Synthesis, Characterization and Property Evaluation of Single Phase MgNb₂O₆ by Chemical route

Kakali Sarkar* and Siddhartha Mukherjee

Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata-700032, India

Email: kakaliece.nano@gmail.com

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ABSTRACT
Columbite - like MgNb₂O₆ single phase powder sample with orthorhombic crystal structure has been successfully synthesized by chemical process with starting material Nb₂O₅ and hydrofluoric acid (HF). MgNb₂O₆ is characterized by thermogravimetric and differential thermal analysis (TG- DTA), X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX). Optical behavior is studied by diffuse reflectance spectroscopy and dielectric property is also measured in this investigation. The effect of annealing temperature, phase formation, chemical composition, morphology, band gap energy and dielectric behavior of single phase MgNb₂O₆ are examined. Average crystallite and particle size of single phase MgNb₂O₆ material is measured around 40nm and 47.5nm from XRD and HRTEM analysis respectively. The direct band gap energy is measured about 3.01eV from diffuse reflectance spectroscopy analysis. Dielectric constant of MgNb₂O₆ material is obtained to be 21.20 at 110MHz frequency.

Keywords: Nanocrystalline MgNb₂O₆, Phase analysis, Chemical composition, Microstructure analysis, Optical Property, Dielectric Property

INTRODUCTION
MgNb₂O₆ (magnesium niobate) shows excellent dielectric properties at microwave frequencies [1–3] and it belongs to the binary niobate compounds. It finds its application in the microwave devices as it has very low dielectric loss and a high dielectric constant. Magnesium niobate having a columbite crystal structure is used for the waveguide fabrication [4–6] as a reference material for investigating the defects induced in LiNbO₃ substrates. Moreover, recently, MgNb₂O₆ is well known as the key precursor material for the successful preparation of single phase relaxor ferroelectric perovskite Pb(Mg₁/₃Nb₂/₃)O₃, which is becoming increasingly important for transducer, electrostrictor and actuator applications [7–11]. However, MgNb₂O₆ is normally prepared by the traditional solid-state route, and needs very high sintering temperature. Therefore, researchers have focused their works on the synthesis of MgNb₂O₆ powders by wet chemical methods [12–16]. The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Camargo et al. synthesized the MgNb₂O₆ powders using NH₄H₂NbO₆(C₂O₄)₂·3H₂O, 4MgCO₃·Mg(OH)₂·5H₂O, citric acid and glycol as raw materials [12]. Srisombat reported that MgNb₂O₆ powders with an average particle size of 100nm can be obtained using NbCl₅, MgCl₂·6H₂O and H₂O₂ by co-precipitation method [13]. More recently, Santos obtained MgNb₂O₆ powders with an average particle size of 60–70nm using niobium oxide penta-hydrated, oxalic acid and magnesium carbonate [14]. The expensive raw materials are used in the above research work. Therefore, it is necessary to discover an improved wet-chemical method to lower the materials cost for preparing MgNb₂O₆ powder.

In this research work, MgNb₂O₆ ceramic material is successfully synthesized by chemical process with low cost precursors and the heating temperature is comparatively lower than mixed oxide process (1150°C) [17]. The aim of this work is to highlight the successful synthesis of MgNb₂O₆ through chemical method, which to the best of our knowledge not much reported.

MATERIALS AND METHODS
2.1 Synthesis of MgNb₂O₆ material
MgNb₂O₆ material was successfully synthesized by chemical process with starting material Nb₂O₅ and Hydrofluoric acid (HF). In the first step, 1.06gm Nb₂O₅ was mixed with 5ml HF having 48% 

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concentration to form a solution in the Tarsons make container (100mL). 15ml Ammonia solution having 25% concentration was added to the above solution until the pH of the solution was up to 9. The solution was kept in the container for 1 hour. Then the solution was filtered and the residue was repeatedly washed with distilled water in order to get a pH value of 5. After washing the material was taken in a glass beaker and 100ml water was added. Further citric acid (2.51399gm) was added to form complexing reagent. The solution was further heated at 80°C under constant stirring for 3 hours. 0.2334gm of magnesium hydroxide [Mg(OH)$_2$] was added to this solution under constant stirring to get a viscous liquid at 80°C. Then the liquid was subjected to evaporation at 80°C to get yellowish white mass. Finally the chemically treated material was annealed at different temperatures to get MgNb$_2$O$_6$ crystalline ceramic phase.

2.2 Characterization techniques
Thermal analysis of the samples was done by TGA-DTA (Perkin Elmer, Pyris Diamond 480). Cu Ka XRD (RigakuUltima III, 40kV, 30mA) with a wavelength of 1.54Å, which is used for phase identification of the synthesized product. The material was further analyzed by using a confocal Raman imaging system (WITec GmbH) alpha 300RS to evaluate the compound formation. The chemical constituents were identified from EDX spectra (INCA- sight OXFORD Instrument). Morphological investigation of the prepared sample was done by FESEM using Hitachi, S-4800 Instrument. Inter-planer d-spacing and SAED pattern were observed by HRTEM analysis using JEOL, model JEM 2100. Optical behavior was studied using diffuse reflectance spectrometer (cary 5000 Instrument with 600nm/minute scan rate) and dielectric property was evaluated by Agilent 4294A with frequency range of 40Hz to 110MHz.

RESULTS AND DISCUSSION
3.1 Thermal Analysis by TGA-DTA
The thermal behaviour of the synthesized material is recorded in diamond cone TG-DTA with the programmable heating rate of 20°C/minute (Fig. 1). The endothermic peak at about 132°C in DTA is accompanied by 14% weight loss in TG in the temperature range 112- 224°C, is assigned to the loss of free moisture and other volatile fractions [18]. A weight loss of about 14% can be measured secondarily in the temperature range of 333- 479°C that is accompanied by an exothermic peak at 428°C in DTA curve. This exothermic peak originated due to the chemical reaction in presence of organic reagents and citric acid [18, 19]. The exothermic peak at 534°C in DTA curve is associated with the initiation of conversion of the amorphous gel to crystalline phase and also related to the formation of columbite oxide (MgNb$_2$O$_6$) phase [18]. The TGA shows the associated weight loss of about 8% over the temperature range of 479-694°C due to exothermic reaction.

Fig. 1: TGA-DTA curve of yellowish white sample at 20° C/min heating rate.
3.2 Phase Analysis by XRD and Raman Spectra Observations

3.2.1 Analysis by XRD

The phase formation is examined from X-ray diffraction analysis of heat treated MgNb$_2$O$_6$ powder samples. The formation of MgNb$_2$O$_6$ single phase columbite material is confirmed when treated at 1000°C (Fig. 2 (e)) and the respective sample is indexed with JCPDS card number PDF# 33-0875. The scan rate is maintained at 5°/min and the variation of 2θ is kept from 10-80°. This temperature and heating is much lower than that used in traditional mixed oxide reaction process (1150°C and >12 hours) for the formation of MgNb$_2$O$_6$.[17, 20].

Fig. 2(a) shows crystalline phase of Nb$_2$O$_5$ obtained from the yellowish white sample evaporated at 80°C. After annealing the evaporated material at 750°C for 6 hours (Fig. 2(b)), the maximum intensity peak of the respective sample is matched with the peaks of Nb$_2$O$_5$ (JCPDS PDF# 01-071-0005). Some MgNb$_2$O$_6$, NbO$_{2.432}$ (JCPDS PDF# 00-030-0870) and NbO$_{2.49}$ (JCPDS PDF# 00-030-0871) phases are also noticed having low intensity (Fig. 2(a) and Fig. 2(b)). Fig. 2(c) shows the XRD spectra of nanocrystalline MgNb$_2$O$_6$ sample annealed at 800°C for 6 hours. The respective sample has some phases of Nb$_2$O$_5$, NbO$_{2.432}$ and NbO$_{2.49}$ The phase of MgNb$_2$O$_6$ material is obtained at 900°C for 6 hours (Fig. 2(d)) with two peaks of Nb$_2$O$_5$. The MgNb$_2$O$_6$ nanocrystalline single phase formations are confirmed at 1000°C for 6 hours (Fig. 2(e)). Maximum intensity peak of MgNb$_2$O$_6$ crystalline phase is observed at 2θ = 30.42. The (hkl) plane and d-values are found to be (131) and 2.9579Å respectively. The crystallite size of the MgNb$_2$O$_6$ sample heat treated at 1000°C for 6 hours with respect to the maximum intensity peak is measured to be 40nm.

The experimental finding shows that a pure phase formation could be achieved by heat treating the samples at 1000°C for 6 hours in this novel chemical route.

Fig. 2: XRD Analysis of synthesized  (a) dried yellowish white sample (80°C) and annealed for 6 hours at (b) 750°C  (c) 800°C  (d) 900°C & (e) 1000°C.
3.2.2 Analysis by Raman Spectra

Fig. 3 represents the Raman shift of single phase MgNb$_2$O$_6$ sample at 1000°C for 6 hours using a confocal Raman imaging system. Raman vibration modes assignments (in cm$^{-1}$) for orthorhombic MgNb$_2$O$_6$ at 1000°C for 6 hours are shown in Table 1 in detail. From the Raman Spectra, the various modes of the oxygen octahedral are observed. The Raman Spectra are dominated by the symmetric stretching vibration of the NbO$_6$ unit at 924cm$^{-1}$. The columbite structure shows an original linking formation of the octahedral, in which the edges and corners are shared, allowing for the appearance of three types of Nb-O bonds. The terminal oxygen ($O_t$) is bonded to one Nb and two Mg atoms; the bridge oxygen ($O_b$) is bonded to two Nb and one Mg atom; and the chain oxygen ($O_c$) is bonded to three Nb atoms. So we can expect three kinds of Nb-O bond vibration. From the explanation of Raman Spectra we can strongly defend the formation of MgNb$_2$O$_6$ material [21].

3.3 Elemental Analysis by EDX (Energy Dispersive X-Ray Spectroscopy)

The atomic % and weight % of MgNb$_2$O$_6$ material are found out from EDX (Fig. 4). The atomic percentage for Mg, Nb and O are shown in table 2, which is very close to the stoichiometric ratio of pure MgNb$_2$O$_6$.

![Fig. 3: Raman shift of MgNb$_2$O$_6$ ceramic sample at 1000°C for 6 hours.](image)

Table 1: Raman vibration mode assignments (cm$^{-1}$) for orthorhombic MgNb$_2$O$_6$ at 1000°C for 6 hours

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Mode vibration</th>
</tr>
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<tr>
<td>253</td>
<td>Mg-O stretching, chain Nb-O stretching, O-Nb-O bending, O-Mg-O bending [21]</td>
</tr>
<tr>
<td>290</td>
<td>Mg-O stretching, O-Nb-O bending, O-Mg-O bending [21]</td>
</tr>
<tr>
<td>361</td>
<td>chain Nb-O stretching, Mg-O stretching, O-Nb-O bending [21]</td>
</tr>
<tr>
<td>426</td>
<td>chain Nb-O stretching, O-Nb-O bending [21]</td>
</tr>
<tr>
<td>502</td>
<td>Nb-O-Nb stretching [22]</td>
</tr>
<tr>
<td>554</td>
<td>Bridging Nb-O stretching [21]</td>
</tr>
<tr>
<td>645, 681, 1011</td>
<td>Mg-O stretching mode [23, 24]</td>
</tr>
<tr>
<td>866</td>
<td>Nb-O-Mg stretching [25]</td>
</tr>
<tr>
<td>924</td>
<td>terminal Nb-O stretching [21]</td>
</tr>
</tbody>
</table>
Fig. 4: EDX plot of MgNb$_2$O$_6$ crystalline ceramic material at 1000°C for 6 hours.

Table 2: Weight and atomic percentage of MgNb$_2$O$_6$ crystalline ceramic material.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>35.75</td>
<td>67.38</td>
</tr>
<tr>
<td>Mg K</td>
<td>12.85</td>
<td>10.94</td>
</tr>
<tr>
<td>Nb L</td>
<td>51.40</td>
<td>21.68</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 5: FESEM images of MgNb$_2$O$_6$ sample at 1000°C for 6 hours.

3.4 Microstructural Analysis by FESEM and HRTEM

3.4.1 Microstructural analysis by Field Emission Scanning Electron Microscopy (FESEM)
The grain size and structure of magnesium niobate (MgNb$_2$O$_6$) powder samples are examined by FESEM analysis. Grain morphology of MgNb$_2$O$_6$ powder sample prepared by chemical process at 1000°C for 6 hours is agglomerated in nature and irregular tends to spherical curvature in shape. Average grain size of MgNb$_2$O$_6$ material is around 185nm shown in Fig. 5 (b). The merge of spherical particle is quite prominent from the microstructure.

3.4.2 HRTEM (High Resolution Transmission Electron Microscope) Analysis
The microstructure, lattice image and SAED pattern of MgNb$_2$O$_6$ sample at 1000°C for 6 hours are observed by HRTEM analysis (JEOL, model JEM 2100) operated at 200 kV. The microstructure and average particle size of MgNb$_2$O$_6$ material are studied in detail.
The image confirms the clear irregular agglomerated nanoparticles with uniform distribution. The average particle size is measured to be 47.5nm as shown in Fig. 6 (a). The lattice image of the respective sample with interplanar d-spacing (2.947 Å) and diffraction planes (131) are clearly visible in Fig. 6 (b) which is matched with orthorhombic MgNb$_2$O$_6$ material (JCPDS card no. PDF# 33-0875). The SAED pattern of MgNb$_2$O$_6$ polycrystalline sample with different diffraction planes are confirmed in Fig. 6 (c). The sharp diffraction spots in the SAED pattern shows that the prepared sample is well crystallized.

3.5 Optical behavior Evaluation by diffuse reflectance

The direct band gap energy is measured from diffuse reflectance spectroscopy for solid sample in the reflectance mode over a range of 250 – 1500nm in this research work. For the band gap semiconductor, the equation is given below in the reflectance mode (Eqn 1):

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

Where, $R$ = Reflectance

The Fig. 7 shows the relationship of $(F(R_\infty)hv)^{1/2}$ and $hv$. The direct band gap energy is measured to be 3.01eV from the relationship [26].

Fig. 6: (a) Microstructure (b) Lattice image and (c) SAED pattern of MgNb$_2$O$_6$ sample at 1000°C for 6 hours

Fig. 7: Diffuse reflectance spectroscopy curve of MgNb$_2$O$_6$ ceramic material annealed 1000°C for 6 hours.
3.6 Dielectric Property Analysis

The frequency dependence of the dielectric constant is plotted in Fig. 8 (a) in the frequency range of 40Hz – 110MHz. The dielectric constant of MgNb$_2$O$_6$ sample is measured to be $\varepsilon_r = 21.20$ (at 110 MHz frequency) from dielectric property analysis. The decrease of $\varepsilon_r$ with frequency can be explained as follows; at low frequencies the dielectric constant $\varepsilon_r$ for polar material arises due to the multicomponent contribution of polarizabilities of deformational polarization (electronic and ionic polarization) and relaxation polarization (orientational and interfacial polarization). Similar observations were predicted by Shadhukhan [27].

When the frequency is increased, the dipoles will no longer be able to rotate rapidly enough, so that their oscillations begin to lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation polarization will be stopped, so $\varepsilon_r$ decreases at higher frequencies approaching a constant value due to the interfacial or space charge polarization only. Loss tangent (tanδ) versus frequency curve is shown in Fig. 8 (b) and cole-cole plot is shown in Fig. 8 (c). The decrease of tanδ with increase of frequency is clearly visible in Fig. 8 (b).

![Fig. 8: MgNb$_2$O$_6$ ceramic sample at 1000°C for 6 hours: (a) dielectric constant ($\varepsilon_r$) versus frequency (b) loss tangent (tanδ) versus frequency (c) cole-cole plot](image)

CONCLUSIONS

The phase formation of MgNb$_2$O$_6$ nanocrystalline ceramic precursor with orthorhombic crystal structure is obtained at 800°C for 6 hours by chemical route. The pure single phase MgNb$_2$O$_6$ ceramic compound is found at 1000°C for 6 hours. The average crystallite size is measured at 1000°C. The phase formation of MgNb$_2$O$_6$ is confirmed from XRD and Raman Spectra. The chemical composition and atomic percentage of Mg, Nb and O are obtained from EDX study, which is nearly closed to the stoichiometric ratio of pure magnesium niobate. The morphological structure, average grain size and average particle size of MgNb$_2$O$_6$ is measured from FESEM and HRTEM analysis. The direct band gap energy of pure magnesium niobate material synthesized at 1000°C is measured from diffuse reflectance spectra. The dielectric constant of MgNb$_2$O$_6$ single phase sample
is calculated to be $\varepsilon_r = 21.20$ (at 110 MHz frequency).

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