

Liquid phase low temperature sintering of niobate and cerate fine powders

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Abstract The efficiency of simultaneous application of chemically-derived starting powders and melt-forming sintering aids in low temperature sintering has been demonstrated. Doping of cryochemically processed BiNbO_4 powders with $\text{CuO}/\text{V}_2\text{O}_5$ causes reducing sintering temperatures from 850–900°C to 700–720°C. Similar doping of $\text{Zn}_3\text{Nb}_2\text{O}_8$ fine powders allows to obtain ceramics with density 97–98% and $Q \times F$ values up to 40 000 GHz at $T > 720^\circ\text{C}$. The sintering of solution-derived BaCeO_3 powders doped with CuO results in dense ceramics at $T = 1000^\circ\text{C}$. Morphological evolution during sintering was observed using hot stage SEM. Low temperature liquid phase sintering of fine powders is rather sensitive to the traces of secondary phases and to the micromorphology of starting powders though observed reduction of sintering temperatures is substantially larger than for traditional liquid phase sintering of coarse-grained oxide powders.

Keywords Low temperature sintering · Fine powders · Freeze drying · Microwave dielectrics · Barrier materials

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Introduction

The problem of reducing sintering temperatures (T_s) is rather topical for a large number of oxide ceramic materials applied in high and low voltage electronics. Some of them demand complicated and energy-consuming sintering at $T_s \geq 1500^\circ\text{C}$ while in many other cases the reduction of sintering temperature by 100–200°C can be critical for the development of new devices like microwave chip modules based on the LTCC microwave dielectrics. One of the basic methods of sintering temperature reduction is based on the application of finely grained starting powders obtained by intensive grinding or by wet chemical methods. Meanwhile, the effect of their application is often rather small for submicron powders or poorly predictable for nanosized powders due to drastic enhancement of the particle agglomeration influence on the sintering processes.

Another T_s reduction method widely used in the sintering practice is the introduction of small amount (0.1–5%) of sintering aids into the starting powder. Their influence can be based on various mechanisms, while in most cases T_s reduction effect is caused by the formation of thin liquid layer of molten eutectics at the grain boundaries of target material followed by dissolution of intergrain necks, rearrangement of wetted grains and enhanced mass transfer through the liquid phase that promotes the densification at the last stages of sintering [1]. Successful application of this method depends on a large number of factors like eutectic temperatures and solubilities of solid components in the eutectic melts. Proper selection of material/dopant combination can reduce T_s for 500–600°C [2, 3] while in many other cases the effect is rather limited and does not exceed 100–150°C at $T \sim 1500^\circ\text{C}$.

Simultaneous application of both T_s reduction methods could have synergistic effect and promote further

development of low temperature sintering processes. In spite of simplicity of this approach, there is a definite lack of information about sintering behavior of the finely grained systems during liquid phase sintering and the influence of various powder parameters and processing variables on this process. Several results of our studies of dense ceramic materials preparation using liquid phase sintering of fine oxide powders are briefly described in this paper. The comparison of sintering behavior of various materials under these conditions might be useful for the identification of general features and common phenomena for this type of sintering processes.

BiNbO₄ ceramics is known as one of the perspective microwave dielectric materials with reasonable values of dielectric constant ($\epsilon_r = 43\text{--}44$) and dielectric losses ($Q \times F = 15\,000\text{--}22\,000$ GHz) achieved at rather low sintering temperatures ($T_s \leq 950^\circ\text{C}$) [4, 5]. The application of this material in the multilayer microwave chips is complicated by significant chemical interaction with silver at $850\text{--}900^\circ\text{C}$ [6]. T_s of pure single phase BiNbO₄ is $1100\text{--}1150^\circ\text{C}$, though the production of BiNbO₄ ceramics from coarse-grained powders obtained by solid state synthesis method is usually performed at lower temperatures ($900\text{--}930^\circ\text{C}$) using CuO/V₂O₅ sintering aids. Recent studies demonstrated that BiNbO₄ doping with rare earth elements allows T_s to be reduced down to $800\text{--}850^\circ\text{C}$ [7, 8]. The effect of T_s reduction by CuO/V₂O₅ dopant is usually attributed to the liquid phase sintering due to the appearance of eutectic melt in this system at the temperatures as low as 630°C .

Zn₃Nb₂O₈ is another perspective microwave dielectric material with lower values of dielectric constant ($\epsilon_r = 22\text{--}23$) and higher maximum values of $Q \times F$ (up to $80\,000$ GHz). Sintering of the undoped coarse-grained Zn₃Nb₂O₈ is performed at $1100\text{--}1250^\circ\text{C}$ [9, 10] while the introduction of 2% V₂O₅ into starting mixture allows to reach the density over 95% and $Q \times F \sim 60\,000$ GHz at $T = 850^\circ\text{C}$ [11]. Another complex Zn-Nb oxide, ZnNb₂O₆, also demonstrates similar dielectric properties after sintering at $T_s = 1100\text{--}1200^\circ\text{C}$. The sintering temperatures can be reduced down to 900°C by using CuO/V₂O₅ sintering aids.

Main applications of the BaCeO₃-based materials deal with high ionic conductivity of their rare earth-doped derivatives. It is also shown that dense BaCeO₃-based ceramics can be used as barrier material during melt processing of superconducting cuprates [12]. Coarse-grained BaCe_{1-x}Ln_xO₃ ceramics is usually sintered at $1500\text{--}1700^\circ\text{C}$ for $10\text{--}20$ h [13, 14]. The application of the wet chemical methods of starting BaCeO₃ powder preparation causes reducing T_s to $1300\text{--}1400^\circ\text{C}$ [15]. Recent studies demonstrated that the introduction of the CuO sintering aid into chemically derived BaCeO₃ powders allows dense BaCeO₃ ceramics to be obtained at $T \leq 1000^\circ\text{C}$ [16].

Experimental

Both BiNbO₄ and Zn₃Nb₂O₈ fine powders were prepared by two different kinds of cryochemical processing. According to the scheme 1, fixed amounts of Nb hydroxide were precipitated from HNbCl₆ solution by excess of NH₃(aq.); filtered, carefully washed and redissolved in the citric acid (for BiNbO₄) or ammonium oxalate (for Zn₃Nb₂O₈) solutions. As-obtained Cl⁻-free Nb solutions were mixed with stoichiometric amounts of Bi or Zn nitrates solutions, respectively, sprayed to liquid nitrogen and freeze dried in trays at $P = 5 \times 10^{-3}$ mbar using Christ Alpha 2–4 freeze dryer.

According to the scheme 2, Bi-Nb and Zn-Nb hydroxide residues have been coprecipitated from initial stock solutions containing HNbCl₆ and Zn or Bi nitrates, respectively, by mixed 1M ammonia and ammonium carbonate solution 1/1 (for BiNbO₄) or by 1M aqueous n-butylamine (for Zn₃Nb₂O₈). As-obtained residues were filtered, washed until negative Cl⁻ test by AgNO₃ solution and freeze dried under the same conditions.

Thermal decomposition of BiNbO₄ and Zn₃Nb₂O₈ precursors obtained by both methods was performed in air at $T = 400\text{--}800^\circ\text{C}$. Deagglomeration, introduction of Cu/V₂O₅ sintering aid (0.5–2%) and PVA binder (1%) were performed during milling of the powders. Raw mixtures were pressed into pellets and sintered in air at $T = 600\text{--}850^\circ\text{C}$ for $2\text{--}12$ h. Density of ceramics was measured by the geometric method after polishing the pellets.

BaCeO₃ powders were obtained by oxalate coprecipitation from aqueous solution of Ba and Ce nitrates followed by filtering, drying and thermal decomposition of precursor at $T = 1000^\circ\text{C}$ for $1\text{--}12$ h at various heating rate. 1 mass % of CuO sintering aid and PVA binder were also added during wet milling of powders.

A study of the morphological evolution of doped BiNbO₄ and BaCeO₃ ceramics during thermal processing was performed using a hot stage attachment to Philips ESEM XL-30 FEG ($U = 15\text{--}25$ kV, $T = 400\text{--}1000^\circ\text{C}$, heating rate 5 Kmin⁻¹ with 2 min measurement steps, $P = 1\text{--}2$ mbar).

Results and discussion

BiNbO₄

According to the previous reports, the preparation of BiNbO₄ by solid state synthesis method at $800\text{--}850^\circ\text{C}$ results in the formation of orthorhombic (α) polymorph of BiNbO₄ that is transformed into triclinic β -form at $T > 1000^\circ\text{C}$ [17]. The thermal decomposition of citrate precursors causes appearance of the crystalline BiNbO₄ with a structure similar to its high temperature triclinic polymorph [18] while

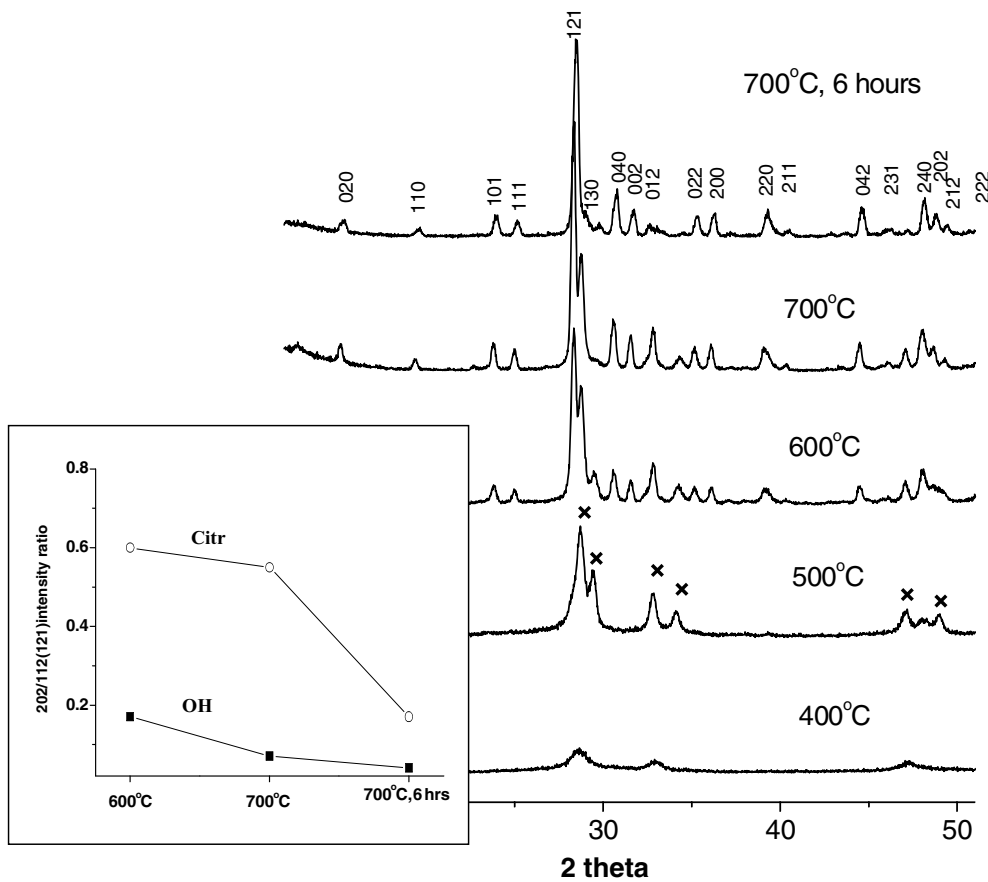


Fig. 1 XRD patterns of the products of thermal processing of the OH-BiNbO₄ precursor at different temperatures for 30 min. x – metastable β' – polymorph. Indexing of α-BiNbO₄ pattern is given according to

JCPDS 16-0295. **Inset:** the influence of thermal processing on the intensity ratio for the 202 (β' – polymorph) to 112 (triclinic) or 121 (orthorhombic) reflections for OH- and Citr-BiNbO₄

little is known about its further transformation. Our studies of the thermal decomposition processes of BiNbO₄ precursors demonstrated that both hydroxide- (OH) and citrate- (Citr) derived primary decomposition products obtained at 400–450°C are usually amorphous. The crystallization of these products at 500–600°C results in formation of the low temperature β' -BiNbO₄ polymorph similar to that observed in [18] (Fig.1). Further thermal processing of as-obtained powders at $T > 600^\circ\text{C}$ causes the irreversible crystallographic transformation of the product into stable orthorhombic form. The rate of this process was rather different for the hydroxide- and citrate-derived BiNbO₄ (Fig. 1, inset), though further sintering of these powders resulted in the fast completion of β' → α phase transition at the early stages of densification irrespectively of their chemical prehistory. More detailed analysis of the BiNbO₄ phase formation from the chemical precursors will be given elsewhere.

The isothermal sintering studies of obtained powders doped with V₂O₅/CuO sintering aid demonstrated their outstanding sinterability resulted in the formation of dense BiNbO₄ ceramics at unusually low temperatures (Fig. 2). Few or no correlations were observed between BiNbO₄

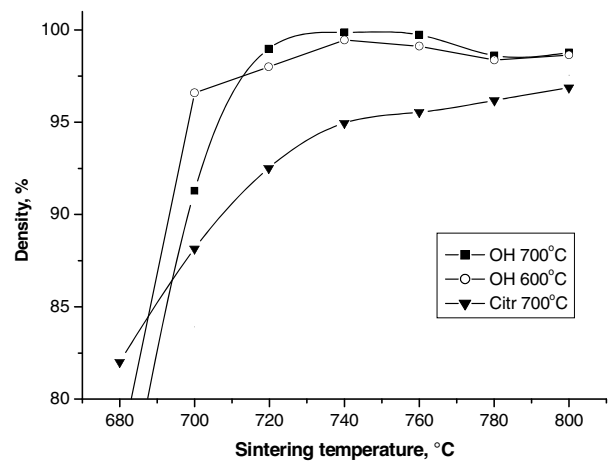


Fig. 2 Density of BiNbO₄ ceramics obtained by isothermal sintering at various temperatures for 2 hrs

polymorph ratio and sintering activity of the corresponding powders. Indeed, BiNbO₄ powders obtained from hydroxide precursor at 600°C and at 700°C demonstrated a rather similar sinterability (Fig. 2) while, according to Fig. 1, they consist mostly of β' - and α-polymorph, respectively. Instead,

the sinterability of BiNbO_4 powders with similar XRD patterns (mostly β' -modification) but obtained from different (OH and Citr) precursors is proved rather different (Fig. 2). This feature correlates quite well with a basic sintering mechanism of fine powders, when the most part of primary densification occurs by rearrangement and repacking of powder crystallites [1, p. 96]. In such a case, internal crystallographic features of crystallites are less critical as the process is controlled mostly by particle morphology and packing parameters of the starting powder.

The analysis of the correlation between micromorphology of obtained powders (Fig. 3) and their sintering activity supports this concept. The thermal decomposition of OH precursors is accompanied by the formation of fine uniform round-shaped BiNbO_4 crystallites. The increase of the processing temperature to 700°C causes evolutionary grain coarsening that keeps almost the same particle shape and packing mode (Fig. 3A, 3B). Instead, the decomposition of citrate precursor at 700°C results in the formation of large irregular BiNbO_4 particles poorly appropriate for easy rearrangement during sintering (Fig. 3C), that correlates quite well with their moderate sintering activity at $T < 750^\circ\text{C}$ (Fig. 2).

The liquid phase character of observed sintering processes was confirmed by *in situ* sintering studies. A direct hot stage ESEM observation of sintering allows, apart from usual *ex situ* methods, to observe a morphological evolution at the fixed spot of sample's surface. The temperature and character of observed changes (Fig. 4) correlate quite well with traditional liquid phase sintering model [1, p. 225]: changes of the particle morphology appear soon after the point of liquid phase formation in the $\text{CuO-V}_2\text{O}_5$ system ($T = 630^\circ\text{C}$ [19]). Further thermal processing leads to the fast particle rearrangement and intergrowth resulted in the formation of monolithic round-shaped grains from agglomerates of the primary crystallites. The temperature range of this fast and deep transformation correlates fairly well with temperatures of intense densification of BiNbO_4 ceramics ($T > 650^\circ\text{C}$, Fig. 2).

Observed grain coarsening has also a positive effect on the microwave dielectric properties of obtained ceramics. A wide application of fine powders in LTCC materials production is complicated by small grain size and, hence, large density of grain boundaries in the ceramics obtained by low temperature sintering of these powders, that is usually associated with high dielectric losses. Grain growth, promoted by $\text{CuO-V}_2\text{O}_5$ eutectic melt, might be a useful tool in solving this problem. Indeed, BiNbO_4 ceramics obtained by proposed method demonstrates a reasonable quality factor ($Q \times F \sim 10\,000$ GHz) even at 700°C while sintering at $720\text{--}740^\circ\text{C}$ allows to obtain materials with $Q \times F$ values of $16\,000\text{--}20\,000$ GHz typical for common BiNbO_4 ceramics sintered at $T \geq 900^\circ\text{C}$.

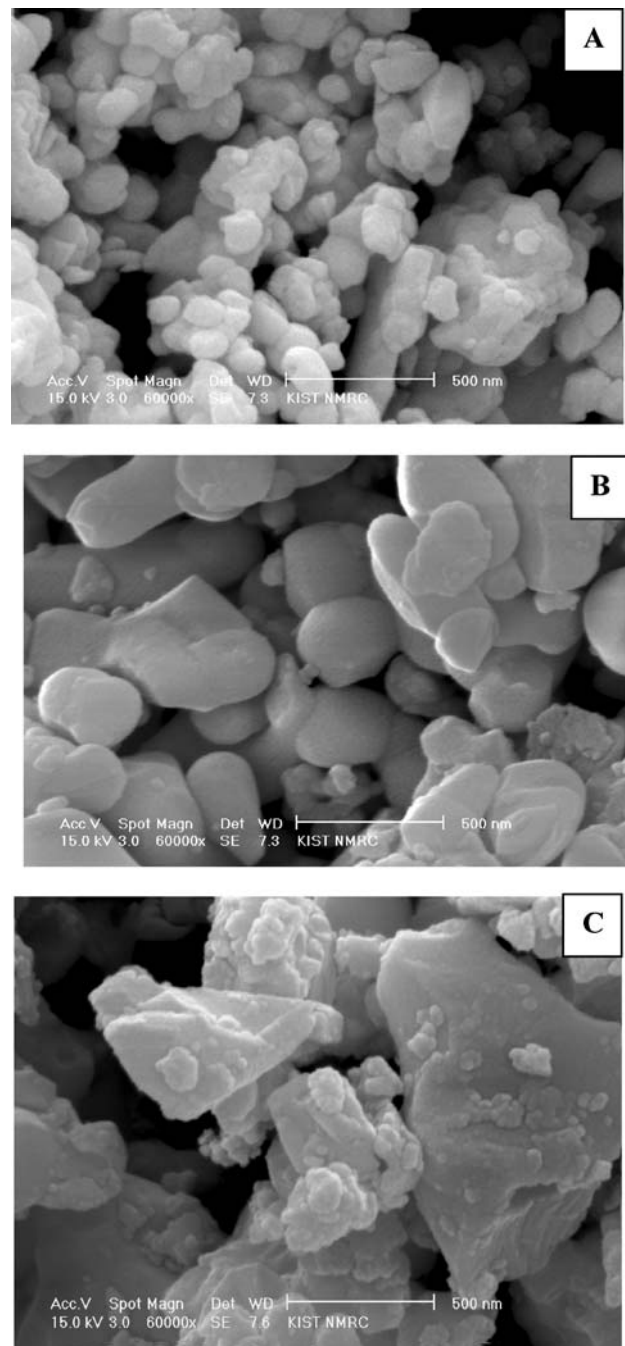


Fig. 3 SEM micrographs of BiNbO_4 powders obtained by thermal decomposition of (A) OH-precursor at 600°C ; (B) OH-precursor at 700°C ; (C) Citr-precursor at 700°C

$\text{Zn}_3\text{Nb}_2\text{O}_8$

An important feature of phase formation processes during the thermal decomposition of $\text{Zn}_3\text{Nb}_2\text{O}_8$ precursors deals with the competitive formation of the target phase and ZnNb_2O_6 . The synthesis of the single phase $\text{Zn}_3\text{Nb}_2\text{O}_8$ directly by thermal decomposition of the precursor is possible from

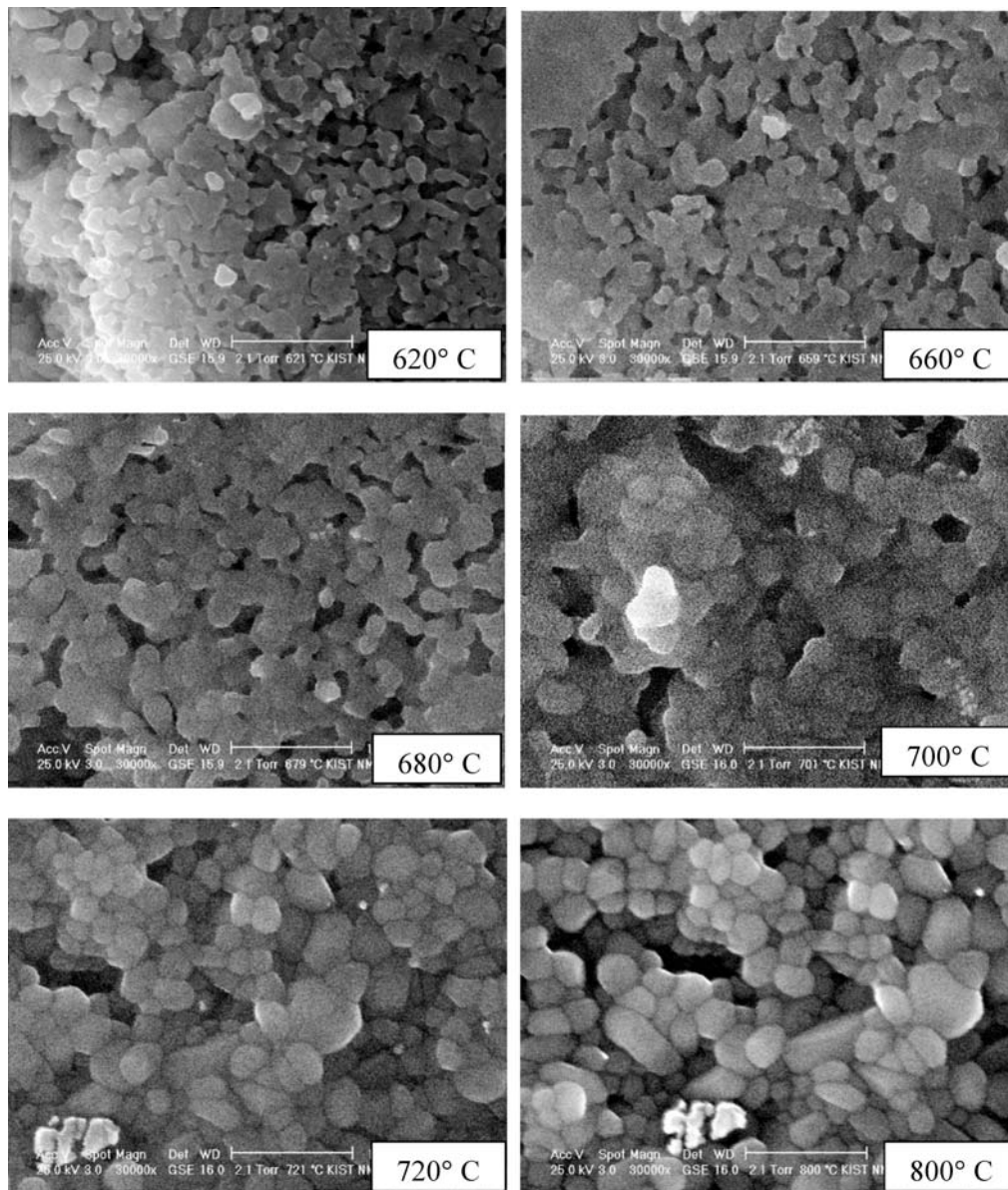


Fig. 4 Hot stage ESEM micrographs of BiNbO_4 ($\text{CuO}/\text{V}_2\text{O}_5$) green pellet heated at 5 K/min until given temperatures

$T = 600^\circ\text{C}$ but the transformation of ZnNb_2O_6 intermediate into the target phase needs higher temperatures; single phase $\text{Zn}_3\text{Nb}_2\text{O}_8$ can be obtained in this case only at $T > 750^\circ\text{C}$. Apart from BiNbO_4 polymorphs, $\text{Zn}_3\text{Nb}_2\text{O}_8$ and ZnNb_2O_6 demonstrate very different sinterability at low temperatures, so that the appearance of ZnNb_2O_6 among thermal decomposition products causes a significant increase in their sintering temperature. Taking into account that the formation of ZnNb_2O_6 is kinetically preferable, the synthesis of $\text{Zn}_3\text{Nb}_2\text{O}_8$ powders with $T_s < 800^\circ\text{C}$ requires a careful optimization of processing conditions. More detailed discussion of the $\text{Zn}_3\text{Nb}_2\text{O}_8$ formation from freeze dried precursors can be found elsewhere [20].

Thermal processing of the coprecipitated hydroxide (OH) precursors at $T \sim 650^\circ\text{C}$ results in the formation of finely

grained $\text{Zn}_3\text{Nb}_2\text{O}_8$ powders with a clearly visible agglomerate structure (Fig. 5A); a size of observed agglomerates correlates quite well with the maximum of particle size distribution obtained by light scattering method (Fig. 5D). The increase in thermal processing temperature just by 50°C promotes an intensive grain growth (Fig. 5B) accompanied by strengthening and coarsening agglomerates (Fig. 5D). Taking into account that the first stage of the sintering proceeds by the rearrangement of powder crystallites [1], such a coarsening should be accompanied by a significant decrease in sinterability that correlates with experimentally observed sintering data (Fig. 6). The sintering activity of the OX- $\text{Zn}_3\text{Nb}_2\text{O}_8$ powders, obtained from freeze-dried oxalate solution, follows the same trend. Complicated crystallization of $\text{Zn}_3\text{Nb}_2\text{O}_8$ during thermolysis of these precursors causes

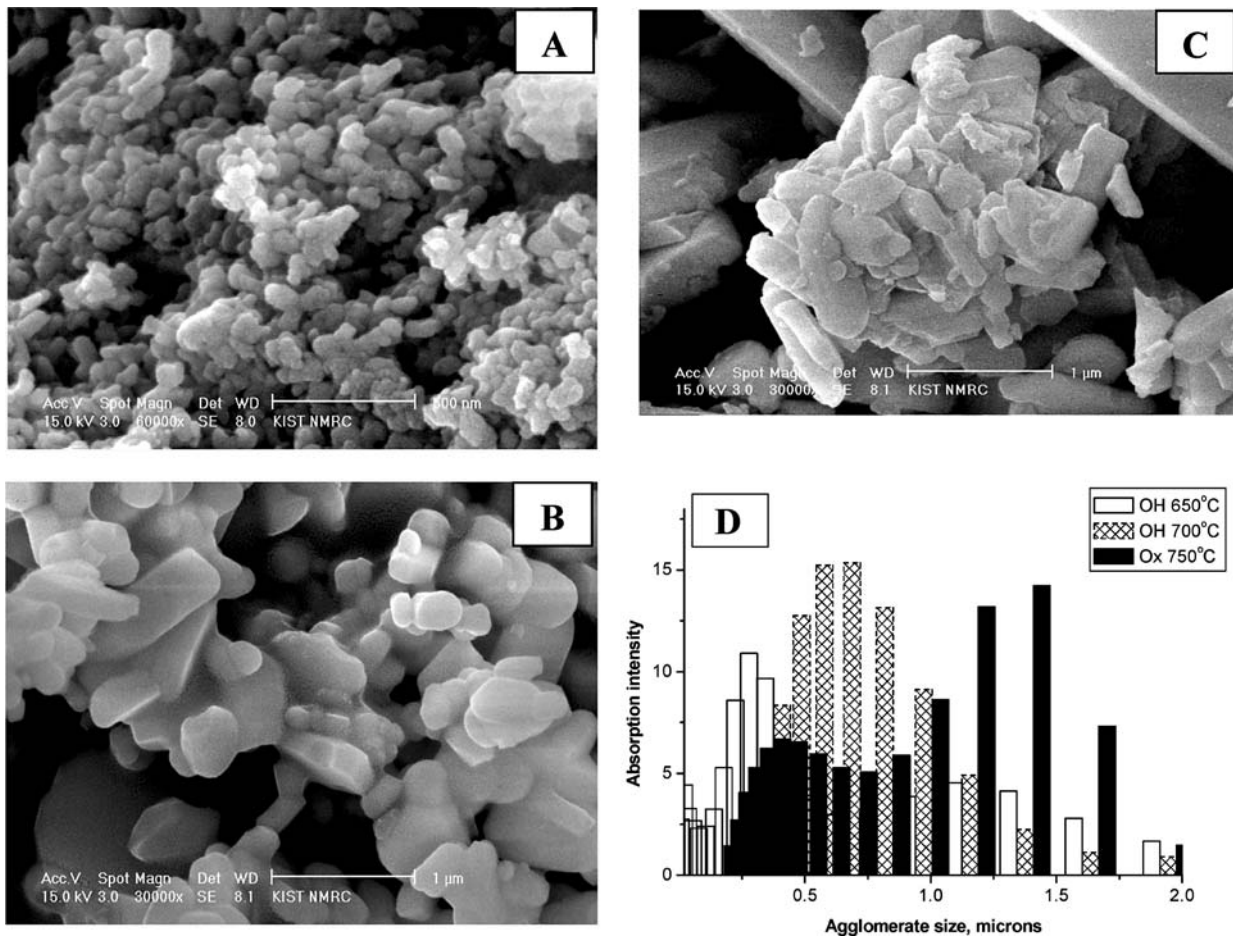


Fig. 5 SEM micrographs of $Zn_3Nb_2O_8$ powders obtained by thermal decomposition of hydroxide precursor at (A) 650°C; (B) 700°C; (C) oxalate precursor at 750°C; (D) Agglomerate size distribution for

$Zn_3Nb_2O_8$ powders obtained from hydroxide (OH) and oxalate (OX) precursors at various thermal decomposition temperatures

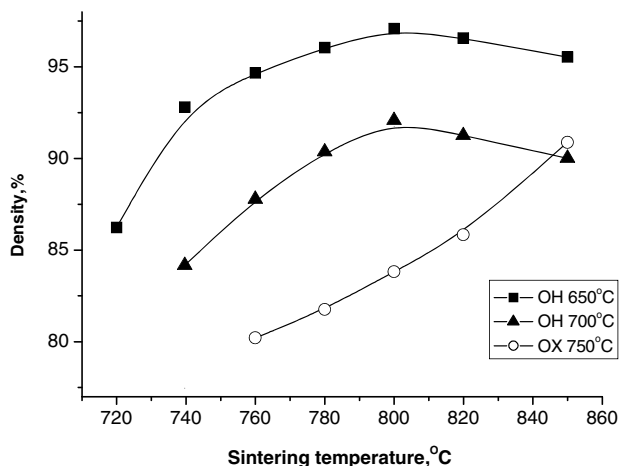


Fig. 6 Density of $Zn_3Nb_2O_8$ ceramics, obtained from several precursors, at different T_s . Sintering time = 2 h

an increase in decomposition temperature to 750°C accompanied by non-uniform and irregular grain growth and their severe agglomeration (Fig. 5C, 5D). As-obtained oxalate-derived $Zn_3Nb_2O_8$ powders demonstrate a rather moderate

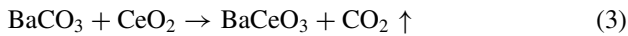
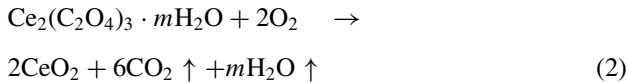
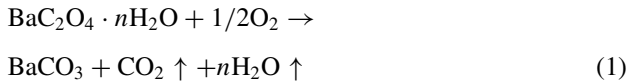
low temperature sintering activity in spite of the presence of sintering aid (Fig. 6).

Another similar feature of the liquid phase sintering of $BiNbO_4$ and $Zn_3Nb_2O_8$ ceramics is an accelerated grain growth during densification that ensures a good level of microwave dielectric properties of obtained materials. Liquid phase-assisted sintering of single phase $Zn_3Nb_2O_8$ powders, obtained from coprecipitated precursors, at $T = 740\text{--}780^\circ\text{C}$ allows to obtain microwave dielectric ceramics with 94–95% density, $\epsilon_r = 20.2\text{--}20.8$ and $Q \times F = 30\,000\text{--}36\,000$ GHz. Further optimization of powder synthesis and processing conditions allowed to reduce the sintering temperature of $Zn_3Nb_2O_8$ ceramics down to 680°C [20].

BaCeO₃

Processes of BaCeO₃ phase formation during thermal decomposition of its carbon-containing precursors are seriously affected by the thermodynamic instability of the final product

in air at $T < 800^\circ\text{C}$ [21]. Due to this fact, a scheme of the thermal decomposition processes of the coprecipitated Ba and Ce oxalates can be summarized as follows [22, 23]:



According to TG data [24], processes (1) and (2) occur almost simultaneously during thermal decomposition of precursor at $T < 800^\circ\text{C}$ while a significant mass change at $T = 800\div 1000^\circ\text{C}$ is associated with process (3). XRD analysis also shows at the presence of considerable amount of BaCO_3 and CeO_2 in reaction products even during thermolysis at $T \geq 900^\circ\text{C}$. Taking into account that secondary phases can have a strong negative effect on the BaCeO_3 sinterability [25], thermal decomposition of the oxalate precursors was usually performed at $T > 950^\circ\text{C}$. However even at these high temperatures, the formation of BaCeO_3 occurs relatively slowly via BaCO_3 and CeO_2 intermediates.

This information can be rather helpful in understanding the different sintering behavior of the BaCeO_3 powders obtained at different heating rates during thermal decomposition (Fig. 7). The intense evolution of water vapor and CO_2 during fast heating causes intense cracking of BaCeO_3 particles and prevents their reagglomeration. However in spite of smaller grain size, this powder demonstrates a significantly lower sinterability at $\tau < 60$ min than coarser BaCeO_3 powder obtained at low heating rate (Fig. 8). This effect can be attributed to the aforementioned strong negative influence

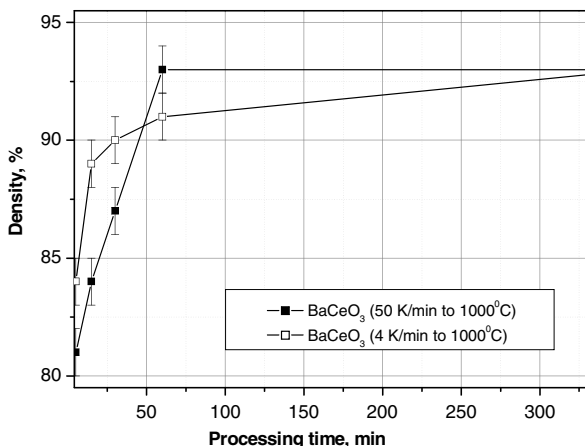


Fig. 7 Density of $\text{BaCeO}_3(\text{CuO})$ pellets ($T_s = 1000^\circ\text{C}$, $\tau = 6$ hrs) vs duration of thermal processing of starting powders at 1000°C during thermal decomposition

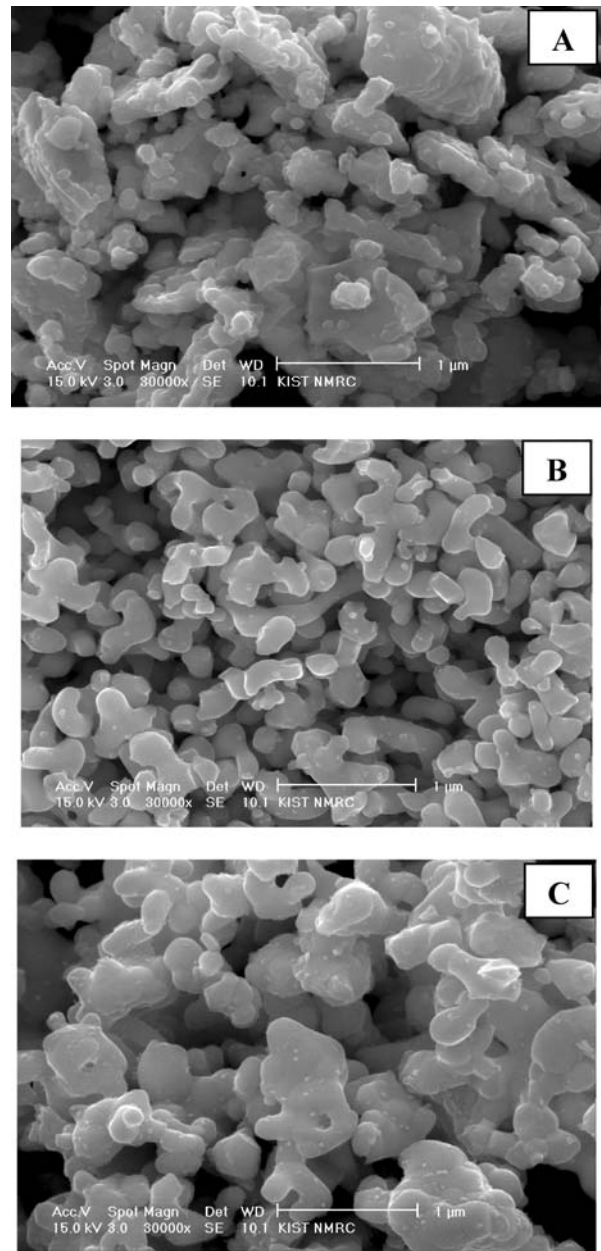


Fig. 8 SEM micrographs of (A) oxalate precursor powder and (B, C) products of its thermal decomposition at 1000°C for 6 hrs. Heating rate is: (B) 50 K/min; (C) 4 K/min

of CeO_2 on BaCeO_3 sinterability, earlier observed in [25], because in spite of smaller grain size, the completion of the process (3) after “fast decomposition” takes at least 20–30 min at $T = 1000^\circ\text{C}$.

The morphological evolution of BaCeO_3 ceramics during CuO-aided sintering is rather similar to the corresponding processes in BiNbO_4 : a microstructure remains intact until the temperature roughly corresponding to the beginning of intense densification (Fig. 9). Further heating causes fast coarsening and complete rearrangement of the granular

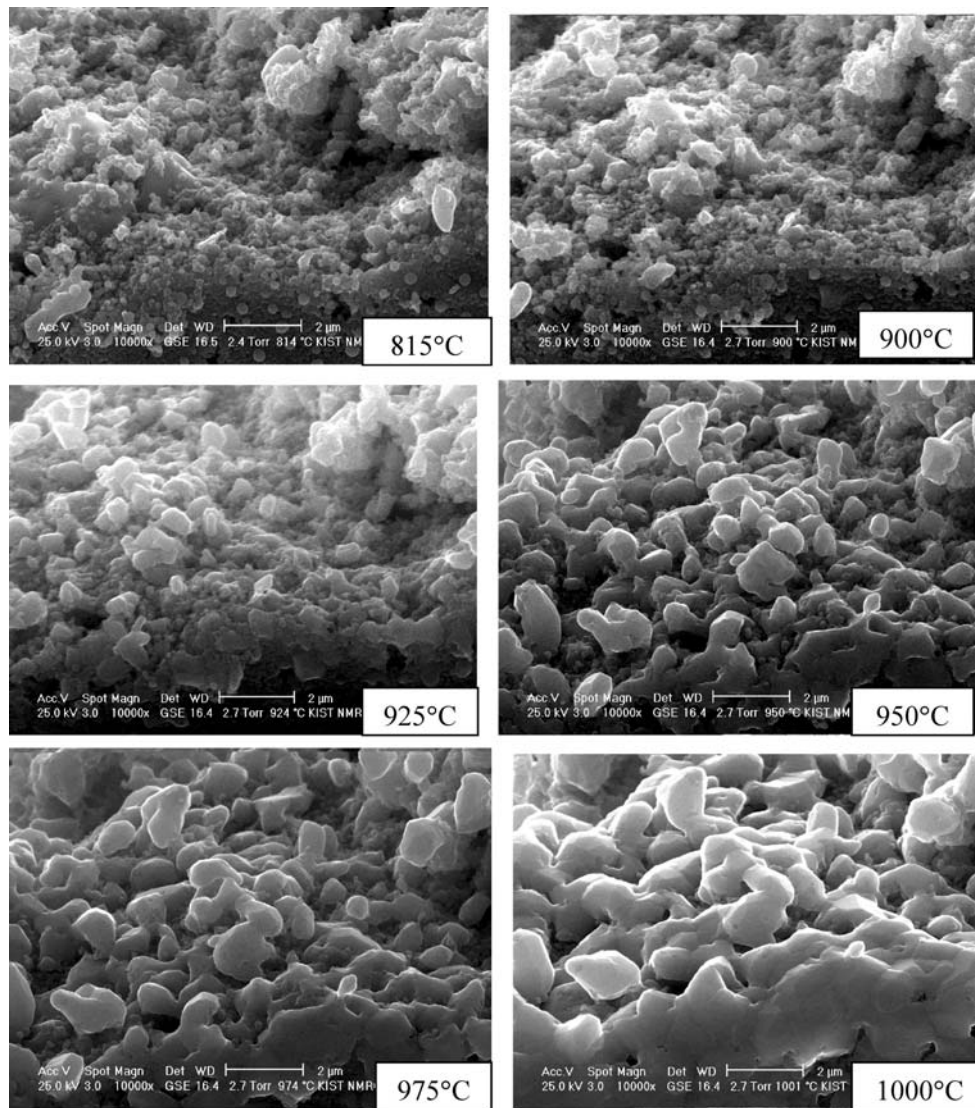


Fig. 9 Hot stage ESEM micrographs of BaCeO_3 (CuO) pellet heated at 5 K/min until given temperatures

structure of ceramics followed by the absence of further changes until the beginning of the bulk diffusion usually associated with the last stages of sintering process. The character of observed morphological evolution correlates quite well with the main features of the classic liquid phase sintering mechanism based on particle rearrangement and fragmentation at the early stages of the process followed by solution-precipitation-driven sintering after the formation of dense packing of primary particles and considerable grain coarsening at the final stage of sintering [1]. However, smaller grain size of chemically derived powders results in their higher mobility at the first stages of sintering that causes the realization of this basic scheme at considerably lower temperatures compared to the traditional liquid phase sintering of common micron-sized powders.

Conclusions

The thermal decomposition of BiNbO_4 precursors results in the formation of the metastable triclinic polymorph that is easily transformed into the stable orthorhombic modification during thermal processing of powder or sintering of ceramics. The formation of fine $\text{Zn}_3\text{Nb}_2\text{O}_8$ powders from chemically derived precursors is complicated by kinetically preferable formation of ZnNb_2O_6 that demonstrates a poorer sintering activity at low sintering temperatures. Intensive grain growth during liquid phase sintering of these ceramics allows to obtain materials with a high level of microwave dielectric properties usually achieved at much higher sintering temperatures. The sintering activity of BaCeO_3 powders is seriously affected by the presence of trace amounts of decomposition intermediates.

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References

1. R.M. German, *Sintering Theory and Practice*, (Wiley Interscience, NY, 1996), p. 228.
2. M. Pollet, S. Marinel, F. Roulland, and G. Allainmat, *Mat. Sci. Eng.*, **B104**, 58 (2003).
3. Min-Han Kim, Sahn Nahm, Woo-Sung Lee, Myong-Jae Yoo, Nam-Kee Kang, Hyo-Tae Kim, and Hwack-Joo Lee, *Jpn. J. Appl. Phys.*, **44**, 3091 (2005).
4. H. Kagata, T. Inoue, J. Kato, and I. Kameyama, *Jpn. J. Appl. Phys.*, **31**, 3152 (1992).
5. Cheng-Fu Yang, *J. Mat. Sci. Lett.*, **18**, 805 (1999).
6. M. Valant and D. Suvorov, *J. Am. Ceram. Soc.*, **83**, 2721 (2000).
7. Eung Soo Kim, Je Hun Kim, Ki Gang Lee, Seung Gu Kang, and Pyung Kyu Kim, *Ferroelectrics*, **262**, 263 (2001).
8. Ning Wang, Mei-Yu Zhao, Zhi-Wen Yin, and Wei Li, *Mater. Res. Bull.*, **39**, 439 (2004).
9. Dong-Wan Kim, In-Tae Kim, Byungwoo Park, Kug Sun Hong, and Jong-Hee Kim, *J. Mater. Res.*, **16**, 1465 (2001).
10. Dong-Wan Kim, Jin-Ho Kim, Jeong-Ryeol Kim, and Kug Sun Hong, *Jpn. J. Appl. Phys.*, **40**, 5994 (2001).
11. Yen-Chi Lee, Cheng-Hsiun Lin, and I-Nan Lin, *Mater. Chem. Phys.*, **79**, 124 (2003).
12. A.V. Orlov, A.L. Vinokurov, O.A. Shlyakhtin, and Yu.D. Tretyakov, *Doklady Chemistry*, **384**, 167 (2002)
13. S. Loidant, L. Abello, E. Siebert, and G. Lucazeau, *Solid State Ionics*, **78**, 249 (1995).
14. K. Katahira, Y. Koichi, T. Shimura, and H. Iwahara, *Solid State Ionics*, **138**, 91 (2000).
15. F. Chen, P. Wang, O. Toft Sorensen, G. Meng, and D. Peng, *Solid State Ionics*, **100**, 63 (1997).
16. A.V. Orlov, A.L. Vinokurov, O.A. Shlyakhtin, and Yu.D. Tretyakov, *Mendeleev Comm.*, (4), 163 (2004).
17. A.W. Sleight and G.A. Jones, *Acta Cryst.*, **B31**, 2748 (1975).
18. Ning Wang, Mei-Yu Zhao, Zhi-Wen Yin, and Wei Li, *Mater. Lett.*, **57**, 4009 (2003).
19. I.I. Ivanova, I.B. Dimitriev, M.R. Marinov, and D. Stavrakeva, *Trans. Bulg. Acad. Sci.*, **27**, 491 (1974).
20. O.A. Shlyakhtin and Young-Jei Oh, *J. Amer. Ceram. Soc.*, **89**, (2006) (in press).
21. M.J. Scholten, J. Schoonman, J.C. van Miltenburg, and E.H.P. Cordfunke, *Thermochim. Acta*, **268**, 161 (1995).
22. F. Chen, O.T. Sorensen, G. Meng, and D. Peng, *J. Therm. Anal. Calorim.*, **53**, 397 (1998).
23. J. Matta, D. Courcot, E. Abi-Aad, and A. Aboukais, *J. Therm. Anal. Calorim.*, **66**, 717 (2001).
24. A.V. Orlov, O.A. Shlyakhtin, A.L. Vinokurov, A.V. Knotko, and Yu.D. Tretyakov, *Inorganic Materials*, **41**, 1354 (2005).
25. D. Shima and S.M. Haile, *Solid State Ionics*, **97**, 443 (1997).