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Tailoring the structural, optical, and dielectric properties of nanocrystalline niobate ceramics for possible electronic application

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Abstract

In the past decades, magnesium niobate materials have been extensively investigated due to their exceptional dielectric characteristics at microwave frequencies and are widely employed in microwave dielectric resonators. In present research, the nanocrystalline $MgNb_2O_6$ having an orthorhombic crystal structure with P b c n space group was successfully synthesized at 1000°C using a chemical route. X-ray diffraction (XRD), Raman spectroscopy, FESEM, impedance analyzer, and diffuse reflectance spectroscopy (DRS) were used to characterize the prepared phase. The average crystallite size, unit cell volume and the X-ray density of the prepared material were evaluated to be 52.55 nm, 407.65 Å^3 and 4.9865 g/cm^3, respectively. The molecular bending and stretching vibrations of metal oxide bonds were examined by Raman spectroscopy, which ranged from 232 cm^{-1} to 1007 cm^{-1}. FESEM analysis of the prepared ceramics revealed uniformly distributed grains with clear grain boundaries bearing the average grain size of 0.78 μm. A high direct band gap of 2.97 eV was investigated from DRS. The impedance analysis of the prepared phase revealed a decrease in the capacitance and dielectric constant between 40 Hz to 10 MHz. At 10 MHz frequency, the dielectric constant of the material was found to be 13.15. The loss tangent also displayed a systematic decrease with the increase in frequency from 40 Hz to 10 MHz.

1. Introduction

Controlling the desirable characteristics of dielectric nanomaterials has become crucial due to the rising need for novel devices, cost effective production, and excellent functionality. The investigation of certain properties, such as homogeneity, composition, grain size, etc., has focused interest on the development of dielectric compounds. Because of its good dielectric and room-temperature luminescence capabilities, $MgNb_2O_6$(MN_2) is thought to be a crucial material in the ceramics family. Some microwave and opto-electronic applications are rendered possible by these exceptional capabilities (Kakali et al.) In the past ten years, consider-

able research has been conducted to synthesize and examine these features for potential uses. Since the 1970s, magnesium niobite compounds have been researched to attain dependable dielectric properties (Kakali et al.). Norin et al. identified the niobate family oxides of magnesium as $MgNb_2O_6$, $Mg_4Nb_2O_9$, and $Mg_5Nb_4O_{15}$ (Norin et al.). According to You et al., the phases with stability amongst such oxides were $MgNb_2O_6$ and $Mg_4Nb_2O_9$ (You et al.). Due to its remarkable opto-electronic characteristics, magnesium niobate is widely employed in the fabrication of lead magnesium niobate, which has demonstrated advantageous for various device applications (Swartz and Shrout Joy and Sreedhar). According to earlier studies, minor amounts of $Mg_4Nb_2O_9$ or MgO are sometimes generated during the formation of $MgNb_2O_6$ (Sreedhar and Mitra). MN_2phase was obtained at 1140^{o}C using a chemical technique by Hsu et al. (Hsu et al.). Employing HF, Sarkar et al. produced $MgNb_2O_6$ and noted its good optical and dielectric abilities (Sarkar). Later, PMN (pyrochlore-free) ceramics with extremely intriguing dielectric characteristics were made using the produced MN_2 phase (Sarkar, V. Kumar, and Mukherjee). $MgNb_2O_6$ was also synthesized using a very productive improved combined oxide method by S. Ananta et al. (Ananta, Brydson, and W Thomas). We are aware that nanomaterials exhibit several intriguing features as a result of their tiny size and high surface energy. To increase the probability of enhanced ceramic implementations in microwave engineering and high optical characteristics, new production techniques are therefore required. Wet Chemical approach is one of the finest ways to create nano-$MgNb_2O_6$(MN_2) ceramics as solid-state reaction process needs a lengthy heat treatment. The aim of this research is to demonstrate how to synthesise nanocrystalline MN_2 efficiently using aqueous chemicals. In addition, this study work's additional objectives for potential applications include optical investigations and dielectric analysis.

2. Materials and Method

2.1. Synthesis of MgNb2O6 material

With Nb_2O_5 (purity 99.99 %), sodium hydroxide (NaOH), citric acid, and analytical-grade magnesium hydroxide, a successful chemical synthesis of $MgNb_2O_6$ material was accomplished. After using Nb_2O_5 as a source of niobium, Nb_2O_5 was added to NaOH. To create niobic acid solution, the mixture of glacial CH_3COOH, Nb_2O_5, and NaOH was first stirred at 80°C for 10 hours (Sarkar and Mukherjee). The niobic acid ($Nb_2O_5.nH_2O$) solution required the addition of citric acid to create the Nb-citric acid combination. To create transparent niobium citrate stock solution, the mixture was stirred at 25°C. This stock solution was combined with Mg $(OH)_2$, and the mixture of Nb^{5+} and Mg^{2+} was heated at 80°C while being constantly stirred to create a viscous liquid, which was subsequently evaporated at 100 ^{o}C to produce a yellow-white substance (Ananta, Brydson, and W Thomas). The chemically processed ceramics was heat-treated at 1000 ^{o}C to produce the ceramic phase of $MgNb_2O_6$. The flowchart of synthesis process is shown in Fig. 1 (Kakali et al.).

2.2. Characterization techniques

For structural characterization, Cu K XRD (Rigaku Ultima III, 40kV, 30mA) was employed. Raman spectroscopy (WITec GmbH alpha 300RS) was used to thoroughly investigate the sample by assessing molecular bonding. FESEM (Hitachi, S-4800) was used to morphologically examine the prepared materials. EDX (INCAX sight OXFORD) was used for elemental identification. Utilizing a diffuse reflectance spectrometer (Cary 5000 Instrument), optical behaviour was investigated, and the Agilent 4294A impedance analyzer was used to assess the dielectric characteristic.

3. Results and Discussion

3.1. Analysis by XRD

XRD characterized the heat-treated $MgNb_2O_6$ powdered materials employing a scan rate of 5°/min with a 2 θ range from 10^o to 70degrees. With minor secondary phases of $Mg_4Nb_2O_9$ and $Mg_5Nb_4O_{15}$, prominent peaks of crystallized $MgNb_2O_6$ were seen in Figure 2 XRD spectra of the $MgNb_2O_6$ phase produced by glacial acetic acid at 1000°C for 6 h. The crystal structure of $MgNb_2O_6$ was determined to be orthorhombic with the P b c n space group, and the crystalline phase was indexed with the COD ID 9012222. The diffraction planes have been ascribed as (200), (110), (111), (400), (311) (020), (411), (510), etc.

The strongest reflection was observed for (311), at 2θ = 30.26, among these diffraction planes. The d-spacing, lattice constants (a, b and c), the cell vol-

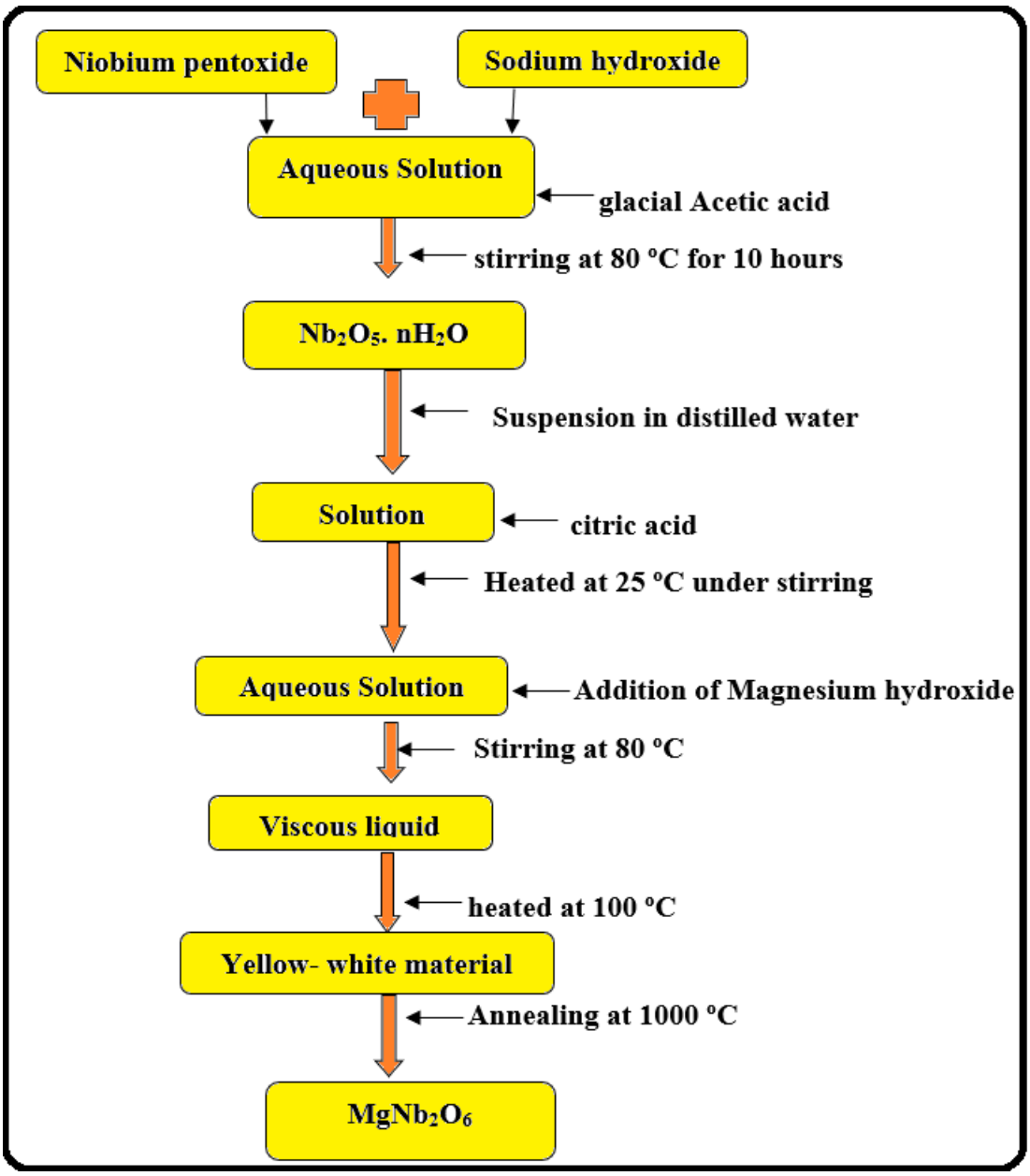

FIGURE 1. **Flowchart of synthesis process**

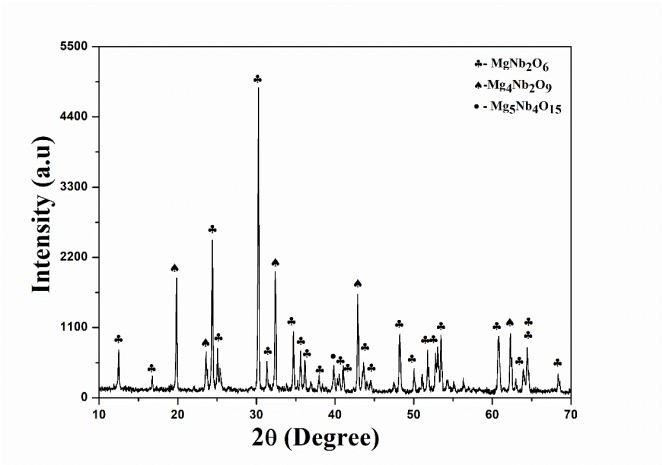

FIGURE 2. **XRD spectra of $MgNb_2O_6$ materials**

ume (V) and the X-ray density (D_x) have been calculated by the following equations:

$$n\lambda = 2dsin\theta \tag{1}$$

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2}\right) + \left(\frac{k^2}{b^2}\right) + \left(\frac{l^2}{c^2}\right) \tag{2}$$

$$V = abc \tag{3}$$

$$D_x = \frac{4M}{Na^3} \tag{4}$$

where, symbols have their usual definitions (Das et al.).

Equation 1 was used to calculate the d spacing for 2θ = 31.34 degrees, and the result was 2.8518 Å. Equation 2 and prominent hkl planes were used to calculate the lattice constants. The estimated values for lattice constants a, b, and c are 14.1512 Å, 5.7036 Å, and 5.0507 Å, respectively. Equation 3 was used to compute the unit cell volume, which resulted in a value of 407.65. Equation 4 was used to determine the X-ray density (D_x), which was estimated as 4.9865 g/cm^3. Using Scherrer's formula, $t = \frac{0.9\lambda}{\beta cos\theta}$ (V. Kumar et al.), where 't' and β describe crystallite size and FWHM, the crystallite size was determined to be 52.55 nm with regard to the greatest intensity peak. Table 1 contains entire structural parameters of $MgNb_2O_6$. Additionally, we prefer the W-H plot for niobate samples, which is shown in Fig. 3 and is stated in Equation 5 (Das et al.) to estimate the strain.

$$\beta cos\theta = \frac{K\lambda}{D} + 4\varepsilon \, sin\, \theta \qquad (5)$$

where, symbols have their general definitions. The lattice strain (ε) for the prepared material was found to be 6.92 $\times$ 10$^{-4.}$

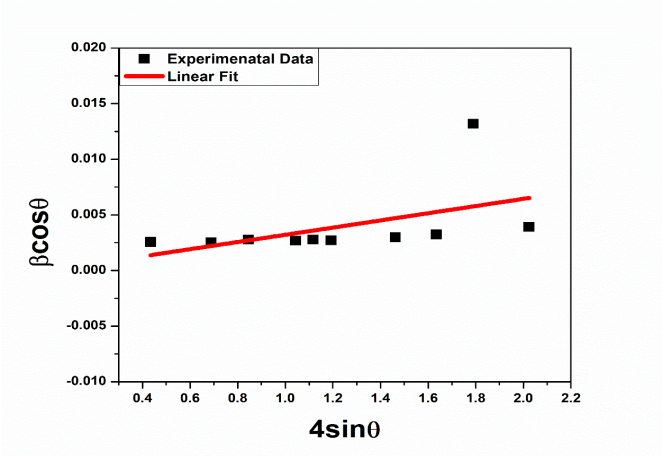

FIGURE 3. Williamson- Hall plot of $MgNb_2O_6$

3.2. Raman Spectroscopy

Using a confocal Raman scanning equipment, Fig. 4 shows the Raman shift of the prepared $MgNb_2O_6$ and lists the Raman vibration mode mappings (in cm^{-1}). Several bending and stretching vibrations of metal oxide bonds are seen in the Raman spectrum (Kakali, V. Kumar, and Mukherjee Sarkar et al.) in Fig. 4. The NbO_6 unit symmetric stretching vibration at 919 cm^{-1} predominated this spectrum. Nb-O bonds can be seen in the columbite

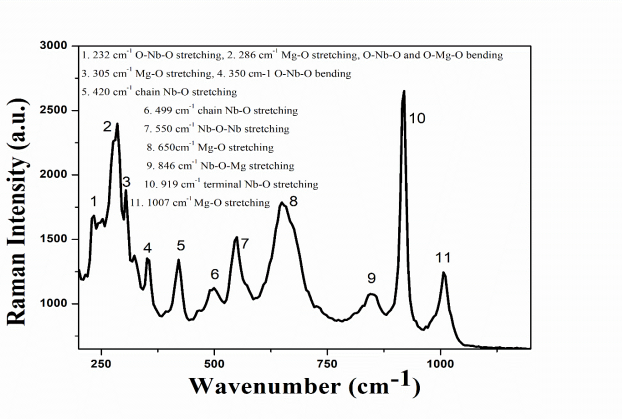

FIGURE 4. Raman shift of $MgNb_2O_6$

structure, where the edges and corners have been shared (Kakali, V. Kumar, and Mukherjee Sarkar et al.). Besides these, strong Mg-O stretching and O-Mg-O bending vibration bands are also present in Raman spectrum.

3.3. FESEM analysis

Figure 5 shows the FESEM morphology of the synthesized $MgNb_2O_6$ ceramics, where grain boundaries are clearly visible. Using Image J software, the mean grain size was determined to be 0.78 m. The histogram used to determine the average grain size is shown in the inset of Fig. 5. The microstructure clearly shows the merging of spherical particles.

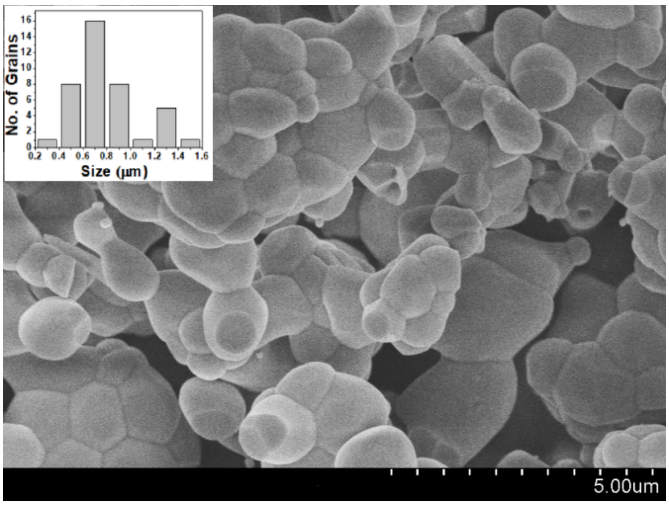

FIGURE 5. FESEM image microscope of $MgNb_2O_6$

3.4. EDX analysis

The atomic peaks of only Mg, Nb, and O were seen in the EDX analysis of nanocrystals of $MgNb_2O_6$, which are shown in Figure 6. This demonstrates

TABLE 1. Structural parameters obtained from XRD.

d-spacing (Å)	a(Å)	b(Å)	c(Å)	Cell volume(Å^3)	X-ray density (g/cm^3)	Crystallite size (nm)	Lattice strain ($\times 10^{-4}$)
2.8518	14.1512	5.7036	5.05.7	407.65	4.9865	52.55	6.92

the purity of the synthesized niobate compound. The estimated weight and atomic percentages of the present elements in $MgNb_2O_6$ are also shown in Table 2. This enables supportive evidence of the $MgNb_2O_6$ phase development.

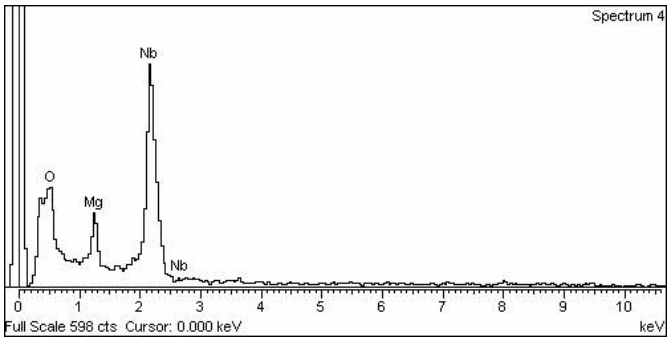

FIGURE 6. EDX spectrum of $MgNb_2O_6$

TABLE 2. EDX compositions of $MgNb_2O_6$

Element	Weight %	Atomic %
O K	34.20	69.42
Mg K	7.69	10.27
Nb L	58.11	20.31
Totals	100.00	

3.5. DRS analysis

In this study, direct band gap (E_g) was determined from DRS measurements spanning a 250–1500 nm wavelength range. The following equation was used to evaluate the function of reflectance (Sarkar, V. Kumar, and Mukherjee Kakali, V. Kumar, and Mukherjee Sarkar et al.):

$$F(R_\infty) = \frac{(1-R)^2)}{2R} \tag{6}$$

where, R = Reflectance and $F(R_\infty)$ = function of reflectance.

According to Fig. 7, E_g was estimated to be 2.97 eV considering the slope of the curve between $(F(R_\infty)\ h\nu)^{1/2}$and $h\nu$ (Sarkar, V. Kumar, and Mukherjee Kakali, V. Kumar, and Mukherjee Sarkar et al.).

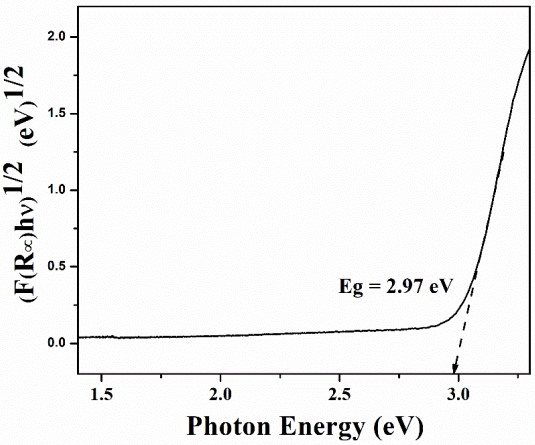

FIGURE 7. DRS curve of $MgNb_2O_6$

3.6. Dielectric Analysis

Figure 8 depicts the capacitance-frequency plot of $MgNb_2O_6$ pellet with applied ohmic contacts, where systematic decrease in capacitance (C) was observed with the increase in frequency. The dielectric constant ($k = \sqrt{\epsilon_r}$), inset of Fig. 8, was obtained from the value of capacitance, which also displayed a systematic decrease with the increase in frequency till 10 MHz. The relation between C and ϵ_r is expressed by the following equation:

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \tag{7}$$

where notations have their general meanings (Sarkar, V. Kumar, and Mukherjee).

The loss tangent, Fig. 9 also demonstrated a decrease with the rise in frequency. k rises at low frequencies as a result of the predominance of the dipolar and interfacial polarizations (Araújo et al. Boukhari, Khalaf, and Awad Sarkar, Mukherjee, and Mukherjee). These mechanisms typically take place as a result of the porosity, oxygen vacancies, and grain structures that result in the dielectric structure's inhomogeneity. Low dielectric constant and frequency-independent stability result from the decrease in dipolar polarization and increase in electronic polarisation at high frequencies (Araújo et al.

Boukhari, Khalaf, and Awad Sarkar, Mukherjee, and Mukherjee). The dielectric constant and loss tangent have been found to be 13.15 and 0.02 at 10 MHz.

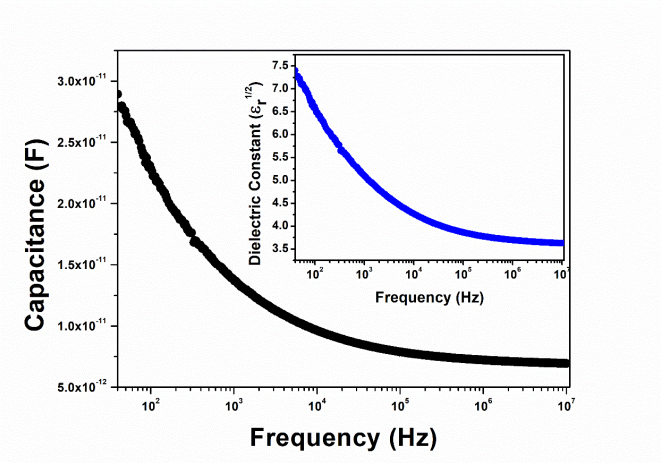

FIGURE 8. Capacitance and dielectric constant Vs Frequency of $MgNb_2O_6$

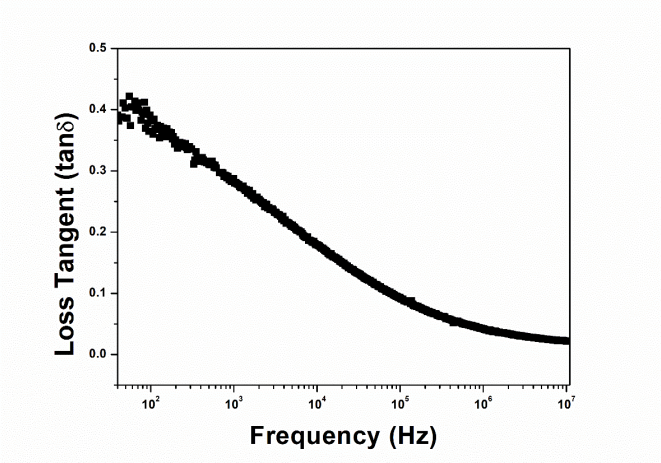

FIGURE 9. Loss Tangent Vs Frequency of $MgNb_2O_6$

4. Conclusions

Orthorhombic $MgNb_2O_6$ nanocrystalline ceramics was prepared by a chemical route, whose phase formation was identified by XRD with a crystallite size of 52.55 nm. Raman spectroscopy reveals various metal oxide bending and stretching vibrations confirming the successful synthesis of nanoceramics. FESEM analysis of the prepared ceramics revealed the merge of spherical grains with the average grain size of 0.78 μm. No elements other than Mg, Fe and O were observed from EDX analysis of $MgNb_2O_6$. A high band gap of 2.97 nm was observed, which may be due to the crystallites in nanoscale, and reflects the insulating behaviour of the prepared ceramics. Between 40 Hz and 10 MHz, the prepared phase capacitance and dielectric constant decreased, according to the impedance study. Additionally, the loss tangent showed a consistent decline from 40 Hz to 10 MHz frequency increase. The decrease in the capacitance and the dielectric constant may be due to the decrease in dipolar polarization and increase in the electronic polarization. The low dielectric loss and a high dielectric constant may facilitate its application in microwave dielectric resonators.

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