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Synthesis, Formation and Characterisation of $MgNb_2O_6$ Powder in a Columbite-like Phase

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Abstract

A modified mixed oxide synthetic route has been developed for the synthesis of the columbite-like phase of magnesium niobate, $MgNb_2O_6$ (MN). Magnesium carbonate hydroxide pentahydrate was employed as a source of magnesium, with the formation of columbite phase investigated as a function of calcination temperature and dwell time by XRD and DTA. The particle size distribution of the calcined powder was determined by laser diffraction, with the morphology, phase composition and crystal structure determined via SEM, TEM and EDX techniques. It has been found that the $Mg_4Nb_2O_9$ phase tends to form together with the columbite-type phase $MgNb_2O_6$, although a single columbite-like phase of $MgNb_2O_6$ was obtained for a calcination temperature of 1150°C with a dwell-time of 4 h. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: calcination, powders – solid state reaction, niobates, magnesium niobates.

1 Introduction

As the demand for new devices, high performance capability, simple processing routes and low cost manufacture in advanced materials has grown over the past few decades, the technologies for controlling the desired properties of resultant materials have become very important. In this respect, the starting material is one of the main variables that critically affects the properties of the final product. The quest for optimal powder characteristics (controlled chemical composition, homogeneity, reactivity, particle size and shape) in the fabrication of materials has directed attention particularly towards powder production techniques.

The columbite-like phase of $MgNb_2O_6$ (MN) has attracted interest for many years,[1–11] with current attention tending to focus on its use in the synthesis of microwave dielectric materials e.g. Ba $(Mg_{1/3}Nb_{2/3})O_3$ (BMN).[2] It is also a suitable reference material for investigating the defects induced in $LiNbO_3$ substrates for waveguide fabrication.[3] Moreover, $MgNb_2O_6$ is well known as the key precursor for the successful preparation of single-phase perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), which is becoming increasingly important for multilayer ceramic capacitor, transducer, electrostrictor and actuator applications.[4–8]

The evolution of a method to produce a particular powder of precise stoichiometry and desired properties is complex, depending on a number of variables such as raw materials, their purities, processing history, temperature, time, etc. For example, the synthesis of stoichiometric lead magnesium niobate (PMN) using $MgNb_2O_6$ (MN) as a key precursor by the conventional columbite process[3,6] requires an additional amount of MgO to convert the unreacted (free) Nb_2O_5 phase to $MgNb_2O_6$. This process, based on the mixed oxide route, has been used with minor modifications in the synthesis of $MgNb_2O_6$ itself.[5,7,8] However, the effect of excess MgO on PMN preparation is still a matter of debate, and appears to depend critically on the amount of MgO added.[9,10] Determination of the appropriate excess of MgO is currently a matter of trial and error. Moreover, production of single-phase columbite $MgNb_2O_6$ is not straightforward, due to the corundum-like $Mg_4Nb_2O_9$ phase being formed alongside the columbite phase.[7,11]

More recently, limited attempts have been made to rationalise experimental results in terms of the starting materials and processing steps involved, in order to improve the yield of $MgNb_2O_6$. One approach is simply to employ a precursor with greater reactivity such as $(MgCO_3)_4.Mg(OH)_2$ $5H_2O$, $Mg(NO_3)_2$ or $MgCO_3$.[5,7,8] However, whereas purity and reactivity are crucial, attention

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2 Method

2.1 Powder preparation

Columbite-like $MgNb_2O_6$ was synthesised by the solid state reaction of appropriate amounts of reagent grade magnesium carbonate hydroxide pentahydrate, $(MgCO_3)_4.Mg(OH)_2.5H_2O$ (Aldrich, 99% purity) and niobium oxide Nb_2O_5 (Alfa [Johnson Matthey], 99·9+% purity), based upon the reaction sequence advocated by Butcher and Daglish[5] [eqn (1)].

$$(MgCO_3)_4.Mg(OH)_2.5H_2O + 5\,Nb_2O_5 \rightarrow \\ 5\,MgNb_2O_6 + 4CO_2 + 6H_2O \tag{1}$$

Powder-processing was carried as shown schematically in Fig. 1. Instead of employing a ball-milling procedure (ZrO_2 media under acetone for 20 h), use was made of a McCrone vibro-mill, milling for 30 min with corundum media in isopropyl alcohol (IPA). Furthermore, the procedure for drying the powder-IPA slurry was modified as follows: the sample dish was placed in a fume cupboard, on a hotplate with a magnetic stirrer, but with the hotplate turned off. Heat was applied to the slurry by means of an infra-red lamp placed above the dish, with the metal hotplate acting as a heat sink, leading to a more uniform heat distribution without boiling the solvent. The magnetic stirring action precluded gravitational separation of the components, which is particularly relevant in the case of dense Nb_2O_5 powders. Although the use of IPA in place of acetone was dictated by the use of the McCrone mill, an associated benefit is the avoidance of unpleasant vapours associated with the use of acetone. Drying was carried out for 1·5 h (not to complete dryness), prior to sieving through a 100 μm mesh.

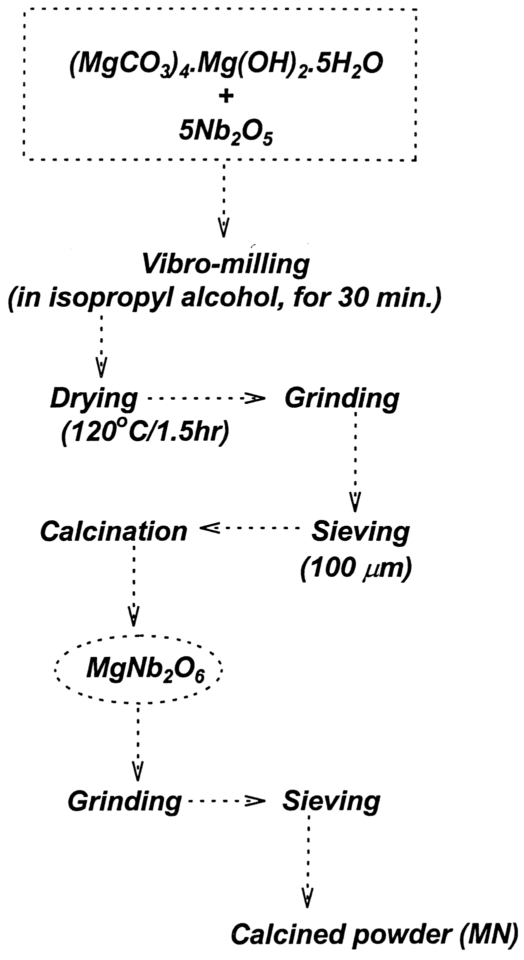


Fig. 1. Preparation route for $MgNb_2O_6$ powder in a columbite-like phase.

Five calcination temperatures were chosen for the reaction to form magnesium niobate: 1000, 1050, 1100, 1150 and 1200°C for 4 h, with heating and cooling rates of 10°C min^{-1}. XRD and analytical SEM were utilised to compare the products obtained at each temperature. Having established the optimum temperature, alternative calcination times of 3 h were applied at this temperature. For completeness, calcination times of 5 h at a temperature 25°C below and 3 h at 25°C above the optimum temperature were also investigated.

2.2 Powder characterisation

Differential thermal analysis (DTA) (Perkin–Elmer, 7 Series Thermal Analysis System) was performed in the temperature range from 600 to 1250°C. As-dried powder (100 mg) was placed into a platinum holder and measured at a heating rate of 10°C min^{-1} in air with alumina powder as a reference. After DTA experiments, calcined powders were examined by X-ray diffraction (XRD) using CuKα radiation to identify the phases formed and the optimum calcination temperature and time for the formation of columbite-like $MgNb_2O_6$.

The particle size distributions of the samples were determined by laser diffraction techniques (MasterSizer, Malvern, UK) with the grain sizes and morphologies of the powders observed by scanning electron microscopy (Hitachi S-700 SEM) interfaced to a digital image capture system. The chemical compositions and structures of the phases formed were elucidated by transmission electron microscopy (CM20 TEM/STEM operated at 200 keV) and an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. Powder samples were dispersed in solvent and deposited by pipette on to 3 mm holey carbon grids for observation by TEM.

3 Results and Discussion

3.1 Identification of the optimum calcination temperature for the formation of magnesium niobate

A DTA curve for the powder is given in Fig. 2, where the exothermic peak at 1192°C and the endothermic peak at 1235°C are shown. XRD analysis was subsequently carried out on the same batch of powder calcined at various temperatures (1000, 1050, 1100, 1150 and 1200°) for 4 h. These were chosen to span the exothermic peak at 1192°C.

Powder XRD patterns of the calcined powders are shown in Figs 3 and 4 respectively. The strongest reflections apparent in the majority of the XRD patterns indicate the formation of the columbite-like phase of magnesium niobate, $MgNb_2O_6$, which could be matched with JCPDS file no. 33–875 (Fig. 5) This major phase possesses an orthorhombic columbite-type structure with lattice parameters

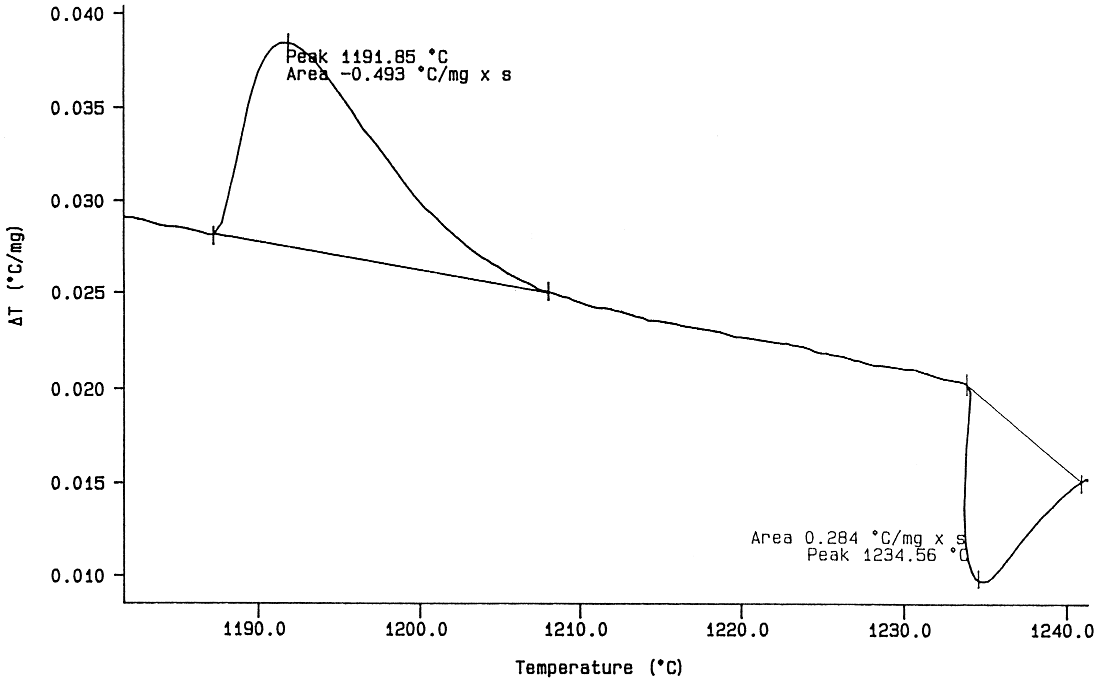


Fig. 2. A DTA curve for the columbite-like phase $MgNb_2O_6$ powder.

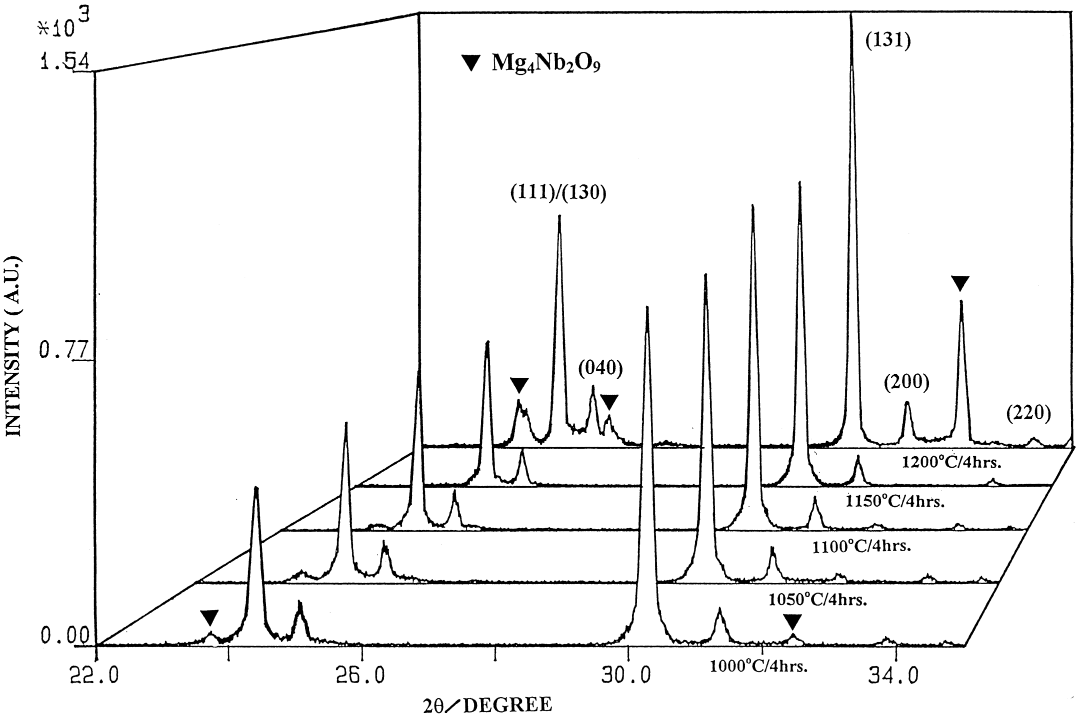


Fig. 3. Powder XRD patterns of the calcined powders at various calcination temperatures with constant dwell time.

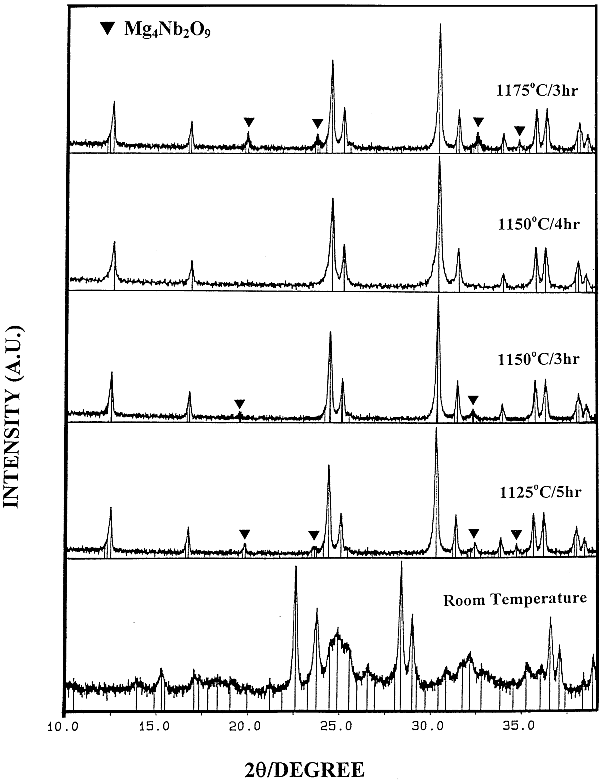


Fig. 4. Powder XRD patterns of the calcined powders at various calcination temperatures and times.

$a = 5{\cdot}70$ Å, $b = 14{\cdot}19$ Å, and $c = 5{\cdot}03$ Å in space group Pcan (No. 60). Moreover, some additional weak reflections are found in the XRD pattern (marked by ▼) which correlate with a $Mg_4Nb_2O_9$ phase (JCPDS file no. 38-1459). This has a corundum-type (α-Al_2O_3) structure with a rhombohedral unit cell ($a = 5{\cdot}16$ Å and $c = 14{\cdot}02$ Å), space group R3c (No. 165).

The amount of the columbite phase present in each calcined powder may, in principle, be calculated from the intensities of the major X-ray reflections for the columbite and corundum phases. In this connection, Joy and Sreed[6] have proposed the use of the following equation:

$$\text{wt\% columbite phase} = \left(\frac{I_{\text{Col}}}{I_{\text{Col}} + I_{\text{Cor}}}\right) \times 100 \qquad (2)$$

In their work, I_{col} referred to the intensity of the (311) columbite peak and I_{cor} to the intensity of the (100) corundum peak, these being the most intense reflections in the XRD patterns of both phases.

In the work reported here, the (104) reflection has been found to be the strongest in the corundum-like phase, rather than (100). Furthermore, this observation is consistent with JCPDS file 38-1459.

For the purposes of estimating the concentrations of corundum-like phase present, eqn (2) has been applied to the diffraction patterns reported here (Table 1). However, the (104) corundum-like peak has been used, rather than the (100) peak. Because of the inherent approximation in eqn (2), which requires, for an accurate evaluation of weight fraction, that the absolute intensities of the two peaks selected from pure columbite, $MgNb_2O_6$, and pure corundum, $Mg_4Nb_2O_9$ are

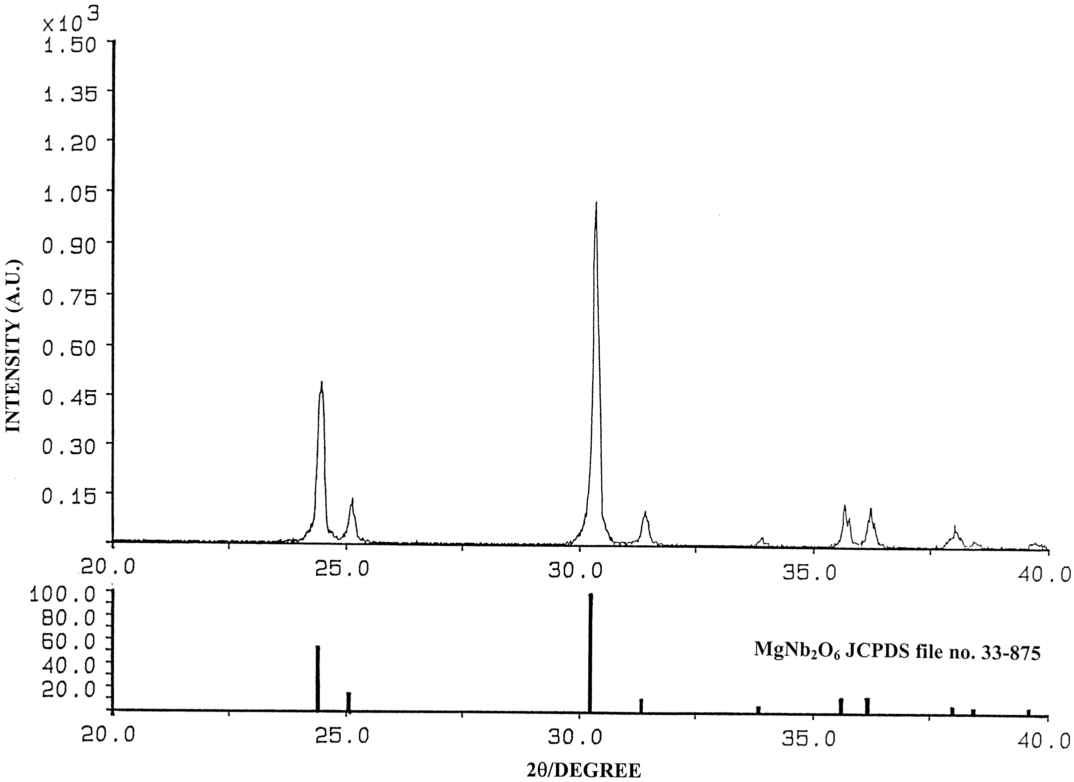


Fig. 5. Computerised JCPDS data-matching (file 33-875) confirms the formation of the columbite-like phase $MgNb_2O_6$.

Table 1. Phase analysis for MN prepared by the modified mixed oxide route

Sample	*Calcination conditions*		*Qualitative concentractions of phases*	
	Temperature (°C)	*Time (h)*	*$MgNb_2O_6$ (wt%)*	*$Mg_4Nb_2O_9$ (wt%)*
MN0	1000	4	97·0	3·0
MN1	1050	4	98·5	1·5
MN2	1100	4	98·8	1·2
MN3	1150	4	100·0	0·0
MN4	1200	4	76·5	23·5
MN5	1150	3	99·5	0·5
MN6	1125	5	99·2	0·8
MN7	1175	3	98·0	2·0

The estimated precision of the concentration values for the two phases is ±0·1%

comparable, the results should be interpreted only in a comparative sense. It is also relevant to point out that peak-heights have been used to represent intensities, rather than peak areas, which would have been more appropriate.

As expected, there is evidence that, even for a wide range of calcination conditions, single phase $MgNb_2O_6$ cannot easily be produced. To date, four possible magnesium-niobium oxides have been identified: $MgNb_2O_6$, $Mg_4Nb_2O_9$, $Mg_5Nb_4O_{15}$ and $Mg_{2/3}Nb_{11(\frac{1}{3})}O_{29}$.[11] In most of this reported work, the formation of columbite required long heat treatments, e.g. 20 h,[7] 22 h[12] and 24 h.[8] Joy and Sreedhar[8] have also reported that their attempts to prepare columbite free of corundum were not successful.

This study shows that a minor amount of the corundum $Mg_4Nb_2O_9$ phase co-exists along with the columbite $MgNb_2O_6$ phase, after calcination in the range 1000–1100°C. By increasing the calcination temperature, the yield of $MgNb_2O_6$ phase increases significantly until 1150°C, whereafter higher temperatures and different dwell times do not enhance the yield of single phase columbite. This observation is, in all likelihood, connected with the exothermic peak observed in the DTA trace centred at 1192°C (Fig. 2). The possibility exists that this peak is associated with formation of the corundum-like phase itself. The optimal calcination conditions for single phase $MgNb_2O_6$ of 1150°C for 4 h found here are in good agreement with those reported earlier.[5] Therefore, by using magnesium hydroxide pentahydrate as a magnesium source, with an optimal calcination condition (1150°C for 4 h in this study), the reproducible, lower cost and faster process involving vibro-milling can produce high purity columbite $MgNb_2O_6$

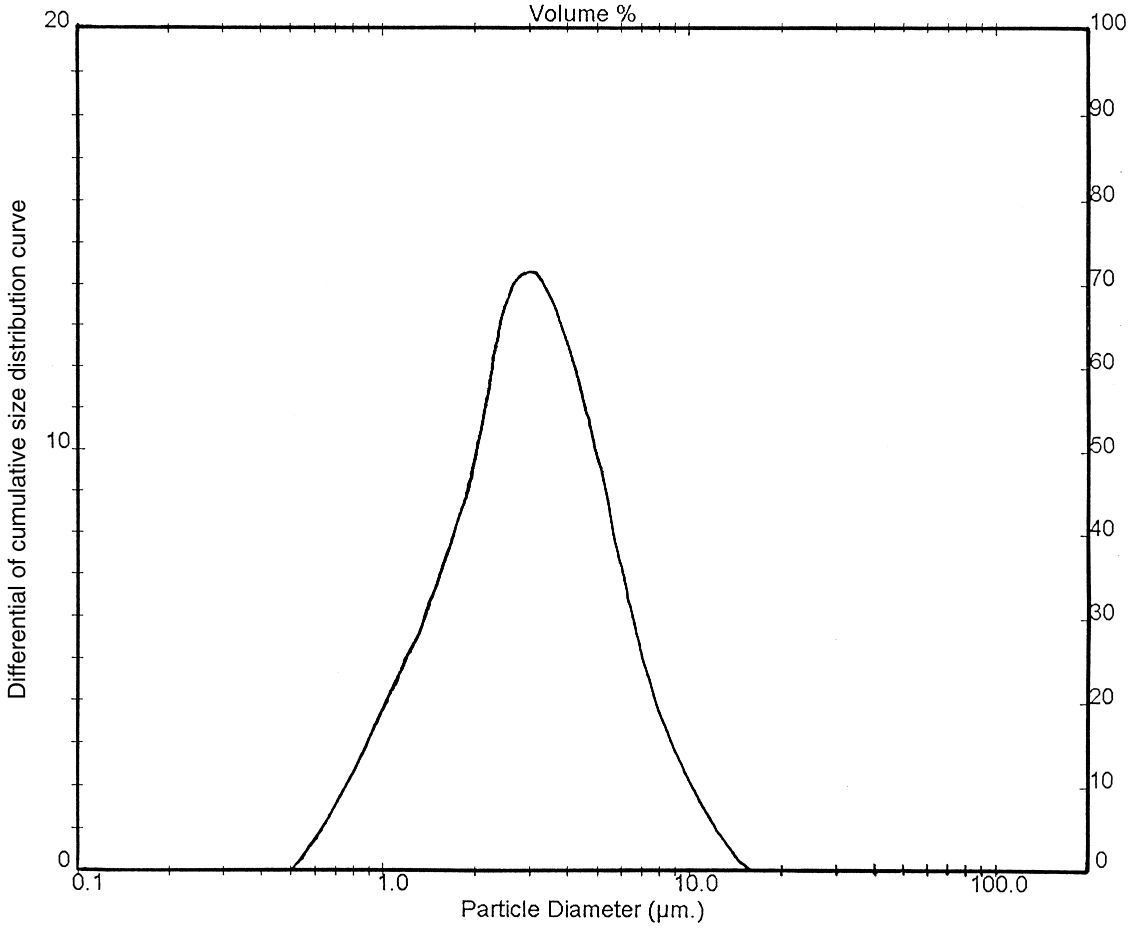


Fig. 6. The particle size distribution curve of the calcined $MgNb_2O_6$ powder.

(with impurities undetected by XRD and SEM/EDX techniques) from laboratory-grade raw materials.

3.2 Particle size analysis of $MgNb_2O_6$ powder

Figure 6 shows the particle size distribution curve of calcined $MgNb_2O_6$ powder, which indicates an appreciable size fraction at about 3 μm within the possible range of 0·5 to 15 μm.

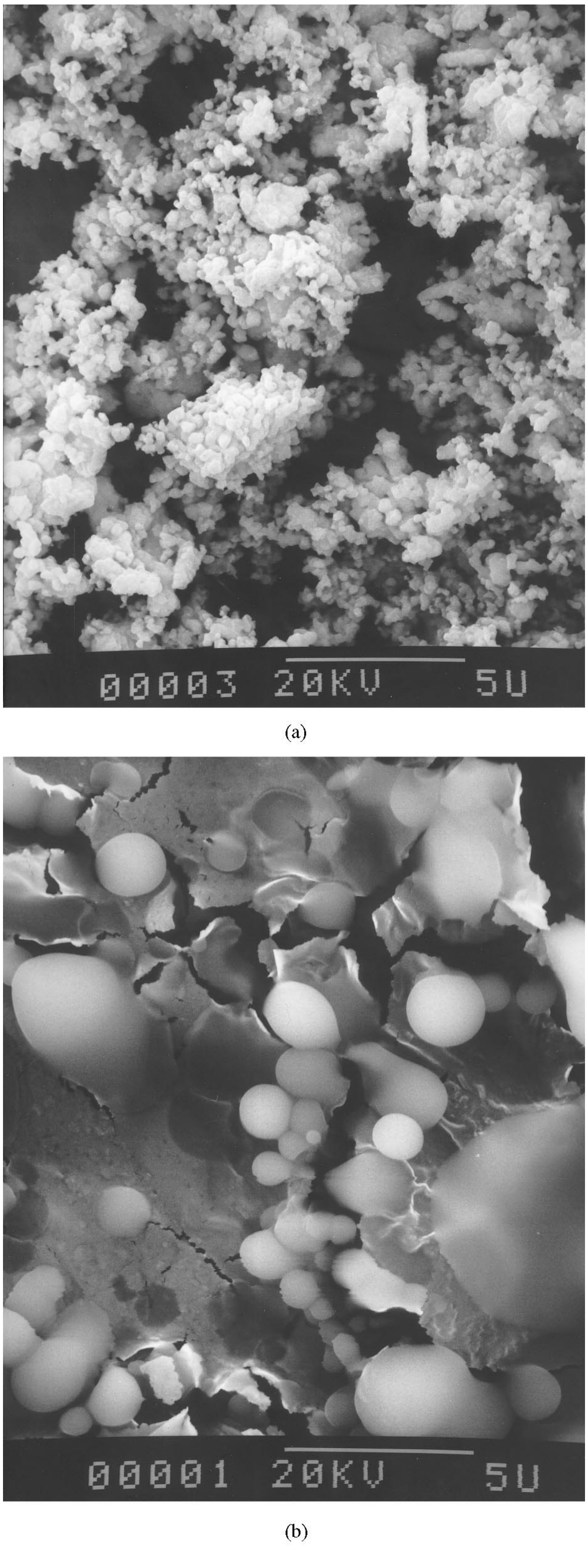


Fig. 7. SEM micrographs of the calcined $MgNb_2O_6$ powder.

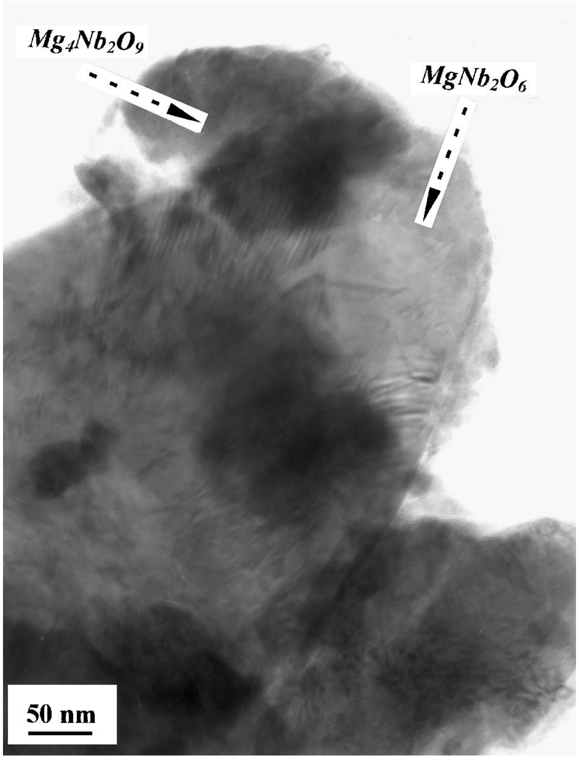


Fig. 8. TEM micrograph of the calcined $MgNb_2O_6$ powder.

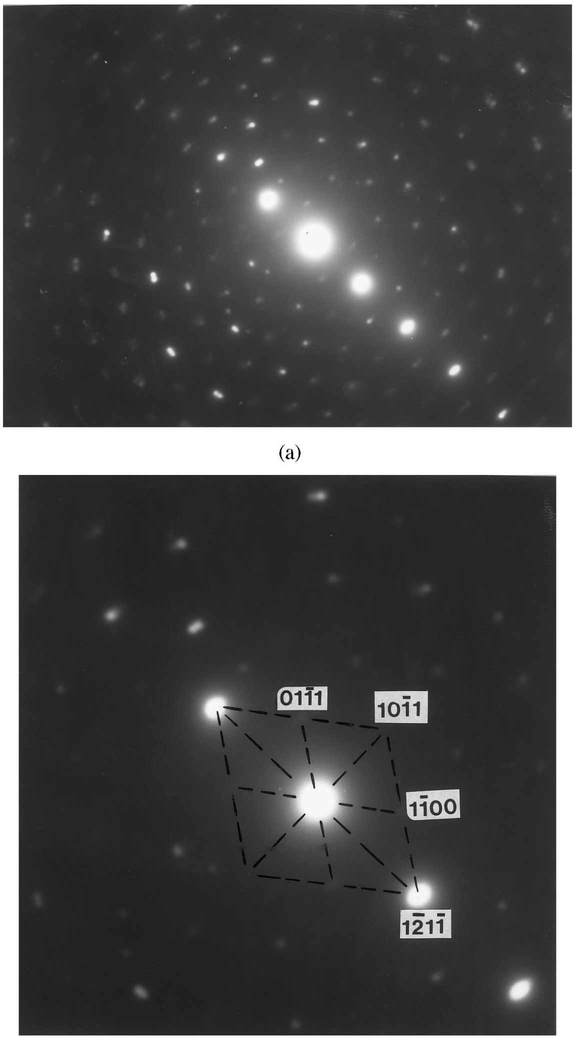


Fig. 9. SAED pattern of the hexagonal $Mg_4Nb_2O_9$ phase.

3.3 Microstructural analysis

SEM micrographs of the calcined $MgNb_2O_6$ powder (1150°C/4 h) are shown in Fig. 7. The particles are agglomerated and basically irregular in shape However, some spherical particles are clearly apparent at high magnification, ranging in diameter from 0·5–3·0 μm, in good agreement with the particle size distribution previously determined (Fig. 6). A TEM bright field image of an agglomerated or intergrown particle of the calcined $MgNb_2O_6$ powder (1150°C/4 h) is shown in Fig. 8, indicating the presence of two co-existing phases: the columbite-like $MgNb_2O_6$ phase (brighter area) and the parasitic hexagonal $Mg_4Nb_2O_9$ phase. The bulk of the particle gave a [Mg]:[Nb] ratio derived from EDX [Fig. 13(a)] of approximately 0·5 and a selected area electron diffraction (SAED) pattern (Fig. 9) characteristic of the columbite-type structure. However, the region marked as $Mg_4Nb_2O_9$ exhibits a [Mg]:[Nb] ratio of 2 [Fig. 13(b)], with a SAED patter which could be indexed as the corundum structure (Fig. 11) The reciprocal lattice patterns of both phases were simulated with the CaRine Crystallography 3·0 software, as demonstrated in Figs 10 and 12. In general, EDX analysis using a 20 nm probe from a large number of particles of the calcined powder confirmed that the

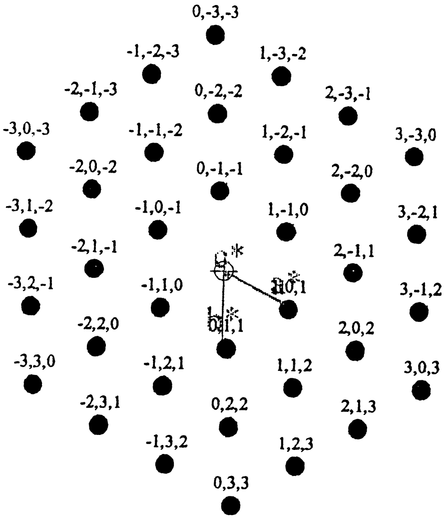
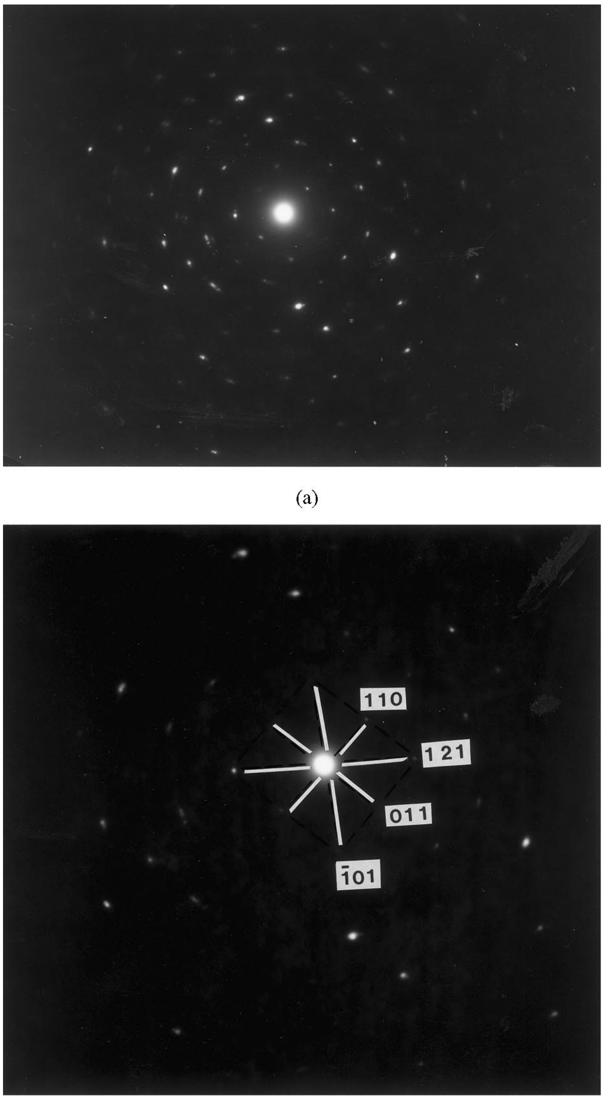


Fig. 10. Reciprocal lattice pattern simulation of $Mg_4Nb_2O_9$ phase.



(a)

(b)

Fig. 11. SAED pattern of the orthorhombic $MgNb_2O_6$ phase.

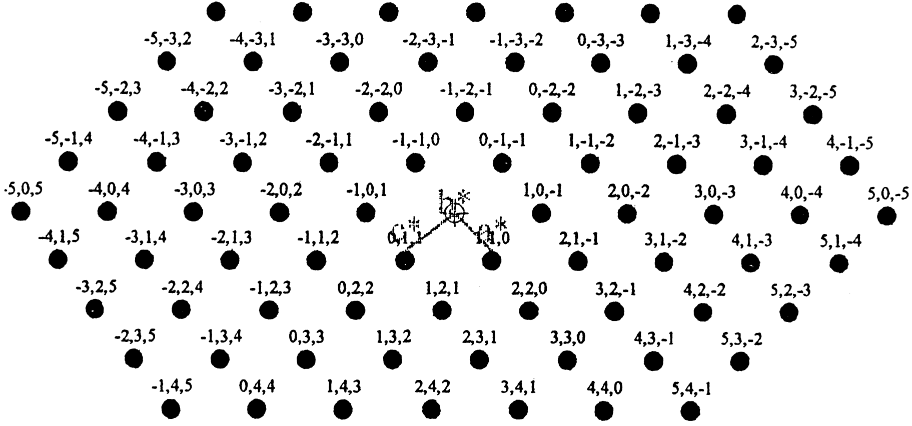
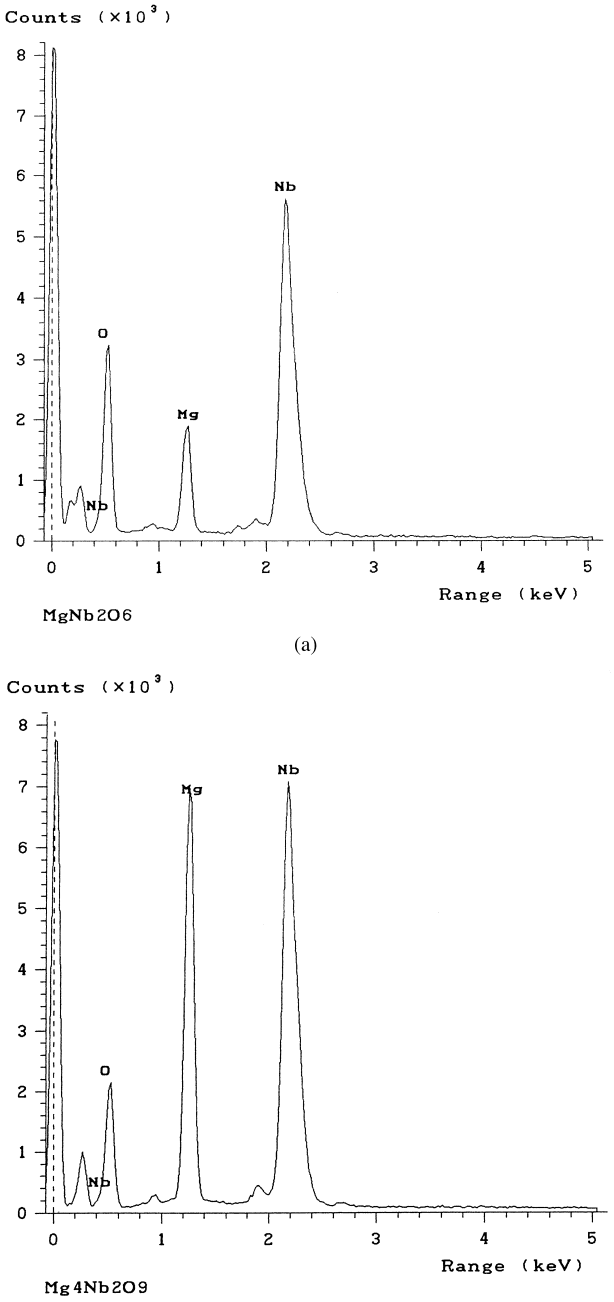


Fig. 12. Reciprocal lattice pattern simulation of the $MgNb_2O_6$ phase.



(a)

(b)

Fig. 13. EDX analysis of the calcined powder, (a) from the $MgNb_2O_6$ phase and (b) from the $Mg_4Nb_2O_9$ phase.

inhomogeneity was confined solely to these two phases, namely $MgNb_2O_6$ and $Mg_4Nb_2O_9$ (Fig. 13), in good agreement with XRD results.

4 Conclusion

Modified, mixed oxide synthetic routes for $MgNb_2O_6$ have been developed which show a high level of reproducibility. These involve the use of laboratory-grade precursors, low milling and drying times of powders, together with moderately low calcination temperatures and times (1150°C for 4 h). They represent significant time-savings compared to synthetic procedures currently advocated, and require only relatively impure laboratory-grade precursors. Moreover, a corundum-free columbite $MgNb_2O_6$ phase has been obtained in this study by using magnesium carbonate hydroxide pentahydrate as a source of magnesium together with a careful calcination treatment.

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