

Comparative study of dielectric properties of MgNb_2O_6 prepared by molten salt and ceramic method

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MS received 10 July 2003

Abstract. Magnesium niobate (MgNb_2O_6) powder was synthesized by the conventional ceramic route as well as by the molten salt route using a eutectic mixture of NaCl–KCl as the salt and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and TiO_2 as the starting materials. Pure phase of MgNb_2O_6 could be obtained by the molten salt method at 1100°C . However, in ceramic method the pure phase of MgNb_2O_6 was obtained by heating at 1025°C for 20 h. On sintering at 1100°C the dielectric constant and dielectric loss of MgNb_2O_6 obtained by the molten salt method was found to be 19.5 and 0.004 at 100 kHz at room temperature. Lower values were obtained for these oxides prepared by the ceramic route, 16.6 and 0.000518, respectively. In both cases the dielectric constant was quite stable with frequency.

Keywords. Ceramics; molten salt route; dielectric constant; dielectric loss.

1. Introduction

In recent years there has been considerable interest in developing dielectric ceramics for their use as resonators at microwave frequency due to the very fast growth of mobile communication systems (Ouchi and Kawashima 1985; Wakino *et al* 1990). Researchers have focussed attention towards the development of materials with high dielectric constant which would allow the reduction of the size of resonators. Since the wavelength (λ) of a dielectric resonator is inversely proportional to $\sqrt{\epsilon_r}$, where ϵ_r is the relative dielectric constant of the resonator (Lee *et al* 1997a; Hsu *et al* 2003), some typical examples of such materials are found in the $\text{BaO}-\text{Re}_2\text{O}_3-\text{TiO}_2$ (Sato *et al* 1987) and $(\text{Pb}_{1-x}\text{Ca}_x)\text{ZrO}_3$ (Wakino *et al* 1984) systems. Many complex perovskite compounds such as $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (Nomura *et al* 1982) and $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (Kawashima *et al* 1983) are also known to have good microwave dielectric properties.

Oxides related to the AB_2O_6 structure, where A is an alkaline-earth metal and B is either Nb or Ta, have also been studied for their microwave dielectric properties (Lee *et al* 1997a, b; Maeda *et al* 1987). Most of the niobium oxides related to AB_2O_6 have the columbite structure with *Pbcn* space group while the tantalates have a variety of related structures, which depends on the A-site cation. MgNb_2O_6 has been earlier investigated by Maeda *et al* (1987) and Lee *et al* (1997a). The microwave dielectric properties of this compound ($\epsilon_r \sim 21.4$, $Q \times f \sim 93,800$ GHz and $t_f \sim -70$ ppm/ $^\circ\text{C}$ at 1300°C ; Lee *et al*

1997a) are suitable for applications in dielectric resonators. Lee *et al* (1997a) have earlier synthesized MgNb_2O_6 at temperatures from 900 to 1025°C by high purity raw materials of Nb_2O_5 and MgO , by the ceramic route and sintered at 1300°C for 2 h in air. However, it has been reported that MgNb_2O_6 was synthesized at 1100°C by using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the source of Mg through conventional ceramic method (Thirumal and Ganguli 2001).

Due to the increasing demand of these materials there has been considerable research on development of easy and cost-effective synthetic methods for dielectric materials. The molten-salt synthesis or flux route had been used earlier to synthesize various oxides like $\text{BaFe}_{12}\text{O}_{19}$ (Arendt 1973), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Yoon *et al* 1995), $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Thirumal *et al* 2001). The flux route allows melt–solid reactions which are faster due to small diffusion distances and higher mobility of oxides in the melt. So reactions may be performed at lower temperatures.

In this paper, we report the synthesis of MgNb_2O_6 using the flux method. We have also synthesized the above oxide at lower heating conditions using the ceramic route by avoiding MgO or MgCO_3 (which have been used earlier) by using hexahydrated magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) instead. A comparative study of the dielectric properties of MgNb_2O_6 obtained by the ceramic route and by the molten salt route is discussed.

2. Experimental

Stoichiometric ratio of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck 99%), and TiO_2 (Fluka 99%), NaCl (Merck 99%) and KCl

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(Merck 99%) were used for the synthesis of MgNb_2O_6 . In the molten salt method stoichiometric amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck 99%), and TiO_2 (Fluka 99%) were used along with eutectic mixture (1 : 1) of NaCl – KCl . The weight of reactant to the salt mixture was in the ratio of 2 : 1. The reactants were thoroughly ground in an agate mortar and then loaded in alumina crucibles in a programmable furnace at 900°C for 6 h. The product was then washed several times with chloride-free hot distilled water to remove salt. The powder was further heated at 1000°C for 20 h and 1100°C for 24 h with intermittent grinding. In the ceramic method, stoichiometric ratio of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and TiO_2 were taken in an agate mortar and properly homogenized. The homogenized mixture was first heated at 900°C for 12 h and was further heated at 1025°C for 20 h. The powder samples of MgNb_2O_6 synthesized by molten salt method and ceramic method were treated with polyvinyl alcohol (PVA) and then pelletized at a pressure of 8 tonnes and sintered at 1100°C for 12 h. Powder X-ray diffraction studies were carried out after each stage of heating on a Bruker D8 advance X-ray diffractometer. The refined lattice parameters were obtained by a least square fit to the observed d -values. Scanning electron micrographs (SEM) were obtained on the sintered disks using a Cambridge Stereoscan 360 electron microscope. The dielectric properties (dielectric constant and dielectric loss) were measured on sintered pellets (coated with Ag-paste as electrodes) using an HP 4284L LCR meter in the frequency range of 50–500 kHz,

at varying temperatures (35 – 200°C). The density of sintered pellets of MgNb_2O_6 were measured by Archimedes principle and the relative density was found to be around 91% and 92%, respectively of theoretical density.

3. Results and discussion

Magnesium niobate was synthesized by both the ceramic and molten salt methods. These compounds were analysed by powder X-ray diffraction. In case of the molten salt synthesis, after the first heating stage (900°C for 6 h) nearly 60% of $\text{Mg}_4\text{Nb}_2\text{O}_9$ was present which decreases to 12% after heating at 1100°C . Pure phase of MgNb_2O_6 was obtained after a further heating at 1100°C for 12 h (figure 1). Magnesium niobate synthesized by the ceramic route led to a biphasic mixture with 12% impurity of $\text{Mg}_4\text{Nb}_2\text{O}_9$ along with the major phase after heating at 900°C . Further heating at 1025°C led to a single phase. The powder diffraction pattern of MgNb_2O_6 prepared by ceramic method at 1025°C has been shown in figure 2. All the peaks could be indexed satisfactorily in the orthorhombic cell as known for the columbite structure of MgNb_2O_6 . The refined lattice parameters were found to be as follows: ' a ' = $14.170(6)$, ' b ' = $5.680(3)$, ' c ' = $5.022(2)$. This is similar to a previous study (Thirumal and Ganguli 2001) where single phase formation occurred at a lower temperature (1100°C) using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as a starting material. MgNb_2O_6 is normally prepared at 1300°C using MgO and Nb_2O_5 oxides.

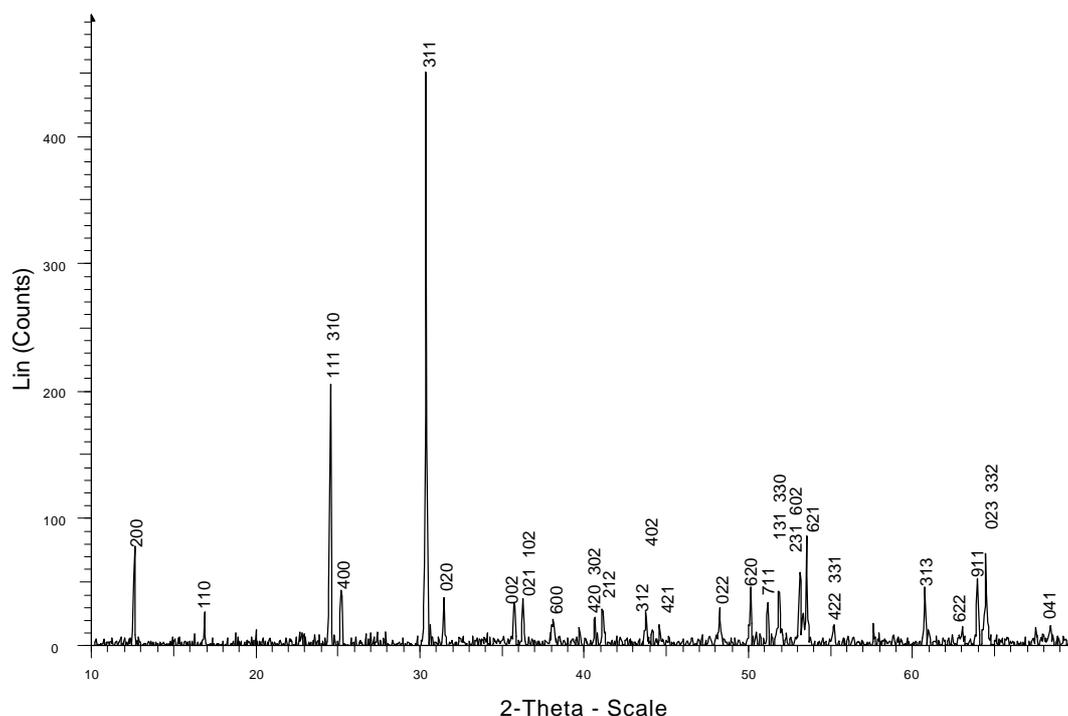


Figure 1. Powder X-ray diffraction pattern of MgNb_2O_6 prepared by the molten salt method after 1100°C heating.

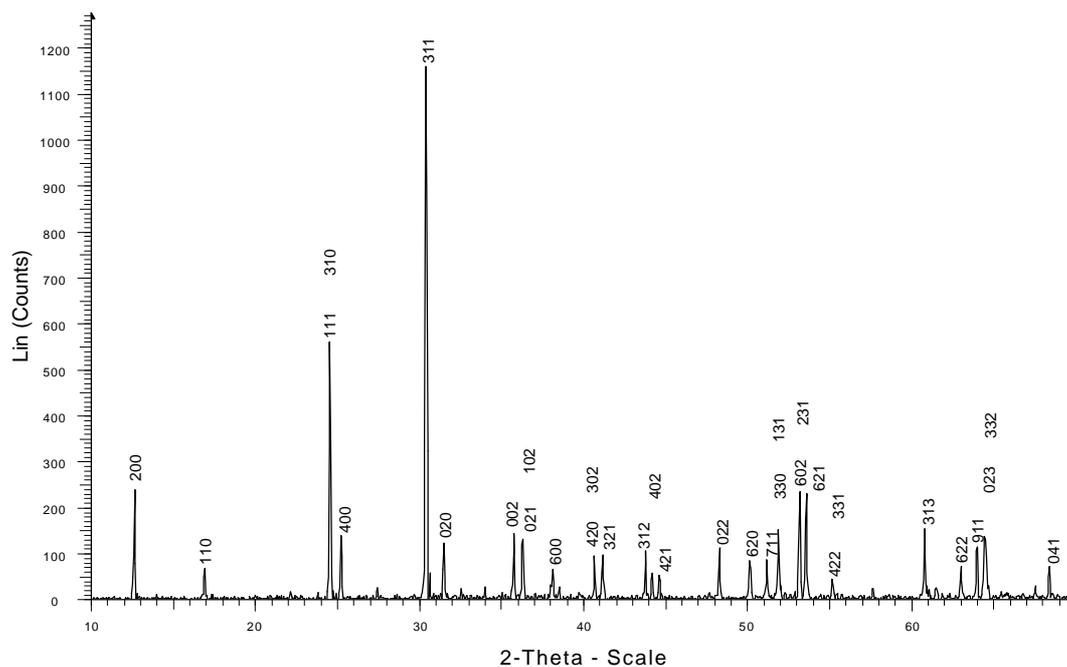


Figure 2. Powder X-ray diffraction pattern of MgNb_2O_6 prepared by ceramic method at 1025°C .

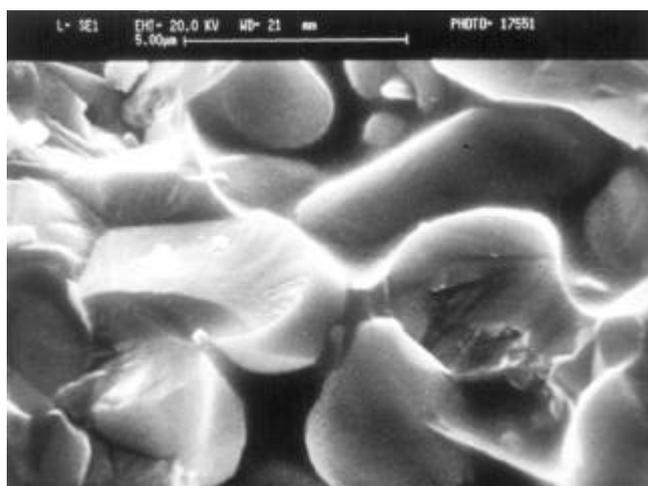


Figure 3. Scanning electron micrograph of MgNb_2O_6 sintered at 1100°C (molten salt method).

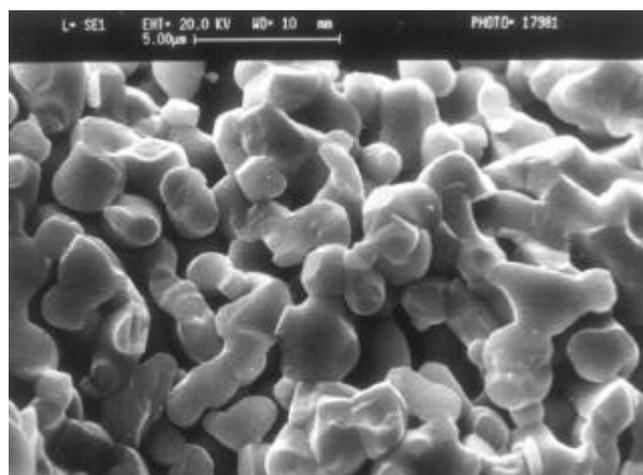


Figure 4. Scanning electron micrograph of MgNb_2O_6 sintered at 1100°C (ceramic method).

Scanning electron micrographs (SEM) of MgNb_2O_6 prepared by the molten salt method at 1100°C show that the grain boundaries are not well defined and the grain size was found to be around $3\text{--}5\ \mu\text{m}$ (figure 3). However, in the oxide obtained by the ceramic route the grain size was around 1.5 to $2.5\ \mu\text{m}$ (figure 4). Earlier reports have shown that the grain size of MgNb_2O_6 prepared by the same (ceramic) method was around $7\text{--}10\ \mu\text{m}$ when sintered at 1200°C (Thirumal and Ganguli 2001). There is considerable increase in the grain size on increasing the sintering temperature from $1100\text{--}1200^\circ\text{C}$.

Detailed studies on the dielectric properties of MgNb_2O_6 was carried out on pellets sintered at 1100°C in the temperature range $35\text{--}200^\circ\text{C}$ and frequency range, $50\ \text{Hz}\text{--}500\ \text{kHz}$. The variation of the dielectric properties with frequency at room temperature for MgNb_2O_6 obtained by the two methods are shown in figures 5 and 6. The dielectric constant (ϵ) was found to be 19.5 and dielectric loss (D) was 0.004 at $100\ \text{kHz}$ for MgNb_2O_6 synthesized by the molten salt route. However, in the ceramic method the dielectric constant and dielectric loss were both found to be lower ($\epsilon = 16.6$; $D = 0.0005$) at the same frequency.

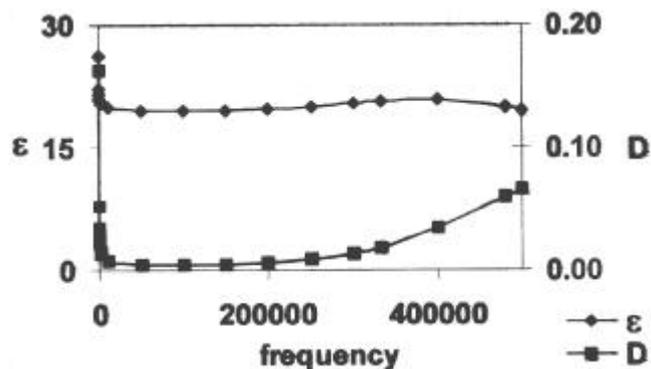


Figure 5. Variation of the dielectric constant (ϵ) and dielectric loss (D) with frequency at room temperature for MgNb_2O_6 prepared by the molten salt method.

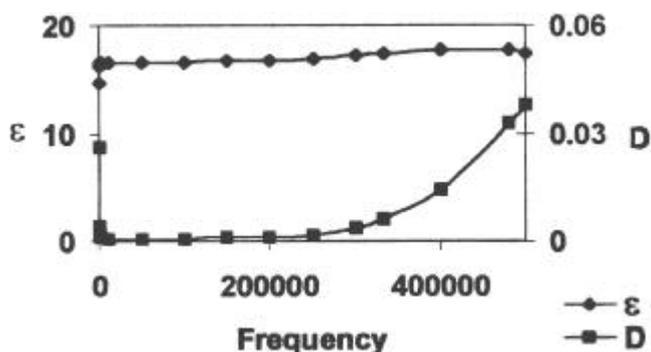


Figure 6. Variation of the dielectric constant (ϵ) and dielectric loss (D) with frequency at room temperature for MgNb_2O_6 prepared by the ceramic method.

Earlier report on MgNb_2O_6 prepared by the ceramic route and sintered at 1200°C showed dielectric constant and dielectric loss of 24 and 0.005, respectively (Thirumal and Ganguli 2001). This increase in the dielectric constant may be due to the difference in the grain size obtained at two sintering temperatures, $1.5\text{--}2.5\ \mu\text{m}$ at 1100°C and $7\text{--}10\ \mu\text{m}$ at 1200°C . The dielectric constant (ϵ) was found to be stable in the range of $10\ \text{kHz}\text{--}500\ \text{kHz}$ irrespective of the preparative method in the present study. The dielectric loss (D) shows very stable value in the frequency

range $1\text{--}200\ \text{kHz}$. However, there is an increase in the dielectric loss beyond $300\ \text{kHz}$ till $500\ \text{kHz}$, which may suggest a well-defined loss peak at higher frequencies. It may be noted that sintering at higher temperatures (1200°C) does not show such an increase in the loss at higher frequencies (Thirumal and Ganguli 2001).

4. Conclusions

We could obtain pure phase of MgNb_2O_6 using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by both the molten salt method and ceramic method. The dielectric constant and loss were found to be slightly higher in the oxide obtained by the molten salt method as compared to ceramic method sintered at the same temperature (1100°C). This may be associated with the larger grain size in the oxide prepared by the molten salt method.

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