A Mixed Oxide Synthetic Route to $Mg_4Nb_2O_9$ Nanopowders in a Corundum-like Phase

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ABSTRACT

An approach to synthesize single-phase magnesium niobate ($Mg_4Nb_2O_9$) nanopowders with a mixed oxide synthetic route is developed via a rapid vibro-milling technique. The powders were characterized by TG-DTA, XRD, SEM and EDX techniques. The effect of calcination temperature on phase formation characteristic of the powders was examined. The calcination temperature was 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 precursors and a columbite $MgNb_2O_6$ tended to form together with the corundum $Mg_4Nb_2O_9$ phase, depending on calcination temperatures. Furthermore, it was observed that optimisation of vibro-milling time and calcination temperature could lead to a single-phase $Mg_4Nb_2O_9$ with particle size of less than 100 nm.

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

INTRODUCTION

Magnesium niobate ($Mg_4Nb_2O_9$; MN) is one of the binary niobate compounds which has been investigated as a potential candidate for the synthesis of microwave dielectric materials (Kan and Ogawa, 2004). It is also a room-temperature photoluminescent material and a suitable buffer layer material for fabricating ferroelectric memory devices (You et al., 1994-b). Recent work on the preparation of a single-phase relaxor perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ or PMN (Lu and Yang, 2001) which is becoming increasingly important for electrostrictor, actuator and capacitor applications (Moulson and Herbert, 2003), has also shown that $Mg_4Nb_2O_9$ is a better precursor than the columbite $MgNb_2O_6$ (Ananta et al., 1999).

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: $Mg_4Nb_2O_6$, $Mg_4Nb_2O_9$, $Mg_5Nb_4O_{15}$ and $Mg_{2/3}Nb_{11(1/3)}O_{29}$ (Pagola et al., 1997). You et al., (1994a) 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 $Mg_4Nb_2O_9$ phase by the conventional method, i.e., by reacting individual oxides, generally results in varying amounts of the columbite $MgNb_2O_6$ phase alongside the corundum phase (Pagola et al., 1997; Sreedhar and Pavaskar, 2002). Thus, a number of chemical routes using expensive precursors, for example, polymerised complex (Camargo et al., 2000) and precipitation (Kan and Ogawa, 2004) methods, have been developed as alternatives to the conventional solid-state reaction of mixed oxides. All of these techniques are aimed at reducing the preparation temperature 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 1,300°C for long times, i.e., 24 h (Joy and Sreedhar, 1997) and 48 h (Sreedhar and Pavaskar, 2002) and has been employed intensively in the last decade (Sreedhar and Pavaskar, 2002; Ananta, 2004(a)). The optimisation of calcination conditions used in the mixed oxide process, however, has not received detailed attention, and the effect of milling time has not yet been studied extensively. Moreover, the advantage of using mechanical milling for preparation of nanosized powders lies in its ability to produce mass quantities of powder in the solid state, using simple equipment and low-cost starting precursors (Kong et al., 2002).

The purpose of this work was to explore a simple mixed oxide synthetic route for the production of $Mg_4Nb_2O_9$ (MN) nanopowders 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 and niobium oxide, Nb_2O_5 (Fluka, 98% purity). The two oxide powders exhibited an average particle size in the range of 3.0 to 5.0 (m. $Mg_4Nb_2O_9$ 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. A rapid vibro-milling technique (McCrone micronising mill) was employed in order to combine mixing capability with a significant time saving (only 12 h instead of 24 h, as required in conventional ball-milling (Ananta, 2004(a)). The milling operation was carried out in isopropanal. High-purity corundum cylindrical media were used as the milling media. After drying at 120°C, various calcination temperatures ranging from 500 to 1000°C, dwell time of 2 h and heating/cooling rates of 30°C/min. were applied in order to investigate the formation of $Mg_4Nb_2O_9$. The reactions of the uncalcined 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 CuK_α 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 $Mg_4Nb_2O_9$, is shown in Figure 1. The TG curve shows two distinct weight losses. In the temperature range from room temperature to ~ 150°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 ~ 1,000°C, the solid-state reaction occurred between MgO and Nb_2O_5 (Ananta, 2004-b; Lu and Yang, 2001). The broad exothermic peak in the DTA curve represents that reaction, which has a maximum at ~ 500°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 MgO-Nb_2O_5 compounds in good agreement with XRD result (Fig. 2) and other workers (Hong et al., 1998; Camargo et al., 2000). However, the DTA curve shows that there are other small peaks at ~ 650 and 780°C. It is to be noted that there is no obvious interpretation of these peaks, although it is likely to correspond to phase transitions as reported in earlier publication (Ananta et al., 1999). These data were used to define the range of temperatures for XRD investigation to between 500 and 1,000°C.

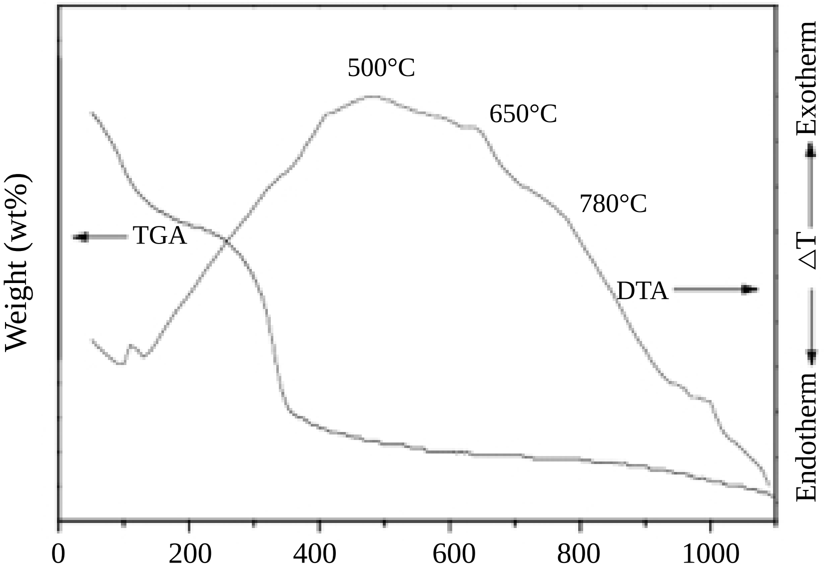

Figure 1. TG-DTA curves for the mixture of MgO-Nb_2O_5 powder.

To further study the phase development with increasing calcination temperature in the powders, they were calcined for 2 h in air at various temperatures, up to 1,000°C, followed by phase analysis using XRD. As shown in Figure 2, for the uncalcined powder, only X-ray peaks of precursors MgO and Nb_2O_5, 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 550°C, little crystalline phase of $MgNb_2O_6$ (∇) was developed, accompanying with MgO and Nb_2O_5 as separated phases. This observation agrees well with those derived from the TG-DTA results and other workers (Yu et al., 2001; Kong et al., 2002). As the temperature was increased to 650°C, the intensity of the corundum-like $Mg_4Nb_2O_9$ peaks was further enhanced. Moreover, the precursor phase of Nb_2O_5 has been found to completely disappear, and crystalline $MgNb_2O_6$ with small amount of MgO are the only detectable phases in the powder. Calcination at 700°C resulted in some new peak (▼) of the corundum $Mg_4Nb_2O_9$ phase, JCPDS file no. 38–1459 (Powder diffraction file ICDD, 2000), mixing with the columbite $MgNb_2O_6$ phase and some residual MgO. Upon calcination at 750°C, the $Mg_4Nb_2O_9$ phase becomes the predominant phase and the residual MgO has been found to completely disappear. However, the traces of minor phase $MgNb_2O_6$ at 2θ ~ 30° could not be completely eliminated. It should be noted that after calcination at 800°C, a single phase of the corundum $Mg_4Nb_2O_9$ is formed. The XRD pattern of this $Mg_4Nb_2O_9$ phase was indexable according to a corundum-type structure with lattice parameters $a = 516$ pm and $c = 1402$ pm, space group $P\bar{3}c1$ (no. 165), in consistent with JCPDS file numbers 38–1459 (Powder diffraction file ICDD, 2000), and literature (Kan and Ogawa, 2004). In conventional mixed oxide route reported earlier (Lu and Yang, 2001; Ananta, 2004(a)), major phase of $Mg_4Nb_2O_9$ was obtained for a calcination temperature above 900°C. However, for the present work, calcination at 800°C already resulted in a single phase of the $Mg_4Nb_2O_9$. This observation could be attributed mainly to the effectiveness of the different milling scheme.

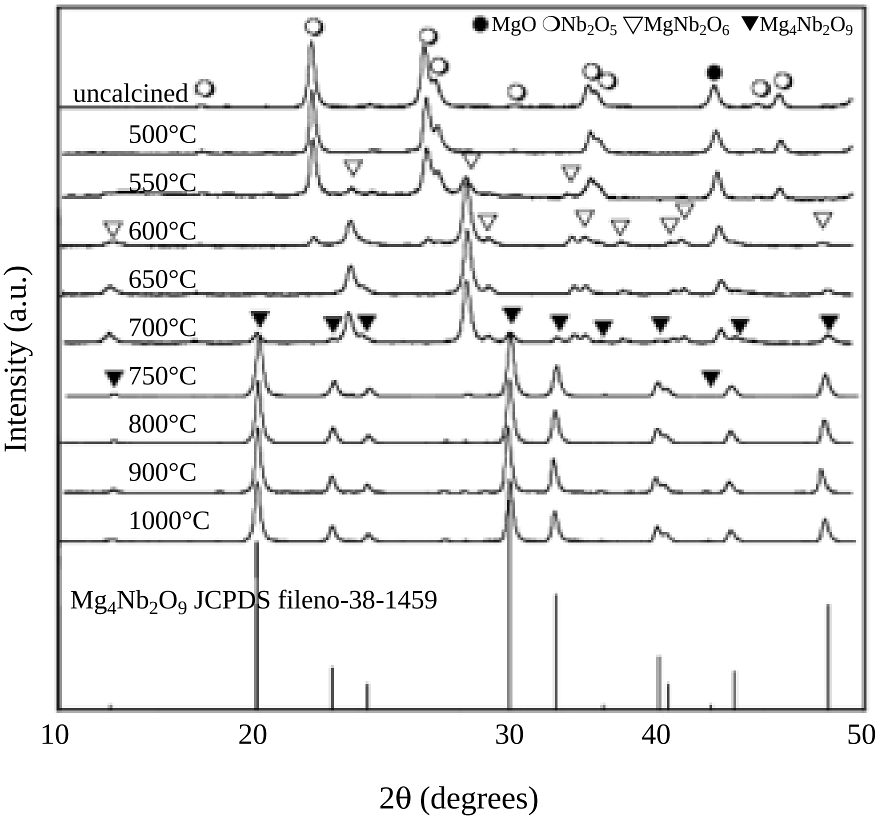

Figure 2. XRD patterns of MN powder calcined at various temperatures for 2 h with heating/cooling rates of 30°C/min.

Based on the TG-DTA and XRD data, it may be concluded that over a wide range of calcination conditions, single-phase $Mg_4Nb_2O_9$ 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 (Lu and Yang, 2001; Sreedhar and Pavaskar, 2002). The experimental work carried out here suggests that the optimal calcination condition for single-phase $Mg_4Nb_2O_9$ (with impurities undetectable by XRD technique) is 800°C for 2 h, with fast heating/cooling rates of 30°C/min. Moreover, the formation temperature for $Mg_4Nb_2O_9$ observed in this work is also lower than those reported earlier (Sreedhar and Pavaskar, 2002; Ananta, 2004(a)).

SEM micrographs of the calcined $Mg_4Nb_2O_9$ powders (800°C for 2 h with heating/cooling rates of 30°C/min.) are given in Figure 3(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 3(b)) showed that they had spherical secondary particles, composing of nanosized primary particulates. The primary particles have sizes of (25–50 nm, and the agglomerates are measured between 71 nm and 1.2 (m. Energy dispersive X-ray (EDX) analysis showed the calcined compositions of these powders to be $Mg_4Nb_2O_9$ in agreement with XRD results. Therefore, in general, the methodology presented in this work provides a simple method for preparing corundum $Mg_4Nb_2O_9$ nanopowders via a simple solid-state mixed oxide synthetic route.

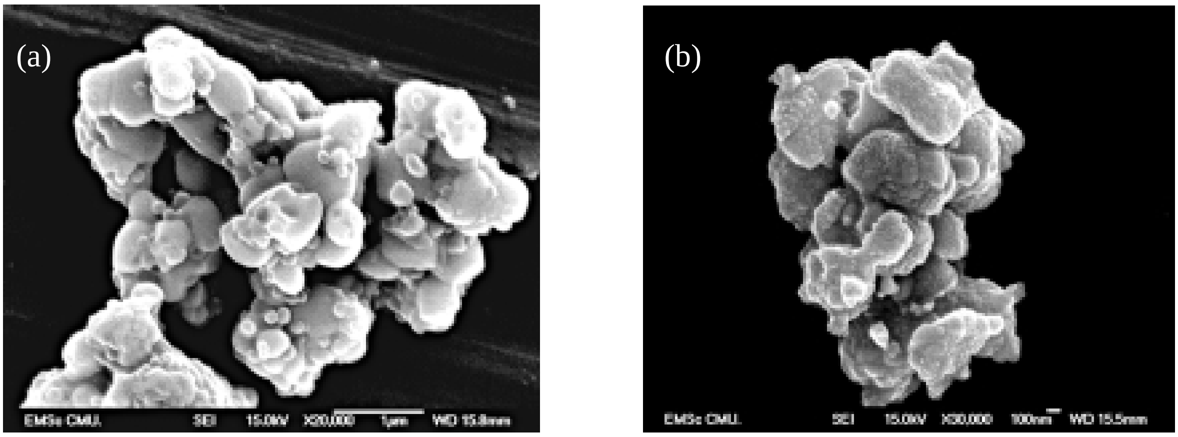

Figure 3. SEM micrographs of the MN powders calcined at 800°C for 2 h, with heating/cooling rates of 30°C/min.

CONCLUSION

This work demonstrated that mass production of a single-phase corundum-type Mg4Nb2O9 nanopowders can be successfully achieved by employing a combination of rapid vibro-milling technique and a careful calcination treatment. Evidence gained from XRD and SEM revealed that the resulting single-phase $Mg_4Nb_2O_9$ nanopowder consists of a variety of agglomerated particle sizes.

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