Dielectric properties of Fergusonite Mg-RE-Nb-O System (RE = La, Pr, Nb, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb) in the Microwave Region

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ABSTRACT: MgCO3-RE Oxide-Nb2O5 (in the ratio 2:1:1) with RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y and Yb were prepared by conventional solid state ceramic route. Structure and dielectric properties of the sintered samples were characterized by XRD and SEM techniques. The Mg-RE-Nb oxides have microwave dielectric properties in the ranges εr = 18 to 21, Qu×f = 17100 to 44400 GHz and τf = -0.3 to -69 ppm/oC. The Mg-La-Nb oxide has near zero τf (-0.3 ppm/oC) with εr = 21 and Qu×f = 23325 GHz.

KEY WORDS: microwave dielectrics, perovskites, Fergusonite, Magnesium rare earth Niobate.

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INTRODUCTION

Microwave dielectric materials been developed for wide applications in telecommunication such as mobile phones, wireless (LAN), intelligent transport systems (ITS) [1] and also an integral part of the cellular phone network. The dielectric characteristics required for a resonator are high relative permittivity in the range of 20-100 for miniaturization, high quality factor greater than 2000 for better selectivity and low temperature coefficient of resonant frequency in the range of –10 to +10 ppm/°C for stable functioning of the device [2]. They have wide microwave applications as oscillators, filters and waveguides in the range of frequencies (300 MHz to 13GHz). In millimetre frequency region small dielectric constant is needed for reducing time delay (TPD) by the relation [3], TPD = $\sqrt{\varepsilon_r}/c$. generally, Mg based perovskites have low ε_r compared to other Ba, Sr and Ca based materials. Ba, Sr and Ca based double perovskites

were studied by many authors, but Mg based similar composition was carried out under study first time in this report.

A wide range of dielectric materials have been developed for microwave applications [4,5,6,7,8,9] in the telecommunication industry. Larger size Ba/Sr in the A-site of ABO_3 type perovskites maintains the cubic structure [10] with the tolerance factor ≥ 0.98.

Perovskite structure of lower symmetry was reported [10,11] for values of $t \geq 0.87$ with cation like Ca^{2+} in A-site. High values of $Q_u \times f$ and ε_r, are needed for base station materials in the microwave range, but low ε_r is needed for wireless materials in the millimetre range. Therefore Mg based low ε_r materials are in demand for millimetre range applications. In this report, we prepared the ceramics oxides with Mg^{2+}, RE^{3+} [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] and Nb^{5+} in the ratio 2:1:1 and their microwave dielectric properties were investigated. The effect of Mg and RE deficiency on the microwave dielectric properties also investigated.

EXPERIMENTAL

Conventional solid state reaction method was adopted for preparing the powders of magnesium-Rare earth-Niobium Oxide (MRNO) samples. High purity powders magnesium carbonate [Aldrich; 99% pure], rare earth oxide [La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Yb_2O_3 [Treibacher; 99.9% pure] and niobium pentoxide [Nuclear Fuel Complex, India; 99.9% pure] were stoichiometrically weighed in the ratio 2:1:1 for the double perovskite type formula (Mg_2RENbO_6). The reagents were stoichiometrically weighed for the compositions Mg_2RENbO_6 [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb], $Mg_{2-x}EuNbO_{6-\delta}$

[x = 0, 0.5, 1, 1.5, 2] and $Mg_2Eu_{1-x}NbO_{6-\delta}$ [x = 0, 0.5, 1]. The raw materials were stoichiometrically weighed and ball milled for 24 h in a polyethylene bottle using zirconia balls and distilled water. The yielded powder mixtures were calcined in the temperature range 1150-1200^oC/4h depending on the composition. Heated powders were ground well and shaped into cylindrical compacts of 18 mm diameter and nearly 9 mm thickness at a pressure of 150 MPa. Poly Vinyl Alcohol (3 wt%; BDH laboratory, Poole, England) solution was added to the ground powder as a binder. 0.5 wt.% CeO_2 was added to the compositions as sintering aid for proper densification.

The green compacts were initially fired at a rate of 6^oC/min up to 600^oC. A dwell time of 30 minutes was given to expel the binder. Then heated at the same rate as before to the sintering temperature of 1350-1400^oC. The sintering temperature was chosen to get maximum density for all compositions. After a dwell time of 4 hours at the sintering temperature, the samples were slowly cooled at the rate of 3^oC/min to the room temperature. Their bulk density was measured using the Archimedes principle. The dielectric properties of the materials were measured in the microwave frequency range using a vector network analyzer (Agilent Technology). The variation of the resonant frequency of the TE01δ mode was studied heating the sample in the temperature range 25-75^oC. The phase purity and structure of the samples were analyzed by X-ray diffraction method using Cuk$_\alpha$ radiation (Philips X'pert PRO MPD X ray diffractometer). The surface morphology of the thermally etched samples was analyzed using Scanning Electron Microscopy (JEOL- Japan) and the formed phases were analysed by EDAX.

Dielectric properties (Q_u, ε_r and τ_f) of the sintered and polished samples were measured using an Agilent Network Analyzer (Agilent Technologies, California). The

dielectric constant (ε_r) was measured by Hakki and Coleman [12] post resonator method using $TE_{01\delta}$ mode of resonance coupled through E-field probes as described by Courtney [13]. The quality factor (Q_u) of the sample was determined using a resonance cavity method proposed by Krupka et al.[14]. The variation of resonant frequency (f_0) of $TE_{01\delta}$ mode in the reflection configuration over a temperature range of 25-75^oC was measured by the end shorted method [12,13].

RE-ion	$r_{(RE)}$ (^oA)	Tolerance factor (t)	%ρ	ε_r	$Q_u \times f$ (GHz)	τ_f (ppm/^oC)
La	1.032	0.6704	96.5	20.9	23325	-0.3
Pr	0.99	0.6768	96.3	20.4	27960	-32.3

RESULTS AND DISCUSSION

X-ray diffraction patterns of Mg-RE-Nb-oxides (MRNO) [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] heated at 1400^oC/4h are shown in Fig. 1. A systematic and regular pattern independent of the rare earth used could be observed. The ionic radii of RE-elements are given in Table 1. The cell volumes of MRNO ceramics vary linear to the ionic radii of RE-elements. The X-ray reflection peaks corresponding to MRNO

***Table 1**; The ionic radii of RE-ions ($r_{(RE)}$), Tolerance factor(t), relative density (%ρ) and dielectric properties of MRNO ceramics.*

Nd	0.983	0.6779	97.5	20.2	29225	-35
Sm	0.958	0.6817	97.6	19.8	35300	-43
Eu	0.947	0.6834	97.5	19.6	44400	-45.6
Gd	0.938	0.6848	96.2	19.3	19480	-46.2
Tb	0.923	0.6872	98.0	19.1	31625	-50
Dy	0.912	0.6889	97.8	18.8	28600	-51.8
Ho	0.901	0.6907	97.0	18.6	25650	-56.7
Y	0.900	0.6908	96.5	18.3	24480	-57.5
Er	0.890	0.6924	96.8	18	19500	-59.4
Yb	0.868	0.6959	97.8	17.8	17100	-69

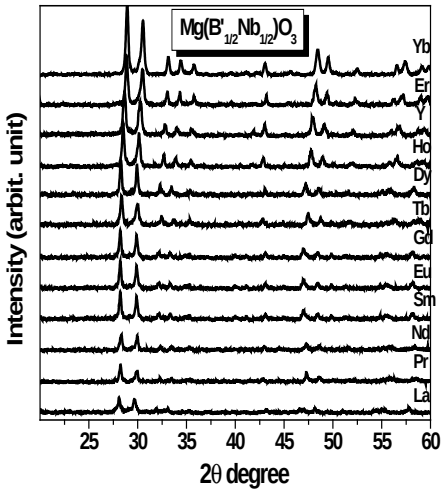

Fig.1; The X-ray diffraction patterns of Mg-RE-Nb-oxides (MRNO) [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] ceramics.

ceramics are very similar to the patterns observed for $RENbO_4$ [RE = La, Nd, Sm, Dy, Er, and Lu] with monoclinic fergusonite-type structure [15]. It is in agreement with the JCPDS file No. 22-1099 of $EuNbO_4$. An additional peak of MgO at $2\theta \approx 43^o$ is also observed in the pattern. The intensities of reflection peaks were found increased and they were shifted towards the higher angle side with the decrease of RE-ionic radii.

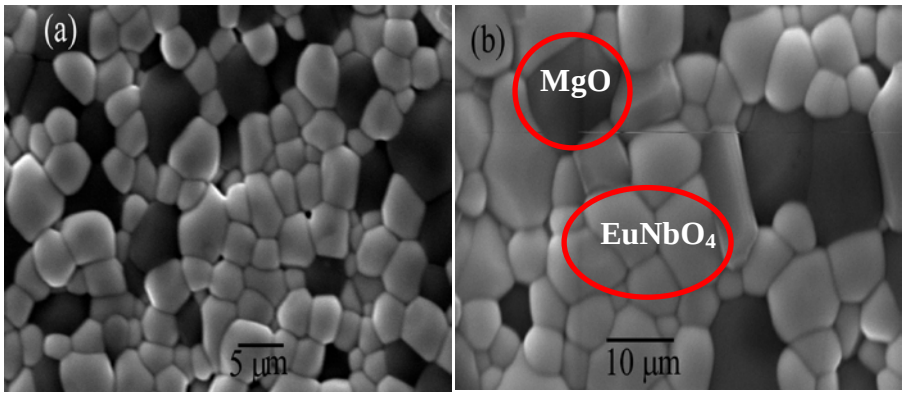

Fig. 2; *Microstructures of (a) pure and (b) 0.5 wt% CeO_2 added Mg-Eu-Nb oxide samples.*

This may be due to the structural transition to lower symmetry with decreasing ionic size of the RE elements. Similar shift of X-ray reflection peaks with decrease of cell volume

was reported by Kim et al.[16]. Though MNRO ceramic composition has similar composition of double perovskite (Mg:RE:Nb = 2:1:1), no perovskite peaks were observed in the XRD pattern.

SEM picture (Fig. 2) also showed two types of grains and by EDAX they were identified as those of $RENbO_4$ (white grains) and MgO (black grains). Similar types of grains were observed for all RE-based MRNO compositions. Based on the double perovskite composition of Mg-RE-Nb oxide with Mg^{2+} in the A-site and RE and Nb in the B-site, the tolerance factors of the compositions were calculated using the following equation and are shown in Table 1.

$$t = \frac{r_{Mg} + r_o}{\sqrt{2}} \left[\frac{r_{RE} + r_{Nb}}{2} + r_o \right]^{-1}$$

(where r_{Mg}, r_O, r_{RE} and r_{Nb} are the ionic radii [17] *of Mg^{2+}, O^{2-}, RE^{3+} and Nb^{5+} respectively)*

The tolerance factor values of MRNO ceramics were far deviated from the tolerance factor range of the perovskite structure (≥ 0.87). Tolerance factor of the present materials is in the range 0.6704-0.6959 (shown in Table 1). This conform the non perovskite structure of MRNO ceramics. Pure MRNO ceramics were densified to 93-95% of their theoretical densities. Addition of 0.5 wt% CeO_2 as sintering aid increased the relative density of these ceramics to 96-98% of their theoretical densities. The surface morphology (Fig. 2b) of Mg-Eu-Nb oxide shows the dense packing of grains with the addition of 0.5 wt% CeO_2 whereas Fig 2a shows that of the material without sintering aid. As the melting point of $CeO_2 \approx 2000^oC$, no liquid phase was expected. With the addition of CeO_2, the grain size was found increased. The relative density of MRNO ceramics with the addition of sintering aid is given in Table 1. Increase in density of the

ceramics with the addition of sintering aid correspondingly improved the microwave dielectric properties of the ceramics.

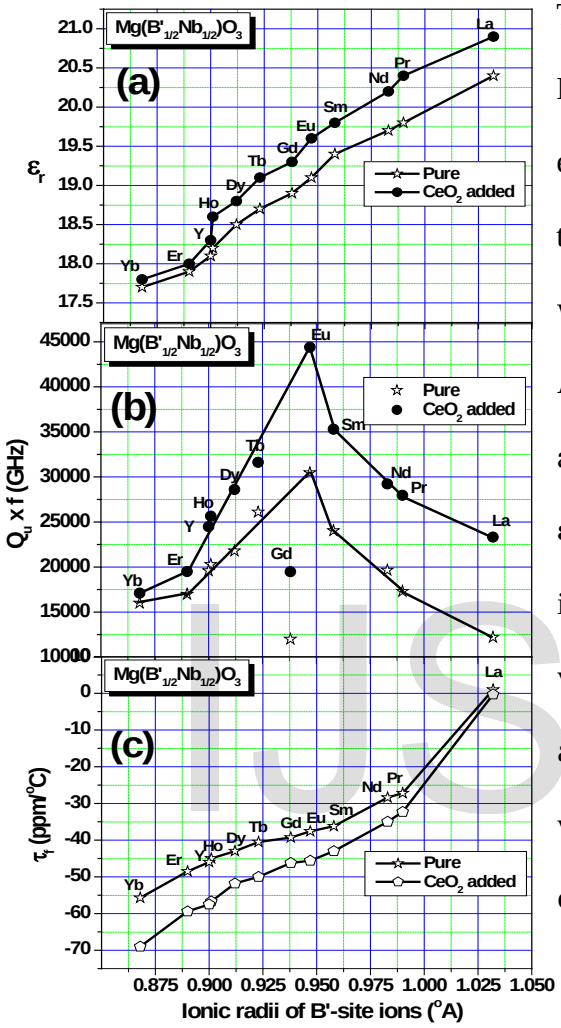

Fig. 3; Variation of (a) ε_r, (b) Q_u x f and (c) τ_f of pure and CeO_2 added MRNO ceramics.

The variations in the dielectric properties of MRNO ceramics versus ionic radii of RE elements are shown in Fig. 3. Fig. 3a shows the linear variation of ε_r of MRNO ceramics with and without the addition of CeO_2. Addition of CeO_2 increased the densification and hence ε_r of the material. The difference in ε_r between them slightly increases with the increases of RE-ionic radii. Fig. 3b shows the variation of Q-factor of MRNO ceramics with and without the addition of sintering aid versus RE-ionic radii. The $Q_u \times f$ of these ceramics increases as the RE elements vary from La to Eu and then decreases towards Yb. Gd based ceramics show an anomaly in the series as shown in Fig. 3b. Similar cases with RE = Gd were reported [9,18,19] for 1:1 type double perovskites. CeO_2 addition considerably increased the Q-factor of MRNO ceramics due to thick packing. Similar results were observed in the case of $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.33PbTiO_3$ also [20]. Mg-Eu-Nb oxide compound show highest Q-factor (44500 GHz) in this series. Here also, the difference in Q-factor of the samples with and without the sintering aid increases with the

increase of RE-ionic radii (see Fig. 3b). The linear variation of τ_f of MRNO ceramics with and without the addition of sintering aid is shown in Fig. 3c. The $|\tau_f|$ of MRNO ceramics decreases to nearly zero value as the RE-elements vary from Yb to La. The difference in τ_f of MRNO ceramics due to with and without CeO_2 addition decreases (as shown in Fig. 3c) as the RE-elements vary from Yb to La. The Mg-La-Nb oxide ceramic has near zero τ_f with and without CeO_2 addition (-0.3 and 1 ppm/^oC respectively).

CONCLUSIONS

Mg-RE-Nb oxide ceramics [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] were synthesized through conventional solid state reaction method by calcining the stoichiometric powders at 1200^{o}C/4h and sintering at 1400^{o}C/4h. The MRNO has been sintered in to dense form with the addition of 0.5 wt% CeO_2. The formed ceramics were a mixture of MgO and $RENbO_4$ with fergusonite structure instead of the expected perovskite structure. The MRNO ceramics have microwave dielectric properties in the ranges ε_r = 18 to 21, $Q_u \times f$ = 17100 to 44400 GHz and τ_f = -0.3 to -69 ppm/^{o}C. The Mg-La-Nb oxide has near zero τ_f with ε_r = 21 and $Q_u \times f$ = 23325 GHz.

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