

Effect of Calcination Condition on Phase Formation Characteristic of Magnesium Niobate Powders Synthesized by the Solid-State Reaction

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ABSTRACT

Magnesium niobate ($MgNb_2O_6$) powders were prepared and characterized by TG-DTA, XRD, SEM and EDX techniques. The effect of calcination temperature, dwell time and heating/cooling rates on phase formation characteristic of the powders were examined. The calcination temperature and dwell time were found to have a pronounced effect on the phase formation of the calcined magnesium niobate powders. It was also found that the minor phases of unreacted MgO and Nb_2O_5 precursor tended to form together with the columbite $MgNb_2O_6$ phase, depending on calcination conditions. Furthermore, it was observed that optimisation of calcination conditions could lead to a single-phase $MgNb_2O_6$ in an orthorhombic phase.

Key words: Magnesium niobate, Powder synthesis, Phase formation, Calcination

INTRODUCTION

Magnesium niobate ($MgNb_2O_6$; MN) is one of the binary niobate compounds which exhibits excellent dielectric properties at microwave frequencies (Ogawa et al., 2003; Zhang et al., 2003). It has very low loss and high dielectric constant and is promising candidate for application in microwave devices. This compound with a columbite crystal structure is also a suitable reference material for investigating the defect induced in $LiNbO_3$ substrates for waveguide fabrication (Hu et al., 1991; Zaldo et al., 1995; Simoes et al., 2002). Moreover, recently, it is well known as the key precursor for the successful preparation of single-phase relaxor perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), which is becoming increasingly important for transducer, electrostrictor and actuator applications (Saha et al., 1994; Joy and Sreedhar, 1997; Haertling, 1999; Uchino, 2000).

It is known that various compositions are possible in the Mg-Nb-O system (Norin et al., 1972). To date, four possible magnesium-niobium oxides have been identified: $MgNb_2O_6$, $Mg_4Nb_2O_9$, $Mg_5Nb_4O_{15}$ and $Mg_{2/3}Nb_{11(1/3)}O_{29}$ (Norin et al., 1972; Pagola et al., 1997). You et al., (1994) reported that $MgNb_2O_6$ and $Mg_4Nb_2O_9$ are the only stable phases that exist at room temperature. It is known that synthesis of $MgNb_2O_6$ phase by the conventional method, i.e. by reacting individual oxides, generally results in varying amounts of the corundum $Mg_4Nb_2O_9$ phase alongside the columbite phase (Saha et al., 1994; Sreedhar and Mitra, 1997; Yu et al., 2001). Thus, a number of chemical routes using expensive precursors, for example,

co-precipitation (Kim, 1997), citrate-gel (Hong et al., 1998) and polymerised complex (Camargo et al., 2001) have been developed as alternatives to the conventional solid-state reaction of mixed oxides. All of these techniques are aimed at reducing the temperature of preparation of the compound even though they are more involved and complicated than the mixed oxide route.

Generally, the mixed oxide method involves the heating of a mixture of magnesium oxide and niobium oxide above 1100 °C for long times, *i.e.* 20 h (Saha et al., 1994), 24 h (Pagola et al., 1997) and 48 h (Sreedhar and Mitra, 1997), and has been employed intensively in the last decade (Swartz and ShROUT, 1982; You et al., 1994; Feng et al. 1999; Camargo et al., 2001; Costa et al. 2002). The optimisation of calcination conditions used in the mixed oxide process, however, has not received detailed attention, and the effects of applied dwell time and heating/cooling rates have not yet been studied extensively.

The purpose of this work was to explore a simple mixed oxide synthetic route for the production of MgNb_2O_6 (MN) powders and to perform a systematic study of the reaction between the starting magnesium oxide and niobium oxide precursors. The phase formation characteristic of the powder calcined at various conditions was also studied and discussed.

MATERIALS AND METHODS

The starting materials were commercially-available magnesium oxide, MgO (periclase: JCPDS file number 71-1176) (Fluka, 98% purity) and niobium oxide, Nb_2O_5 (JCPDS file number 80-2493) (Aldrich, 99.9% purity). The two oxide powders exhibited an average particle size in the range of 3.0 to 5.0 μm . MgNb_2O_6 powder was synthesised by the solid state reaction of thoroughly ground mixtures of MgO and Nb_2O_5 powders that were milled in the required stoichiometric ratio. The milling operation was carried out for 24 h in isopropanol. High purity corundum balls with diameter of 10 mm were used as the milling media. After drying at 120 °C, various calcination conditions, *i.e.* temperatures ranging from 500 to 1100 °C, dwell times ranging from 0.5 to 5 h and heating/cooling rates ranging from 5 to 25 °C/min. were applied in order to investigate the formation of MgNb_2O_6 . The reactions of the uncalcined MN powders taking place during heat treatment were investigated by thermogravimetric and differential thermal analysis (TG-DTA, Shimadzu), using a heating rate of 10 °C/min. in air from room temperature up to 1100 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer), using Ni filtered $\text{CuK}\alpha$ radiation to identify the phases formed and optimum calcination conditions for the manufacture of MN powder. The powder morphology was examined, using scanning electron microscopy (SEM; JEOL JSM-840A). The chemical compositions of the phases formed were elucidated by an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. EDX spectra were quantified with the virtual standard peaks supplied with the Oxford Instruments eXL software.

RESULTS AND DISCUSSION

The TG-DTA simultaneous analysis of a powder mixed in the stoichiometric proportions of MgNb_2O_6 is shown in Figure 1. The TG curve shows two distinct weight losses. In the temperature range from room temperature to $\sim 150^\circ\text{C}$, both small exothermic and endothermic peaks are observed in the DTA curve in consistent with the first weight loss. These observations can be attributed to the decomposition of the organic species from the milling process. Increasing the temperature up to $\sim 1000^\circ\text{C}$, the solid-state reaction occurred between MgO and Nb_2O_5 (Saha et al., 1994; Kong et al., 2002). The broad exothermic peak in the DTA curve represents that reaction, which has a maximum at $\sim 500^\circ\text{C}$. This is supported by a second fall in sample weight over the same temperature range. No further significant weight loss was observed for the temperatures above 500°C in the TG-curve, indicating the minimum firing temperature to get $\text{MgO-Nb}_2\text{O}_5$ compounds in good agreement with XRD result (Fig. 2) and other workers (Norin et al., 1972; Yu et al., 2001). However, the DTA curve shows that there are another small peaks at ~ 660 and 1000°C . It is to be noted that there is no obvious interpretation of these peaks, although it is likely to correspond to a phase transition reported earlier (You et al., 1994; Sreedhar and Mitra, 1997; Yu et al., 2001). These data were used to define the range of temperatures for XRD investigation to between 500 and 1100°C .

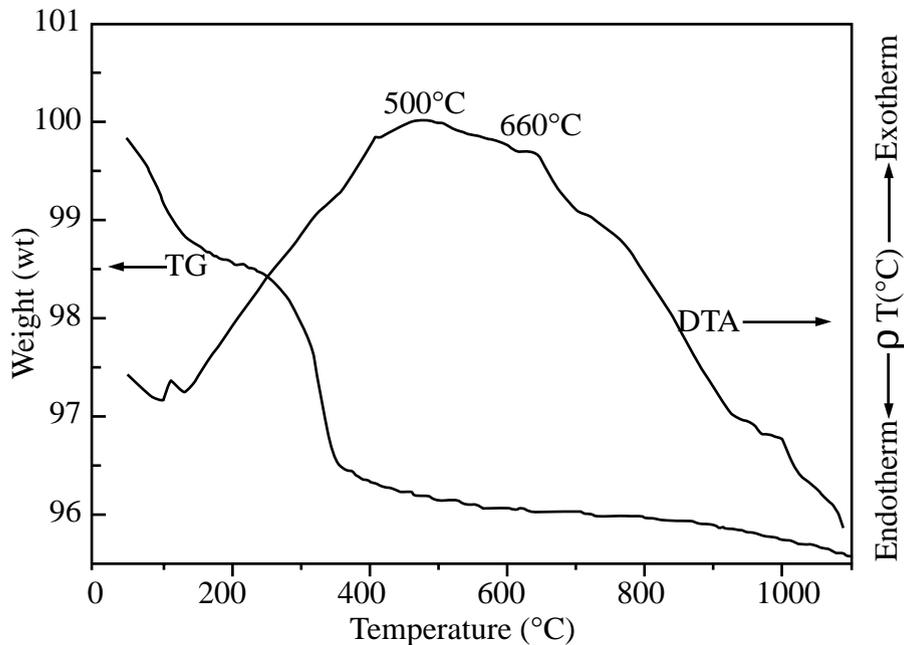


Figure 1. TG-DTA curves for the mixture of $\text{MgO-Nb}_2\text{O}_5$ powder.

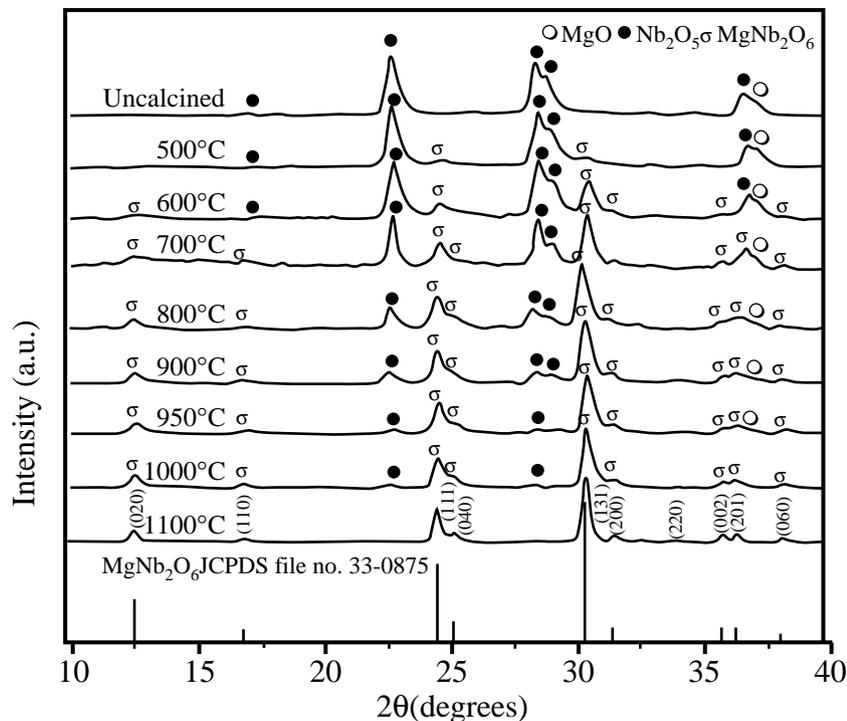


Figure 2. XRD patterns of MN powder calcined at various temperatures for 3 h with heating/cooling rates of 10 °C/min.

To further study the phase development with increasing calcination temperature in the powders, they were calcined for 3 h in air at various temperatures, up to 1100 °C, followed by phase analysis using XRD. As shown in Figure 2, for the uncalcined powder, only X-ray peaks of precursors MgO and Nb₂O₅, which could be matched with JCPDS file numbers 71-1176 and 80-2493 (Powder diffraction file ICDD, 2000), respectively, are present, indicating that no reaction had yet been triggered during the milling process. After calcination at 500 °C, little crystalline phase of MgNb₂O₆ (σ) was developed, accompanying with MgO and Nb₂O₅ as separated phases. This observation agrees well with those derived from the TG-DTA results and other workers (Yu et al., 2001). As the temperature increased to 700 °C, the intensity of the columbite-like MgNb₂O₆ peaks was further enhanced. Upon calcination at temperatures ranging from 800-1000 °C, the MgNb₂O₆ phase became the predominant phase. It should be noted that after calcination at 1000 °C, the peak corresponding to MgO disappeared (not detectable), whereas the traces of minor phase of unreacted Nb₂O₅ could not be completely eliminated.

The XRD pattern of this MgNb₂O₆ phase was indexable according to an orthorhombic columbite-type structure with lattice parameters $a = 570$ pm, $b = 1419$ pm and $c = 503$ pm, space group $Pcan$ (no. 60), in consistent with JCPDS file numbers 33-875 (Powder diffraction file ICDD, 2000), and literature (Pagola et al., 1997; Sreedhar and Mitra, 1997). In conventional mixed oxide route reported earlier (Swartz and Shrout, 1982; Saha et al., 1994; You et al., 1994; Sreedhar and Mitra, 1997), major phase of MgNb₂O₆ was obtained for a

calcination temperature above 1100 °C. However, for the present work, calcination at 1100 °C already resulted in a single phase of the $MgNb_2O_6$.

Apart from the calcination temperature, the effect of dwell time was also found to be quite significant. From Figure 3, it can be seen that the single phase of $MgNb_2O_6$ (yield of 100% within the limitations of the XRD technique) was found to be possible in powders calcined at 1100 °C with dwell time of 3 h or more. In earlier work (Saha et al., 1994; Pagola et al., 1997; Sreedhar and Mitra, 1997), long heat treatments at ~1100-1300 °C for 20 h, 24 h and 48 h were proposed for the formation of $MgNb_2O_6$ by a conventional mixed oxide synthetic route, although no details on phase formation were provided. In the present study, it was found that there were no significant differences between the powders calcined at 1100 °C with dwell time ranging from 3 to 5 h, as shown in Figure 3. In this study, an attempt was also made to calcine MN powders under various heating/cooling rates (Figure 4). In this connection, it indicated that the yield of $MgNb_2O_6$ phase did not vary significantly with different heating/cooling rates ranging from 5 to 25 °C/min. This is in good agreement with the early results reported by Ananta et al., (2003) for the mixture of the two kinds of refractory oxides.

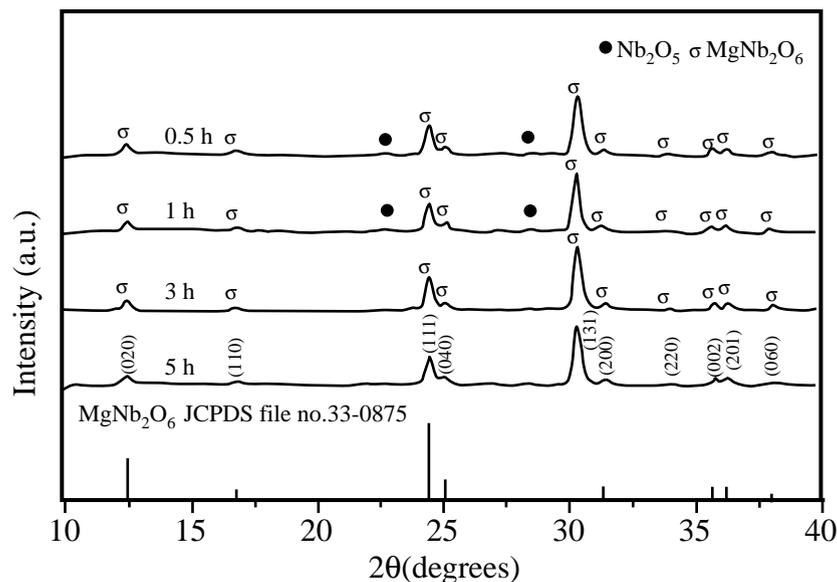


Figure 3. XRD patterns of MN powder calcined at 1100 °C for various dwell times with heating/cooling rates of 10 °C/min.

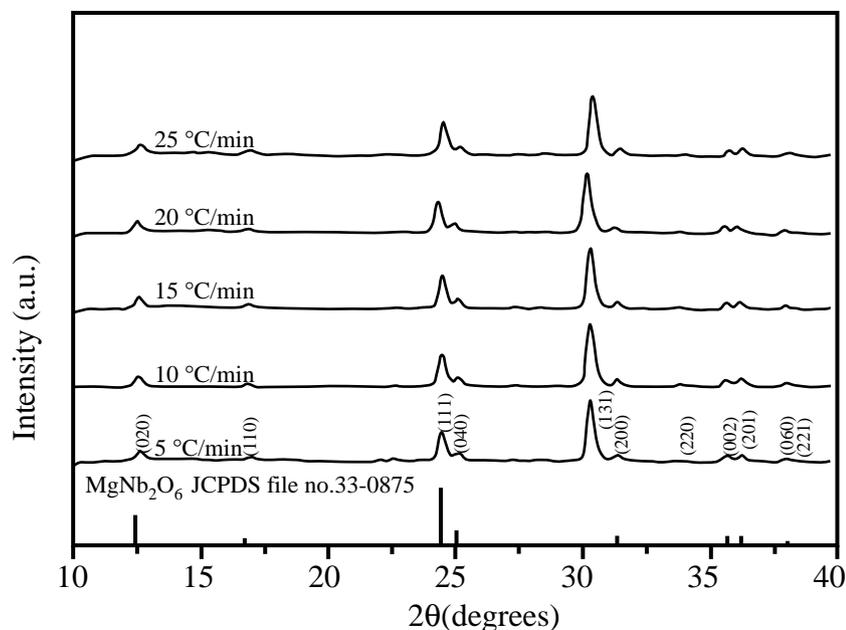
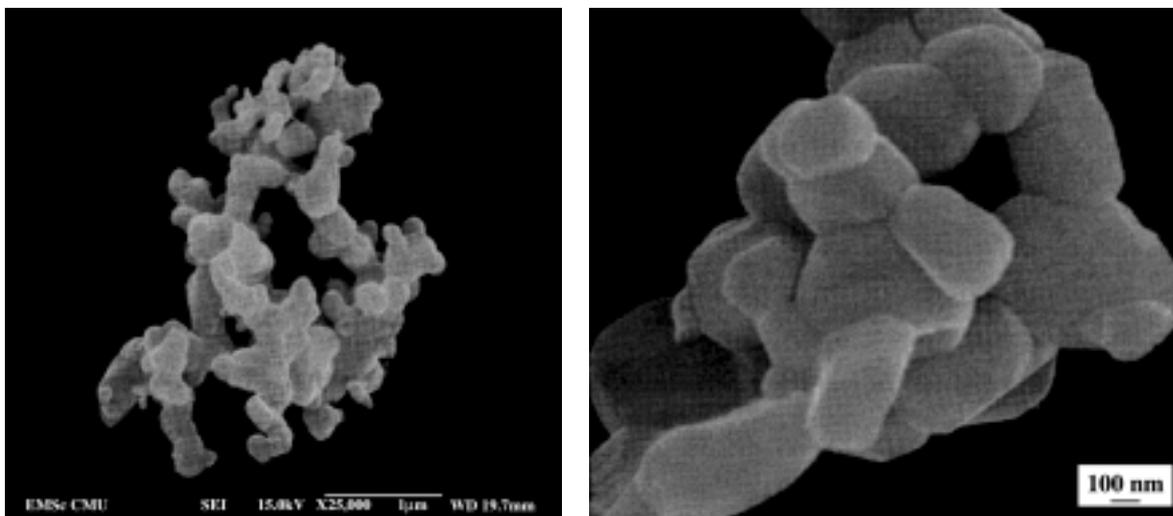


Figure 4. XRD patterns of MN powder calcined at 1100 °C for 3 h with various heating/cooling rates.

Based on the TG-DTA and XRD data, it may be concluded that over a wide range of calcination conditions, single phase MgNb_2O_6 cannot be straightforwardly formed via a solid-state mixed oxide synthetic route. It is well documented that powders prepared by a conventional mixed oxide method have spatial fluctuations in their compositions. The extent of the fluctuation depends on the characteristics of the starting powders as well as the processing schedules (Swartz and Shrout, 1982; Saha et al., 1994; Yu et al., 2001). It is rather surprising that no evidence of the corundum $\text{Mg}_4\text{Nb}_2\text{O}_9$ (You et al., 1994; Yu et al., 2001) was found in this study, nor was there any indication of the $\text{Mg}_5\text{Nb}_4\text{O}_{15}$ (Pagola et al., 1997) being present. The experimental work carried out here suggests that the optimal calcination condition for single phase MgNb_2O_6 (with impurities undetectable by XRD technique) is 1100 °C for 3 h, with heating/cooling rates as fast as 25 °C/min. Moreover, the formation temperature and dwell time for MgNb_2O_6 observed in this work are also lower than those reported earlier (You et al., 1994; Sreedhar and Mitra, 1997; Yu et al., 2001; Costa et al., 2002).

SEM micrographs of the calcined MgNb_2O_6 powders (1100 °C for 3 h with heating/cooling rates of 25 °C/min.) are given in Figures 5(a) and (b). In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size and morphology. A detailed study at high magnification (Figure 5(b)) showed that these agglomerates consisted of ~ 250 - 750 nm MgNb_2O_6 particles. In general, EDX analysis using a 20 nm probe from a large number of particles of the calcined powders confirmed the parent composition to be MgNb_2O_6 (Figure 6) in agreement with XRD results.



(a)

(b)

Figure 5. SEM micrographs of the MN powders calcined at 1100 °C for 3 h, with heating/cooling rates of 25 °C/min.

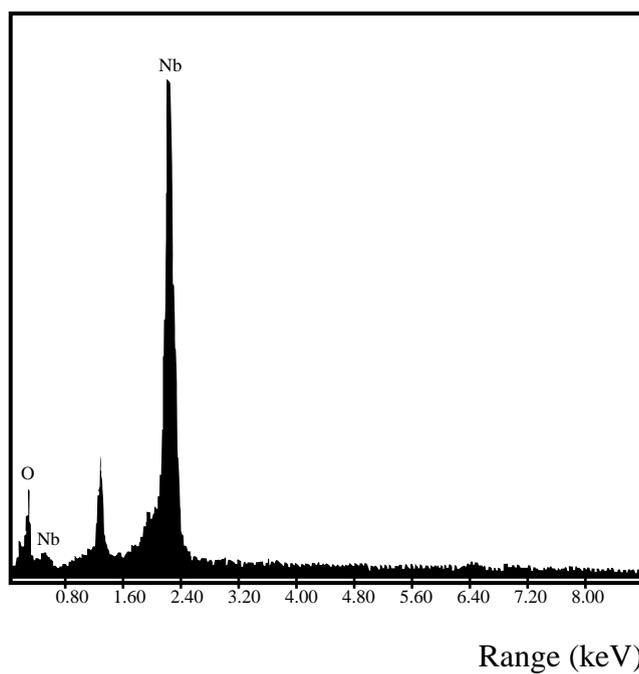


Figure 6. EDX analysis of the MN powders calcined at the optimised condition.

CONCLUSIONS

The columbite-type compound MgNb_2O_6 was prepared by a solid-state mixed oxide synthetic route. The preparative method involved the use of inexpensive and widely available oxide precursors, moderately low calcination temperatures and dwell times, together with fast heating/cooling rates. Evidence gained from XRD revealed that single phase of columbite MgNb_2O_6 powder had been obtained in this study by using a calcination temperature of 1100°C for 3 h, with heating/cooling rates of $25^\circ\text{C}/\text{min}$.

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REFERENCES

- Ananta, S., R. Tipakontitikul, and T. Tunkasiri. 2003. Synthesis, formation and characterization of zirconium titanate (ZT) powders. *Mater. Lett.* 57: 2637-2642.
- Camargo, E.R., M. Kakihana, E. Longo, and E.R. Leite. 2001. Pyrochlore-free $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ prepared by a combination of the partial oxalate and the polymerised complex methods. *J. Alloy. Compd.* 314: 140-146.
- Costa, A.L., C. Galassi, and E. Roncari. 2002. Direct synthesis of PMN samples by spray-drying. *J. Eur. Ceram. Soc.* 22: 2093-2100.
- Feng, C., X. Li, C. Li, and Z. Yin. 1999. Study of dielectric relaxation behaviour and B-site ordering of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN). *Ferroelectrics* 231: 73-78.
- Haertling, G.H. 1999. Ferroelectric ceramics: history and technology. *J. Am. Ceram. Soc.* 82: 797-818.
- Hong, Y.S., H.B. Park, and S.J. Kim., 1998. Preparation of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Powder using a citrate-gel derived columbite MgNb_2O_6 precursor and its dielectric properties. *J. Eur. Ceram. Soc.* 18: 613-619.
- Hsu, C.S., C.L. Huang, J.F. Tseng, and C.Y. Huang. 2003. Improved high-Q microwave dielectric resonator using CuO-doped MgNb_2O_6 ceramics. *Mater. Res. Bull.* 38: 1091-1099.
- Hu, L.J., Y.H. Chang, I.N. Lin, and S.J. Yang. 1991. Defects of lithium niobate crystals heavily doped with MgO. *J. Cryst. Growth.* 114: 191-197.
- Joy, P.A., and K. Sreedhar. 1997. Formation of lead magnesium niobate perovskite from niobate precursors having varying magnesium content. *J. Am. Ceram. Soc.* 80: 770-772.
- Kim, N.K. 1997. Synthesis chemistry of MgNb_2O_6 and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. *Mater. Lett.* 32: 127-130.
- Kong, L.B., J. Ma, H. Huang, and R.F. Zhang. 2002. Crystallization of magnesium niobate from mechanochemically derived amorphous phase. *J. Alloy Compd.* 340: L1-L4.
- Norin, R., C.G. Arbin, and B. Nalander. 1972. Note on the phase composition of $\text{MgO-Nb}_2\text{O}_5$ system. *Acta Chim. Scand.* 26: 3389-3390.

- Ogawa, H., A. Kan, S. Ishihara, and Y. Higashida. 2003. Crystal structure of corundum type $Mg_4(Nb_{2-x}Ta_x)O_9$ microwave dielectric ceramics with low dielectric loss. *J. Eur. Ceram. Soc.* 23: 2485-2488.
- Pagola, S., R.E. Carbonio, J.A. Alonso, and M.T. Fernández-Díaz. 1997. Crystal structure refinement of $MgNb_2O_6$ columbite from neutron diffraction data and study of ternary system $MgO-Nb_2O_5-NbO$, with evidence of formation of new reduced pseudobrookite $Mg_{5-x}Nb_{4+x}O_{15-δ}$ ($1.14 \leq x \leq 1.60$) phases. *J. Solid State Chem.* 134: 76-84.
- Powder Diffraction File No. 71-1176. International Centre for Diffraction Data, Newton Square, PA, 2000.
- Powder Diffraction File No. 80-2493. International Centre for Diffraction Data, Newton Square, PA, 2000.
- Powder Diffraction File No. 33-875. International Centre for Diffraction Data, Newton Square, PA, 2000.
- Saha, D., A. Sen, and H.S. Maiti. 1994. Solid-state synthesis of precursor $MgNb_2O_6$ for the preparation of $Pb(Mg_{1/3}Nb_{2/3})O_3$. *J. Mater. Sci. Lett.* 13: 723-724.
- Simoës, A.Z., A.H.M. Gonzalez, A.A. Cavalheiro, M.A. Zaghete, B.D. Stojanovic, and J.A. Varela. 2002. Effect of magnesium on structure and properties of $LiNbO_3$ prepared from polymeric precursors. *Ceram. Inter.* 28: 265-270.
- Sreedhar, K., and A. Mitra. 1997. Formation of lead magnesium niobate perovskite from $MgNb_2O_6$ and $Pb_3Nb_2O_8$ precursors. *Mater. Res. Bull.* 32: 1643-1649.
- Swartz, S.L., and T.R. Shrout. 1982. Fabrication of perovskite lead magnesium niobate. *Mater. Res. Bull.* 17: 1245-1250.
- Uchino, K. 2000. *Ferroelectric devices*. Marcel Dekker, Inc. New York.
- You, Y.C., H.L. Park, Y.G. Song, H.S. Moon, and G.C. Kim. 1994. Stable phases in the $MgO-Nb_2O_5$ system at 1250 °C. *J. Mater. Sci. Lett.* 13: 1487-1489.
- Yu, Y., C. Feng, C. Li, Y. Yang, W. Yao, and H. Yan. 2001. Formation of columbite-type precursors in the mixture of $MgO-Fe_2O_3-Nb_2O_5$ and the effects on fabrication of perovskites. *Mater. Lett.* 51: 490-499.
- Zaldo, C., M.J. Martin, C. Coya, K. Polgar, A. Peter, and J. Paitz. 1995. Optical properties of $MgNb_2O_6$ single crystals: a comparison with $LiNbO_3$. *J. Phys.: Condens. Matter.* 7: 2249-2257.
- Zhang, Y.C., Z.X. Yue, Z. Gui, and L.T. Li. 2003. Microwave dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics. *Mater. Lett.* 57: 4531-4534.

