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Effect of calcination conditions on phase formation of microwave dielectric cobalt niobate (CoNb₂O₆) powders via a mixed oxide synthesis route

Nopsiri Chaiyo and Naratip Vittayakorn*

King Mongkut's Institute of Technology Ladkrabang Nanotechnology Research Center (NRC), King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand 10520

Cobalt niobate $(CoNb_2O_6)$ powders have been prepared using a mixed oxide synthesis route. The formation of the $CoNb_2O_6$ phase in the calcined powders has been investigated as a function of calcination conditions by differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques. The morphological evolution was determined by scanning electron microscopy (SEM). It has been found that the minor phases of unreacted Co_3O_4 and the orthorhombic-Nb₂O₅ and monoclinic- β -Nb₂O₅ phase tend to form together with the columbite $CoNb_2O_6$ phase, depending on calcination conditions. It is seen that optimization of calcination conditions can lead to a single-phase orthorhombic $CoNb_2O_6$. The calcination temperature and dwell time have been found to have a pronounced effect on the phase formation of the calcined cobalt niobate ($CoNb_2O_6$) powders. Optimization of calcination conditions can lead to a single-phase $CoNb_2O_6$ in a columbite phase.

Key words: CoNb₂O₆, Calcination, Powder synthesis.

Introduction

Advances in wireless communication systems are very dependent upon improvements in microwave dielectric materials. In particular, centimetre and millimetre wave wireless applications require high-Q materials that would be less expensive than the known high-Q perovskitestructure, barium-tantalate-based microwave dielectrics and would not need high sintering temperatures [1]. Cobalt niobate CoNb₂O₆ is a potential candidate for mechanical filter coatings and electrical applications such as for resonators and capacitors which has a columbite structure having the general formula AB_2O_6 , with a *Pcan* (no.60) space group and can be used for capacitors or dielectric resonators for microwave applications due to its low tangent loss (tan δ) and high dielectric constant (ε_r) [1, 2]. Figure 1 shows the columbite structure of $CoNb_2O_6$. Regarding the structure, $[M-O_6]$ (M = Co or Nb) octahedra share edges forming chains along the c-axis. Parallel Co-O₆ and Nb-O₆ chains alternate along the *b*-axis. CoNb₂O₆ is well known as the key precursor for the successful preparation of single-phase perovskite $Pb(Co_{1/3}Nb_{2/3})O_3$ (PCoN), which is becoming increasingly important for multilayer ceramic capacitor, transducer, electrostrictor and actuator applications [3, 4]. The objective of this investigation was to study the reaction between the starting cobalt oxide and niobium oxide precursors, phase formation, microstructure and microwave dielectric properties of columbite-structure cobalt niobate ceramics.

*Corresponding author:

Fax: +66-2-3264415

E-mail: naratipcmu@yahoo.com



Fig. 1. Crystal structure of CoNb₂O₆ compound.

Experimental

Ceramics with the composition CoNb₂O₆ were produced by the conventional mixed-oxide route. All samples in this study were prepared from reagent-grade oxides: Co₃O₄ (99.99%, Aldrich, U.S.A.) and Nb₂O₅ (99.9%, Aldrich, U.S.A.). Co₃O₄ and Nb₂O₅ powders were weighed and mixed by ball-milling in a polyethylene bottle together with methyl alcohol and partially stabilized zirconia media. Methyl alcohol was removed by heating at 80 °C for appropriate durations. After drying, the reaction of the uncalcined powders taking place during heat treatment was investigated by differential thermal analysis (DTA; Perkin-Elmer 7 series) using a heating rate of 10 Kminute⁻¹ in air from room temperature up to 1350 °C. Based on the DTA results, various calcinations conditions, i.e. temperature ranging from 700-1100 °C and dwell time ranging from 15 to 240 minutes, were applied with a heating/ cooling rate of 5 Kminute⁻¹, in order to investigate the formation of CoNb₂O₆.

Tel : +66-9-700-2136

All powders were subsequently examined by room temperature X-ray diffraction (XRD; Bruker D8 Advance) using Ni-filtered CuK_{α} radiation to identify the phases formed and optimum calcination conditions for the formation of CoNb₂O₆ powders. The relative proportions of CoNb₂O₆, Co₃O₄, orthorhombic-Nb₂O₅ and monoclinic- β -Nb₂O₅ have been calculated according to the following approximate relationship, by analogy with our treatment of the yield of CoNb₂O₆ in a related synthesis [5, 6]:

Wt% columbite phase

$$= \left(\frac{I_{col}}{I_{col} + I_{Co_3O_4} + I_{Otho-Nb_2O_5} + I_{\beta-Nb_2O_5}}\right) \times 100$$
(1)

here I_{col} , $I_{Co_3O_4}$, $I_{Otho-Nb_2O_5}$ and $I_{\beta-Nb_2O_5}$ refer to the intensities of the (311) columbite peak, (311) cubic-Co₃O₄ peak, (180) orthorhombic-Nb₂O₅ and (400) monoclinic- β -Nb₂O₅ peak respectively, these being the strongest reflections in all cases. Microstructural analysis of the ceramic samples was performed by means of scanning electron microscopy (LEO 1455VP, Cambridge, England).

Results and Discussions

Figure 2 shows the DTA curves for the mixture of Co_3O_4 and Nb_2O_5 with a molar ratio of 1 : 3. From Fig. 2, three endothermic peaks centered at 100.6, 357 and 810 °C are observed. The first endothermic peak at 100.6 °C is attributed to the evaporation of water molecules [7]. The second endothermic peak occurring at 357 °C should correspond to the decomposition of the organic species from the milling process [8]. The different temperature, intensities, and shapes of the thermal peaks are probably related to the different nature of the organic species and consequently, caused by the removal of species bounded differently in the network [7, 8]. The third endothermic peak at 810 °C is assigned to the formation of CoNb₂O₆ by combination reactions of Co₃O₄ and Nb₂O₅. According



Fig. 2. DTA curve for the mixture of Co_3O_4 -Nb₂O₅ powders.



Fig. 3. XRD patterns of $CoNb_2O_6$ powder calcined at various temperatures for 4 h with heating/cooling rates of 20 K minute⁻¹.

to the DTA measurements, these data were used to define the range of calcination temperature for XRD investigation between 700 $^{\circ}$ C and 1100 $^{\circ}$ C.

XRD paterns of all calcined powders are given in Fig. 3. It is seen that $CoNb_2O_6$ crystallites were already developed in the powder at a calcination temperature as low as 700 °C, accompanied with cubic-Co₃O₄ (JCPDS files No 78-1969), orthorhombic-Nb₂O₅ (JCPDS files No 27-1003), monoclinic- β -Nb₂O₅ (JCPDS files No 26-0885). No evidence of a cubic phase of CoO was found. The strongest reflection from Co₃O₄, (200), was located at $2\theta = 36.8$ whereas the observed temperature variation of Nb₂O₅ in terms of the intensity and position of the peaks attested to a number of phase changes. In niobium oxide synthesis through precipitation from solution, the calcination temperature has a significant effect on the crystal structure of the resulting oxide. The XRD patterns show that the transformation from the orthorhombic- Nb_2O_5 to monoclinic- β - Nb_2O_5 takes place as the calcination temperature increases, which was reported earlier by Belous et al. [9]. As the temperature increased to 800 °C, the intensity of the columbite CoNb₂O₆ peaks was further enhanced and it became the only phase. Upon calcination at 900, 1000 and 1100 °C, an essentially single of CoNb₂O₆ phase was obtained. This CoNb₂O₆ phase was able to be indexed according to an orthorhombic columbite-type structure with lattice parameters a = 571 pm, b = 1414 pmand c = 504 pm, space group *Pcan (no. 60)*, consistent with JCPDS file number 32-0304. Having established the optimum calcination temperature, dewll times ranging from 15 minute to 120 minute with constant heating/cooling rate of 5 Kminute⁻¹ were applied at 800 °C, as shown in Fig. 4. It can be seen that a single-phase of $CoNb_2O_6$ powders was also successfully obtained with a calcinations temperature of 800 °C and a dwell time of 120 minutes or more applied. This was apparently a consequence of the enhancement in crystallinity of the $CoNb_2O_6$ phase with increasing dwell time. The disappearance of monoclinic- β -Nb₂O₅ and orthorhombic-Nb₂O₅ phase indicated that full crystallization has occurred at relative shorter calcinations



Fig. 4. XRD patterns of $CoNb_2O_6$ powder calcined with heating/ cooling rates of 20 Kminute⁻¹ at 800 °C for 15-240 minutes.



Fig. 5. Fraction of the columbite phase formed in $CoNb_2O_6$ specimens (a) as a function of calcination temperature (calcined for 4 hours) (b) as a function of calcination time (calcined at 800 °C).

times. The observation that the dwell time may also play an important role in obtaining a single phase product is also consistent with other systems [10, 11]. The columbite phase formation at various calcination temperatures and time is shown in Fig. 5(a) and (b). By increasing the calcination temperature from 700 to 1100 °C, the yield of the columbite phase increased significantly until at 800 °C, a single phase of CoNb₂O₆ was formed. However, form the present study, there are no significant differences between the powders calcined at temperatures ranging from 800 to 1100 °C. This observation agrees well with those derived from the DTA results. Apart from the calcination temperature, the effect of dwell time was also found to be quite significant (Fig. 4). It is seen that the single phase of $CoNb_2O_6$ (yield 100% within the limitations of the XRD technique) was found to be in powders, calcined at 800 °C with a dwell time of 120 minutes or more. The average grain sizes were determined from XRD patterns according to the Scherrer's equation:

$$D = \frac{k\lambda}{\beta\cos\theta_B} \tag{2}$$

where D is the average grain size, k is a constant equal to 0.89, θ_B is the (311) peak angle, λ is the X-ray wavelength equal to 1.5406 Å and β is the half peak width. The average grain size of CoNb₂O₆ powders at 800 °C with a dwell time of 120 minutes was about 280 nm.

Because the raw materials used were multiphase, the formation reaction of the columbite phase belongs to a heterogeneous system. A model used to treat multiphase reaction kinetics was derived by Johnson and Mehl and the equation for this reaction is:

$$\ln[1/(1-y)] = (kt)^{n}$$
(3)

where y is the constant of the columbite phase formed, k the reaction rate constant, t the calcination time and n is the reaction order [12, 13]. The relation of ln $[\ln 1/(1-y)]$ versus ln t is plotted in Fig. 6. From this graph, it was found that the phase transformation of the columbite phase obeys this theory of phase transformations [14]. This phenomenological model is based on the theory of nucleation and growth and is accurate for a large number of systems. The fact that the data in Fig. 6 closely follow Eq. (3) indicates that the columbite phase grows at a constant rate from a random distribution of point nuclei [14]. SEM micrographs of the calcined CoNb₂O₆ powders are given in Fig. 7(a) and 7(b). In general, the particles are agglomerated



Fig. 6. Johnson-Mehl-Avrami-type for the formation of columbite phase in CoNb₂O₆ specimens isothermally heat treated at 800 °C.



Fig. 7. Scanning electron micrographs of the CoNb2O6 powders calcined at 800 °C for 2 h, with heating/cooling rate 5 °C/min.

and basically irregular in shape, with a substantial variation in particle size and morphology. The particle size can be estimated from SEM micrographs to be in the range of 70-300 nm. A detailed study at higher magnification (Fig. 7(b)) showed that the particles had spherical secondary particles, composed of nano-sized primary particulates.

Conclusions

Polycrystalline powder of CoNb₂O₆ was synthesized using solid state synthesis using oxides as starting materials. Evidence has been obtained for a 100% yield of CoNb₂O₆ at a calcination temperature of 800 °C for 120 minutes with heating/cooling rates of 5 Kminute⁻¹. XRD showed the compound to have the columbite structure, having orthorhombic lattice parameters of a = $5.06880(\pm 0.0014)$ Å, b = 14.1348 (± 0.0046)Å and c = 5.2230 (± 0.0072)Å.

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