Trans. Nonferrous Met. Soc. China 19(2009) s92−s95

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Synthesis and characterization of $Ba(Co_xNb_{1-x})O_3$ nanoparticles by hydrothermal processing

Hyun-Ju KIM[1], Min-Cheol CHU[2], Seong-Jai CHO[2], Dong-Sik BAE[1]

1. School of Nano & Advanced Materials Engineering, Changwon National University, Gyeongnam 641-773, Korea;
2. Materials Evaluation Center, Korea Research Institute of Standards and Science, Yuseong, Daejeon 305-600, Korea

Received 2 March 2009; accepted 30 May 2009

Abstract: The nanosized $Ba(Co_xNb_{1-x})O_3$(BCN) particles were prepared under high temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. $Ba(Co_xNb_{1-x})O_3$ powders were obtained in the temperature range of 170−210 ℃ for 6 h. The results show that the average size of the synthesized particles increases with increasing reaction temperature. The average size of the synthesized particles is about 10 nm. The crystalline phase of the synthesized particles is found to be $Ba(Co_xNb_{1-x})O_3$. Ceramics derived from the nano BCN powders could achieve high sintering density at a relatively low sintering temperature.

Key words: $Ba(Co_xNb_{1-x})O_3$ powders; nanoparticles; hydrothermal processing

1 Introduction

One of the present challenges in material science is the production of materials in the form of nanometric particles with a controlled composition and structure, because the nanometric size can provide new physical and chemical properties to these materials[1]. Ceramic dielectrics are used extensively in microwave communication systems including cellular phone, direct broadcasting satellite and global positioning systems. The advantage of using microwave dielectric ceramics is the size reduction of microwave components. Requirements for these dielectric materials include a high relative permittivity (ε_r), low dielectric loss (high $Q\times f$ value) and a near-zero temperature coefficient of resonant frequency (τ_f). These three parameters are related to the size, frequency selectivity and temperature stability of the system, respectively. To satisfy the demands of microwave circuit designs, each dielectric property should be precisely controlled. Several complex perovskites ceramics $A(B'_{1/3}B''_{2/3})O_3$ (B′=Zn, Co, Ni or Mg; B″=Ta or Nb) have attracted a great deal of attention due to their very low losses[2].

Accordingly, complex perovskites with general formula $A(B_xB'_{1-x})O_3$, where $A=Ba^{2+}$, $B=Mg^{2+}$, Zn^{2+} or Ni^{2+}, $B'=Ta^{5+}$ or Nb^{5+} show very interesting properties at microwave frequencies, such as high permittivity ε', low dielectric loss ε'' and small temperature coefficient of resonance frequency[3−4]. Therefore, these materials are commonly used as resonators in microwave devices. High Q-factor is of the most concern. Recently, due to the high cost of Ta_2O_5, niobium based complex perovskites has attracted much attention[5−7]. For example, $Ba(Co_xNb_{1-x})O_3$ (BCN) has a relative permittivity of 32, a quality factor ($Q\times f$) greater than 50 000 GHz and a negative temperature coefficient of resonant frequency (τ_f) which can be adjusted to zero by Zn substitution[8−11]. BCN crystallizes in either a disordered cubic structure or in an ordered hexagonal structure. The ordered structure results from the 1:2 ordering of B′ and B″ cations along the ⟨111⟩ directions of the cubic unit cell. It is well established that B-site cation ordering in complex perovskites has a significant influence on the dielectric losses at microwave frequencies[12−13]. Stoichiometry of the B-site may also affect the ratio of 1:2 ordering. The $A(B_xB'_{1-x})O_3$-type complex perovskite may also have a disordered structure. $A(B_xB'_{1-x})O_3$ is commonly synthesized by solid-state reaction. This kind of synthesis method has not yet

Corresponding author: Dong-Sik BAE; Tel: +82-55-2133715; E-mail: dsbae7@changwon.ac.kr

achieved consistent results in producing in a high purity fine $A(B_xB'_{1-x})O_3$ powders.

Hydrothermal processes have the potential for the direct preparation of crystalline ceramic powders and offer a low-temperature alternative to conventional powder synthesis techniques in the production of oxide powders[14]. This process can produce fine, high-purity, stoichiometric particles of single and multi-component metal oxides. Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent are carefully controlled, the desired shape and size of the particles can be produced[15−16]. A uniform distribution of the particles is important for optimal control of grain size and microstructure to maintain a high reliability. It has been demonstrated that such powders are composed of much softer agglomerates and sinter much better than those prepared by calcination decomposition of the same oxides[17]. These powders could be sintered at low temperature without calcination and milling steps [18−19].

The objective of this study is to prepare BCN particles by hydrothermal process and to determine the influence of the processing conditions on the formation and phase of the powders.

2 Experimental

$Ba(Co_xNb_{1-x})O_3$ particles were prepared by hydrothermal method using barium nitrate ($Ba(NO_3)_2$, cobalt nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$, niobium chloride $NbCl_5$ as raw materials. The niobium sol was obtained by dissolving $NbCl_5$ in ethanol followed by hydrolysis with excessive water. The sol solution of $Ba(Co_xNb_{1-x})O_3$ was prepared by mixing the aqueous solution of barium and magnesium nitrates with the niobium hydroxide precipitates at a molar ratio of Ba^{2+}:Co^{2+}:Nb^{5+}=3:1:2. And then pH was adjusted by adding 1 mol/L potassium hydrate (KOH). The resulting suspension was placed in a 1 L stainless steel pressure vessel. The vessel was then heated to the desired temperature at a rate of 5 ℃/min. During heating, pressure was usually maintained below 1 MPa during the holding period. The reaction products were washed at least five times by repeated cycles of centrifugation and re-dispersion in water. The recovered powders were analyzed for phase composition using X-ray diffraction at 20°−80° with rate of 2.5(°)/min. The morphology of the synthesized particles was observed using scanning electron microscope(SEM) and transmission electron microscope (TEM, JEM 2100F).

3 Results and discussion

The conditions of hydrothermal processing have significant effects on the formation, phase component, morphology and particle size of BCN powders. The pH in the reaction medium significantly affects the formation of BCN powders. The reaction temperature has a great effect on the particle size of the products and the agglomeration among particles[20]. Lowering reaction temperature leads to decreasing grain size and increasing agglomeration among particles[20]. It has been proposed that crystallization under hydrothermal conditions proceeds by dissolution-precipitation and structural rearrangement. The reaction time plays an important role in the phase transformation from hydroxide to oxide.

Fig.1 shows the SEM images of synthesized $Ba(Co_xNb_{1-x})O_3$ particles at different reaction temperatures. It can be seen from Fig.1 that the average size of the synthesized particles increased with increasing reaction temperature of 190−210 ℃ for 6 h. The size and size distribution of the synthesized particles are unclear and broad, respectively.

Fig.2 shows the TEM image of synthesized particles reacted at 190 ℃ for 6 h. The average size of the synthesized particles is about 10 nm.

Fig.3 shows the XRD patterns of the synthesized particles at different reaction temperatures. It can be seen from Fig.3 that the crystalline phase of the synthesized particles is $Ba(Co_xNb_{1-x})O_3$ in the reaction temperature range of 170 ℃−210 ℃ for 6 h. In addition, the as-prepared nanoparticles reveal good sintering abilities at

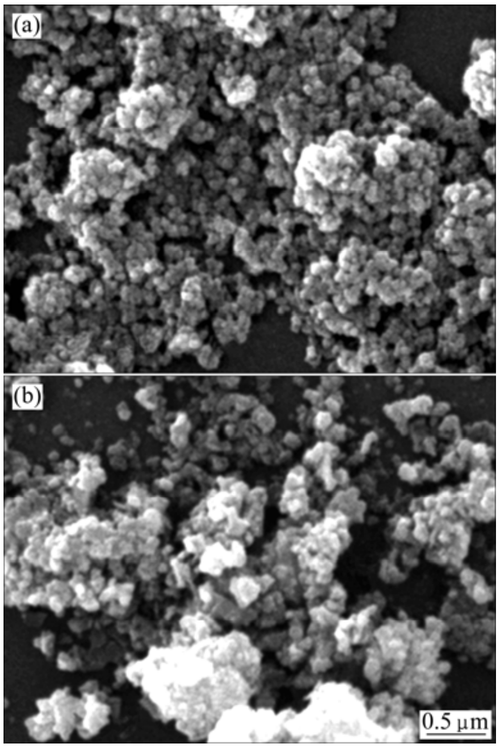

Fig.1 SEM images of synthesized $Ba(Co_xNb_{1-x})O_3$ particles at different reaction temperatures for 6 h: (a) 190 ℃; (b) 210 ℃

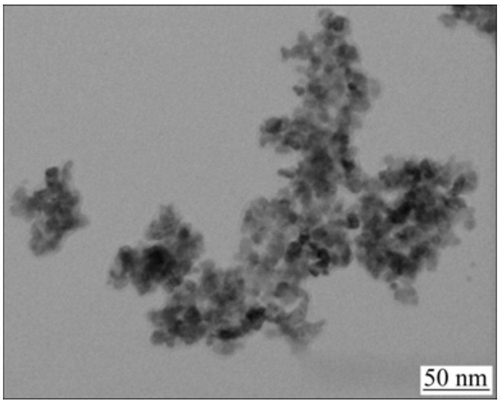

Fig.2 TEM image of synthesized $Ba(Co_xNb_{1-x})O_3$ particles sintered at 190 ℃ for 6 h

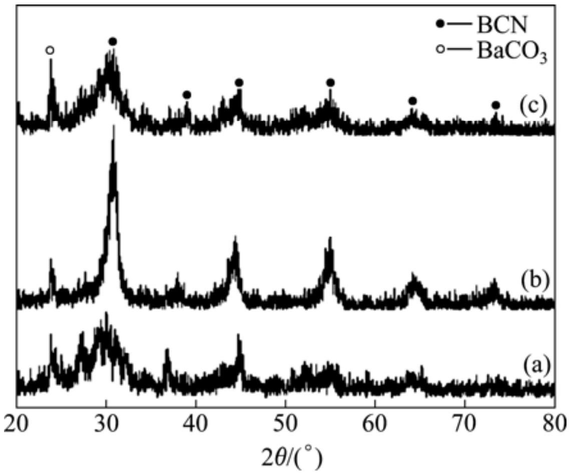

Fig.3 XRD patterns of synthesized $Ba(Co_xNb_{1-x})O_3$ particles at different reaction temperatures for 6 h; (a) 170 ℃, (b) 190 ℃, (c) 210 ℃

low temperature.

Fig.4 shows the surface microstructure of the synthesized $Ba(Co_xNb_{1-x})O_3$ sintered at 1 100 ℃ for 2 h. The average grain size and distribution of the $Ba(Co_x$-$Nb_{1-x})O_3$ sintered body are below 500 nm and broad, respectively.

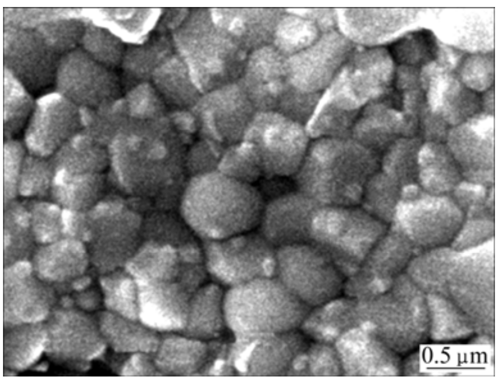

Fig.4 SEM image of synthesized $Ba(Co_xNb_{1-x})O_3$ particles sintered at 1 100 ℃ for 2 h

4 Conclusions

1) The nanosized $Ba(Co_xNb_{1-x})O_3$ particles were prepared under high temperature and high pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. $Ba(Co_xNb_{1-x})O_3$ powders were obtained in the temperature range of 170 ℃−210 ℃ for 6 h.

2) The average size of the synthesized particles increases with increasing reaction temperature.

3) The average size of the synthesized particles is about 10 nm.

4) The crystalline phase of the synthesized particles is found to be $Ba(Co_xNb_{1-x})O_3$. Ceramics derived from the nano BCN powders could achieve high sintering densities at a relatively low sintering temperature.

Acknowledgment

This research was financially supported by the Ministry of Education, Science Technology (MEST) and Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Regional Innovation.

References

[1] TORRES R, CARETTI I, GAGO R, MARTÍN Z, JIMÉNEZ I. Bonding structure of BCN nanopowders prepared by ball milling [J]. Diamond and Related Materials, 2007, 16(4/7): 1450−1454.

[2] RIAZIKHOEI P, AZOUGH F, FREER R. The influence of $ZnNb_2O_6$ on the microwave dielectric properties of $ZrTi_2O_6$ ceramics [J]. Amer Ceram Soc, 2006, 89(1): 216−223.

[3] NOMURA S, TOYAMA K, KANETA K. $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with temperature-stable high dielectric constant and low microwave loss [J]. Jpn J Appl Phys, 1982, 21: 624−626.

[4] ONADA M, KUWATA J, KANETA K, TOYAMA K, NOMURA. $Ba(Zn_{1/3}Nb_{2/3})$-O_3–$Sr(Zn_{1/3}Nb_{2/3})O_3$ solid solution ceramics with temperature-stable high dielectric constant and low microwave loss [J]. Jpn J Appl Phys, 1982, 21: 1707−1717.

[5] AZOUGH F, LEACH C, FREER R. Effect of cation order micro wave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics [J]. Key Eng Mater, 2002, 264/268: 1153−1156.

[6] AZOUGH F, LEACH C, FREER R. The effect of additives and processing parameters on the microstructure and microwave dielectric properties of $Ba(Me_{1/3}Nb_{2/3})O_3$ complex perovskites (Me=Zn, Co, Ni and Mg) [C]//Microwave Materials and Their Applications (MMA20002), York, UK, 2002(poster 23): 1153−1156.

[7] FUKUI T, SAKURAI C, OKUYAMA M. Preparation of $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics as microwave dielectrics through alkoxide-hydroxide route [J]. J Mater Res, 1992, 7(7): 1883−1887.

[8] ENDO K, FUJIMOTO K, MURAKAWA K. Dielectric properties of ceramics in $Ba(Co_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Nb_{2/3})O_3$ solid solutions [J]. J Am Ceram Soc, 1987, 70(9): C215−C218.

[9] AHN C W, JANG H J, NAHM S, PARK H M, LEE H J. Effect of microstructure on the microwave dielectric properties of

$Ba(Co_{1/3}Nb_{2/3})O_3$ and $(1-x)Ba(Co_{1/3}Nb_{2/3})O_3-xBa(Zn_{1/3}Nb_{2/3})O_3$ solid solutions [J]. J Eur Ceram Soc, 2003, 23: 2473−2478.

[10] AZOUGH F, LEACH C, FREER R. Effect of V_2O_5 on the sintering behaviour, cation order and properties of $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ ceramics [J]. J Eur Ceram Soc, 2005, 25: 2839−2841.

[11] HUGHES H, IDDLES D M, REANEY I M. Niobate-based microwave dielectrics suitable for third generation mobile phone base stations [J]. Appl Phys Lett, 2001, 79(18): 2952−2961.

[12] DAVIS P K, TONG J, NEGAS T. Effect of ordering induced domain boundaries on low-loss $Ba(Zn_{1/3}Nb_{2/3})O_3$ $BaZrO_3$ perovskite microwave dielectrics [J]. J Am Ceram Soc, 1997, 80(7): 1724−1740.

[13] KIM I T, KIM Y H, CHUNG S J. Order-disorder transition and microwave dielectric properties of $Ba(Ni_{1/3}Nb_{2/3})O_3$ ceramics [J]. Jpn J Appl Phys, 1995, 34(part 1, No.8A): 4096−4103.

[14] GERHARDT R, NOWICK A S. Electrical measurements [J]. J Ame Ceram Soc, 1986, 69(9): 641−646.

[15] CHIANG Y M, LAVIK E B, KOSACKI I, TULLER H L, YING J Y. Defect and transport properties of nanocrystalline CeO_{2-x} [J]. Apl Phys Lett, 1996, 69: 186−187.

[16] HIRANO S. Hydrothermal processing of ceramics [J]. Am Ceram Soc Bull, 1987, 66: 1342−1344.

[17] DAWSON W J. Hydrothermal synthesis of advanced ceramic powder [J]. Am Ceram Soc Bull, 1989, 67: 1673−78.

[18] CHO S B, VENIGALLA S, ADAIR J H. Morphological control of α-Al_2O_3 in 1,4-butanediol solution [C]// Science, Technology, and Applications of Colloidal Suspensions. Westerville, OH: American Ceramic Society, 1995: 139−150.

[19] HABERKO K, PYDA W. Preparation of Ca-stabilized ZrO_2 micropowders by a hydrothermal method, science and technology of zirconia, Ⅱ. Advances in ceramics [J]. etc Am Cream Soc, 1984, 12: 774−83.

[20] ROZMAN M, DROFENIK M. Hydrothermal synthesis of manganese zinc ferrites [J]. J. Am Ceram Soc, 1995, 78(9): 2449−55.

(Edited by LI Xiang-qun)