-EDAX and can be observed in Figure 2c.$Mg_6Nb_2O_{11}$ ceramic has grains similar to that of $Mg_2Nb_2O_7$ and $Mg_3Nb_2O_8$ with the presence of an unidentified second phase. The $Mg_6Nb_2O_{11}$ ceramic has smaller grains (≈ 5-10 µm) compared to $Mg_2Nb_2O_7$ and $Mg_3Nb_2O_8$ ceramics. The X-ray diffraction pattern of $Mg_6Nb_2O_{11}$ ceramic (Figure 1f) is an entirely different one from the other ceramics in this series. Detailed study is needed to identify its structure.

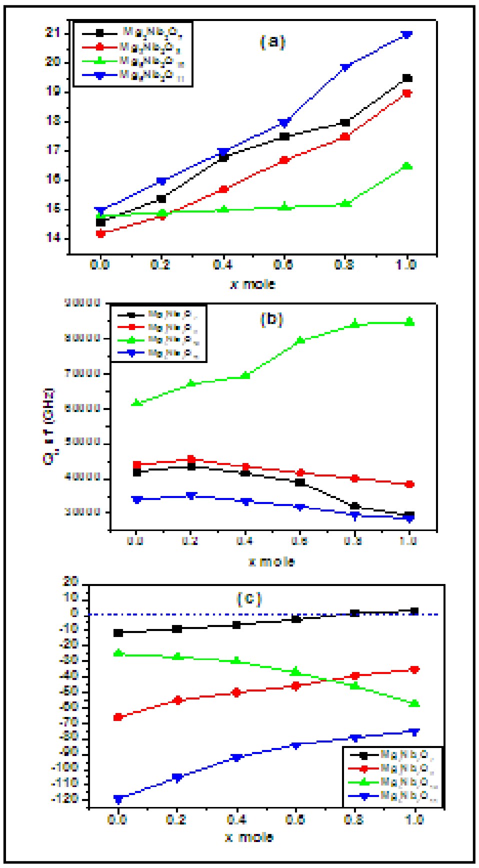

Figure 5: Variation in the dielectric properties of (x) MgO-(1-)Nb_2O_5-(5y/2) TiO_2 forx = 2, 3, 5 & 6 and y = 0-1.

material	Density (gm/cc)	ε_r	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
$MgNb_2O_6$	4.85	21.5	104600	-61
$Mg_2Nb_2O_7$	4.11	14.7	44000	-11
$Mg_3Nb_2O_8$	4.02	14.2	42000	-66
$Mg_4Nb_2O_9$	4.14	14.6	116000	-66
$Mg_5Nb_2O_{10}$	4.16	14.8	61500	-25
$Mg_6Nb_2O_{11}$	4.18	15.0	34000	-119

Table 1: Dielectric properties of $Mg_xNb_2O_{x+5}$ ceramics for x = 1-6

More over the synthesis and characterization of the series $Mg_7Nb_2O_{12}$, $Mg_8Nb_2O_{13}$, etc. are under study in our group. From the grain type of SEM pictures (Figs. 2&3) of $Mg_xNb_2O_{x+5}$ ceramics $MgNb_2O_6$, $Mg_4Nb_2O_9$ and $Mg_5Nb_2O_{10}$can be categorized in to one group (shown in Figure 2) and $Mg_2Nb_2O_7$, $Mg_3Nb_2O_8$ and

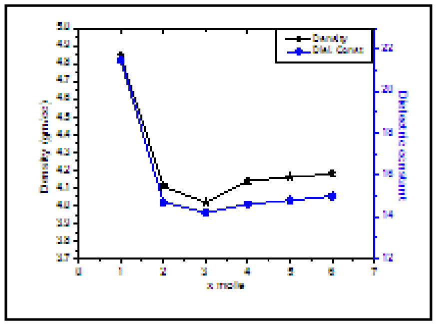

Figure 4: variation of density and dielectric constant of$Mg_xNb_2O_{x+5}$ ceramics for x = 1-6

$Mg_6Nb_2O_{11}$ in to another group (shown in Figure 3).

The density and microwave dielectric properties of $Mg_xNb_2O_{x+5}$ ceramics for x = 1 to 6 are shown in Table 1. The microwave dielectric properties of $MgNb_2O_6$ and $Mg_4Nb_2O_9$ ceramics were previously reported [xviii] with low dielectric constants and high Q-factors. It is in agreement with the present report. Figure 4 shows a corresponding variation of density and dielectric constant (ε_r) of $Mg_xNb_2O_{x+5}$ ceramics for x = 1 to 6. Among these compositions, $MgNb_2O_6$ ceramic has high dielectric constant (ε_r = 21.5). Density and ε_r of $Mg_xNb_2O_{x+5}$ ceramics decreases for x value up to 3 and then increases. ε_r of $Mg_xNb_2O_{x+5}$ ceramics vary from14.2 to 21.5, quality factor is in the range 34000-116000 GHz and the τ_f variation is -11 to -119 ppm/^{o}C (see Table 1).

- Tuning the dielectric properties of $Mg_xNb_2O_{x+5}$ ceramics [for x = 2, 3, 5 and 6]

We have previously reported the dielectric properties of $MgNb_2O_6$ and $Mg_4Nb_2O_9$ with the substitution of Nb_2O_5 with TiO_2, following the chemical formulae MgO-(1-y)Nb_2O_5-(5y/2)TiO_2 and 4MgO-(1-y)Nb_2O_5-(5y/2)TiO_2. In this report, the variation in the dielectric properties of $Mg_xNb_2O_{x+5}$ ceramics for x = 2, 3, 5 & 6was observed by the substitution of Nb_2O_5 with TiO_2, following the chemical formulae,

(x)MgO-(1-y)Nb_2O_5-(5y/2)TiO_2

for x = 2, 3, 5 & 6 and y = 0-1.

Figure 5a shows the variation of ε_r of $Mg_xNb_2O_{x+5}$ ceramics by the substitution of Nb_2O_5 with TiO_2, following the chemical formula (x)MgO-(1-y)Nb_2O_5-(5y/2)TiO_2 for x = 2, 3, 5 & 6 and y = 0-1. For$y$ = 1, $Nb_2O_5$is completely substituted by TiO_2.

With the introduction of TiO_2, the ε_r of the ceramics increased due to the presence of TiO_2 in the unreacted form. The ε_r of $Mg_5Nb_2O_{10}$ ceramic shows an increase (from 14.8 to 16) with the rutile introduction. This is due to the further formation of $MgTiO_3$ by reacting TiO_2 with the second phase MgO in the ceramic.$MgTiO_3$ has a low dielectric constant of ≈ 18.$MgTiO_3$ phase is observed in the XRD pattern of TiO_2 substituted $Mg_5Nb_2O_{10}$ sample (excluded here).

Figure 5b shows the variation in Q-factor of $Mg_xNb_2O_{x+5}$ ceramics for x = 2, 3, 5 & 6 by the substitution of Nb_2O_5 with TiO_2. The Q-factor of $Mg_xNb_2O_{x+5}$ ceramics for x = 2, 3 & 6 increases up to 0.2 mole of TiO_2substitution and then decreased while that of $Mg_5Nb_2O_{10}$ ceramic show a large increase up to 0.8 mole substitution (85500GHz) and then a slight decrease. This might be due to the high Q-factor of the newly formed second phase $MgTiO_3$ (Q_u×f ≈ 130000 GHz).

Figure 5c shows the variation of τ_f of (x)MgO-(1-y) Nb_2O_5-(5y/2) TiO_2 for x = 2, 3, 5 & 6 and y = 0-1. For$x$ = 2, 3 & 6, the τ_f of the ceramics show a trend of variation towards the positive side. This may due to the rutile content in the precursor.$Mg_2Nb_2O_7$ ceramic attained near zero τ_f with 0.8 mole TiO_2 substitution. TiO_2substitution shifted the τ_f of $Mg_5Nb_2O_{10}$ceramic to more negative side due to the formation of $MgTiO_3$(See Figure 5c).$MgTiO_3$ has a τ_f of -55 ppm/^{o}C [xviii].

4. Conclusion

A series of new $Mg_xNb_2O_{x+5}$ ceramics in the composition (x) MgO-(1-y)Nb_2O_5-(5y/2) TiO_2 for x = 2, 3, 5 & 6 and y = 0 were prepared in the solid state reaction method and their dielectric properties were reported. Dielectric properties of the series vary in the ranges ε_r = 14.2-21.5, Q_u×f = 34000-61500 GHz and τ_f = -11 to -119 ppm/^{o}C. By TiO_2 substitution (for y = 0-1), the negative τ_f of $Mg_xNb_2O_{x+5}$ ceramics (for x = 2, 3 & 6) shifted to positive side while that of $Mg_5Nb_2O_{10}$ ceramic to more negative side. $Mg_2Nb_2O_7$ ceramic attained near zero τ_f with 0.8 mole of TiO_2 substitution.

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