

Preparation of nanocrystalline $\text{Mg}_4\text{Nb}_2\text{O}_9$ by citrate gel method

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Abstract. A gel was formed when a aqueous solution of $\text{Mg}(\text{NO}_3)_2$, NbF_5 and citric acid in stoichiometric ratio was heated on a water bath. No precipitation was observed at acidic pH and gellation was complete with evaporation of the solvent. This gel on decomposition at 750°C produced nanocrystallites of ternary oxide, $\text{Mg}_4\text{Nb}_2\text{O}_9$ (M4N2). The phase contents and lattice parameters were studied by powder X-ray diffraction (XRD) at various temperatures. Particle size and morphology were studied by transmission electron spectroscopy (TEM). For comparison, M4N2 powders were also prepared by conventional ceramic route at 900°C .

Keywords. Ceramics; oxides; electron microscopy; X-ray methods; magnesium niobate.

1. Introduction

Magnesium niobate (2 : 1) with corundum like structure has attracted interest because of possible application as microwave dielectric material due to its low dielectric loss and high dielectric constant (Cheng *et al* 1997; Joy 1997; Lu and Yang 2001; Sreedhar and Pawaskar 2002; Ananta 2004; Kan and Ogawa 2004). It also has room temperature photoluminescent material. It is also used as a suitable buffer layer material for fabrication of ferroelectric memory devices. Recently, Lu and Yan (2001) have shown that $\text{Mg}_4\text{Nb}_2\text{O}_9$ (M4N2) is a better precursor material for the successful preparation of single phase relaxor ferroelectric perovskite ($\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$) which is becoming increasingly important for transducer, electrostrictor and actuator applications. Generally, M4N2 powders are prepared by conventional ceramic route at 900°C . It could also (Joy 1997) be prepared using potassium niobate precursor. The purpose of this study was to prepare ultrafine M4N2 powder using citrate gel technique from simple inorganic salts. The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Different chemical methods, e.g. co-precipitation, sol-gel, hydrothermal and colloid emulsion technique, have been used to efficiently control the morphology and chemical composition of prepared powder. Among these wet chemical techniques, alkoxide sol-gel, hydrothermal and colloid emulsions are time consuming and involve the use of highly unstable alkoxides and dif-

ficult to maintain reaction conditions. This citrate gel process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The citrate gel process offers a number of advantages for the preparation of fine powders of many complex oxides as quoted in the literature (Dhage *et al* 2003, 2004a, b; Gaikwad *et al* 2004). This process involves complexation of metal ions by poly functional carboxyl acids such as citric acid or tartaric acid having one hydroxyl group. On heating this mixture, the solvent (water) evaporates resulting in increased viscosity. On complete removal of water, the mixture turns to a polymeric glass and its constituents mixed at atomic level. This glass on heating at higher temperature produces the respective oxides. This method has not been reported in the literature for the preparation of M4N2 powders.

2. Experimental

For preparing $\text{Mg}_4\text{Nb}_2\text{O}_9$ niobium (V) oxide, magnesium nitrate and citric acid were used as starting materials, and all were of AR grade (Loba chemie, 99.9% purity). A stoichiometric amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water and Nb_2O_5 was dissolved in minimum amount of HF after heating in hot water bath for 20 h. The aqueous solution containing magnesium and niobium was mixed with required quantity of citric acid. The ratio of the total metal cations to citric acid was one. Since there was no precipitation during mixing of citric acid and these metal salts, the pH (~2) of the solution was not varied. On heating on a water bath at 100°C a gel was formed after evaporation of water. Subsequently, the gel was decomposed at various

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temperatures ranging from 400–800°C for 8 h. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consisted of very light and homogeneous flakes of very small particle size. For comparison, M4N2 samples were also prepared by the conventional ceramic route. The magnesium oxide and niobium pentoxide were taken in stoichiometric ratio, mixed, ground several times and heated at 900°C for 12 h. Various techniques such as X-ray diffraction (XRD), BET surface area measurements (Nova 1200 instrument) and TEM were employed to characterize these powders. The powder X-ray diffraction pattern were recorded for citrate derived samples

calced at various temperatures by using Philips PW-1710 model X-ray diffractometer using $\text{Cu-K}\alpha$. The X-ray diffractometer was operated at 20 kV and 20 mA with nickel as filter. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10–80° for a period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the unit cell parameters. The transmission electron microscope (TEM) picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. The morphology of both ceramic and citrate derived powders were observed by TEM.

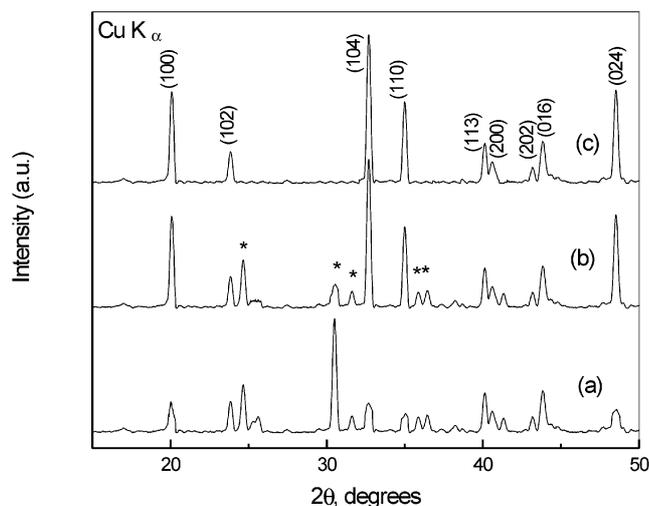


Figure 1. XRD of citrate derived M4N2 powder calcined at (a) 400°C, (b) 600°C and (c) 750°C for 8 h. ‘*’ marked peaks indicate MgNb_2O_6 phase.

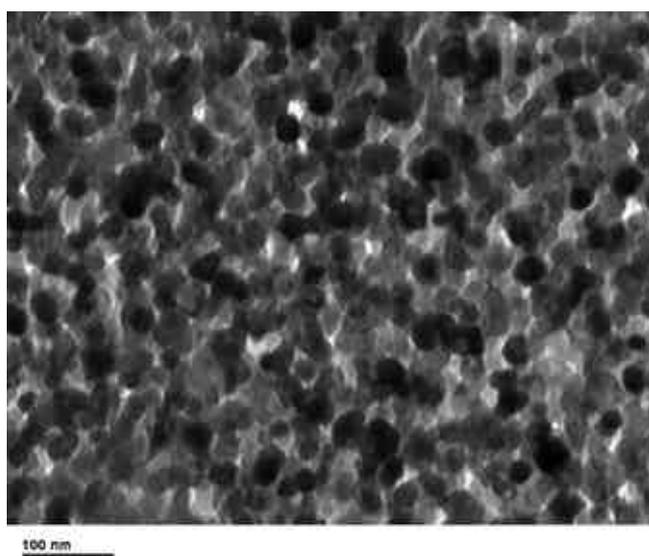


Figure 2. TEM of citrate gel derived M4N2 powder calcined at 750°C.

3. Results and discussion

The citric acid added acts as a complexing agent. The mixture of citric acid and aqueous metal salts on heating on a water bath forms a gel which decomposes at higher temperatures (>300°C). During calcination process, a black fluffy mass (foam-like) is formed which occupies large volume of the furnace. As the temperature increases, the black mass turns to white in colour with the removal of carbon. Samples calcined at 500°C for 40 min shows <1% of carbon. At higher calcination temperatures no carbon was found to be present. The minimum ratio of citric acid to total metal cations was found to be 1 for the formation of the required phase at given duration. The pH was found to be 2 and the gellation was continued as no precipitation was found to occur. At higher concentration of citric acid, the carbon content was found to be more, but no precipitation occurred. Figure 1 shows the XRD pattern of the powders calcined at different temperatures ranging from 400–750°C for 8 h. At initial stages of heating up to 600°C, coulombite MgNb_2O_6 phase was found to be formed along with M4N2. This phase disappears on longer duration of heating at higher temperatures (750°C). The crystal structure of M4N2 is hexagonal and all the d -lines of the pattern match with reported values (JCPDS 38–1459, $a = 5.118 \text{ \AA}$ and $c = 14.039 \text{ \AA}$). The lattice parameters calculated by least square fit are $a = 5.12 \text{ \AA}$ and $c = 14.047 \text{ \AA}$. The measured surface area was found to be $65 \text{ m}^2/\text{g}$.

Conventional solid state method also forms M4N2 phase at 900°C (figure 3) after prolonged heating (12 h) with comparatively larger particle size of $\sim 1 \mu\text{m}$. The particle size and morphology of the calcined powders were examined by transmission electron microscopy. Particle morphology of calcined powder (750°C for 6 h) prepared by citrate process was irregular in shape, with an average primary particle size of around 40 nm (figure 2). The crystallite size calculated from Scherrer’s formula

$$t = KI/B\cos\theta_B,$$

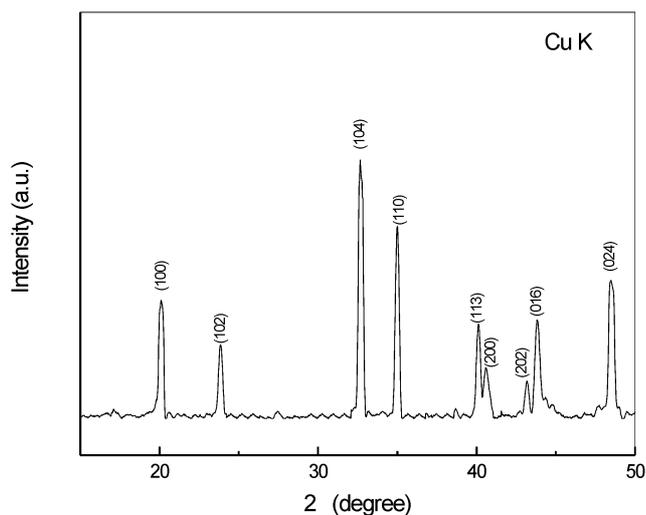


Figure 3. XRD of conventional ceramic route derived M4N2 powder calcined at 900°C.

where t is the average size of the particles, assuming particles are spherical, $K = 0.9$, λ the wavelength of X-ray radiation, B the full width at half maximum of the diffracted peak (after correcting for instrumental broadening) and q_B , the angle of diffraction, is 60 nm.

4. Conclusions

A simple citrate gel method was used to prepare ultrafine particles of M4N2. The M4N2 phase was found to be formed at 750°C with average particle size of 40 nm. At temperatures up to 600°C, coulombite $MgNb_2O_6$ phase was found to be in the initial stages which in turn gives M4N2 after longer durations of annealing at 750°C.

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