

Niobate Ceramics from Chemical Precursors at $T < 800^\circ\text{C}$

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Dense BiNbO_4 and $\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics are obtained at sintering temperatures below 750°C from fine precursor powders prepared by freeze drying method. The processes of target phase formation are complicated in both cases by easy crystallization of stable intermediates. Low temperature sintering of BiNbO_4 is accompanied by rather small grain growth, leading to finely grained ceramics. The processes of morphological evolution in $\text{Zn}_3\text{Nb}_2\text{O}_8$ occur more readily; sinterability of these powders demonstrates substantial dependence on chemical prehistory and powder processing conditions. Continuous processing of both materials at $T > 780^\circ\text{C}$ is accompanied by significant dedensification and exaggerated grain growth. Optimization of processing conditions allows to obtain $\text{Zn}_3\text{Nb}_2\text{O}_8$ microwave dielectric ceramics with $Q \cdot f > 35,000$ GHz.

Key words: microwave dielectrics, low temperature sintering, freeze drying, BiNbO_4 , $\text{Zn}_3\text{Nb}_2\text{O}_8$

1. INTRODUCTION

BiNbO_4 and $\text{Zn}_3\text{Nb}_2\text{O}_8$ are considered as perspective dielectric materials for multilayer microwave components demanding sintering at low temperatures in order to ensure co-firing with internal Ag electrodes [1-4]. Currently applied methods of reducing sintering temperatures of these materials are based on the application of low-melting sintering aids and coarse grained powders obtained by solid state synthesis method. It is anticipated that producing dense ceramics from fine niobate powders, obtained by solution processing, would result in further decrease of sintering temperatures (T_s). However, the processes of synthesis and densification of such a powders are not studied yet. The following investigation was performed in order to estimate the possibility to obtain dense ceramics with reasonable microwave properties at $T_s < 800^\circ\text{C}$ by sintering of BiNbO_4 and $\text{Zn}_3\text{Nb}_2\text{O}_8$ fine powders obtained by cryochemical processing techniques.

2. EXPERIMENTAL

Two main synthesis methods were used, based on the freeze drying of true solutions and coprecipitated residues, respectively. During solution drying $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was first precipitated by aqueous ammonia, washed on the filter and redissolved in citric acid or in ammonium oxalate solutions and mixed with Zn or Bi-containing components. In coprecipitation scheme the aqueous solutions of HNbCl_6 and $\text{Bi}(\text{NO}_3)_3$ or $\text{Zn}(\text{NO}_3)_2$ were mixed in stoichiometric ratio and added dropwise to ammonium hydroxide, ammonium carbonate or butylamine solutions with following filtering and washing the residue.

As-obtained mixed solutions or coprecipitated residues were frozen by liquid nitrogen and freeze dried in Alpha 2-4 (Christ, Germany) laboratory freeze drier at

$P = 5 \times 10^{-2}$ mBar. Thermal processing of freeze dried powders was performed in air at $T = 400 \sim 700^\circ\text{C}$. After thermal decomposition the powders were deagglomerated by the rotary ball mill or by planetary ball mill in ethanol with zirconia milling media. This procedure was usually combined with introducing the sintering aids (mixture of V_2O_5 and CuO) and PVA binder. The powders were pressed into pellets and sintered in air at $T = 700 \sim 850^\circ\text{C}$.

The bulk density of polished pellets was measured by geometric method. Microwave properties of obtained ceramics were studied by modified Hakki-Coleman method using HP 8720C network analyzer. Particle (agglomerate) size analysis was performed by light scattering method in water using Microtrac UPA 150 analyzer.

3. RESULTS AND DISCUSSION

3.1 BiNbO_4 .

Thermal decomposition of various freeze dried salt precursors of BiNbO_4 terminates at $300 \sim 400^\circ\text{C}$ for all chemical prehistories though the product of decomposition at this temperature is amorphous. Further annealing at $600 \sim 700^\circ\text{C}$ results in the crystallization of BiNbO_4 and various complex niobates (Fig.1). Phase composition of powders at this stage and the rate of completion of BiNbO_4 formation during further annealing depend greatly on the chemical prehistory, i.e. on the anion composition of the salt precursors.

The micromorphology of decomposition products is proved to be rather similar even for powders obtained by different synthesis pathways. Comparison of SEM data with particle size analysis curves, obtained by light scattering method, demonstrates that powders contain mostly $400 \sim 600$ nm agglomerates consisting of several primary $100 \sim 200$ nm crystallites.

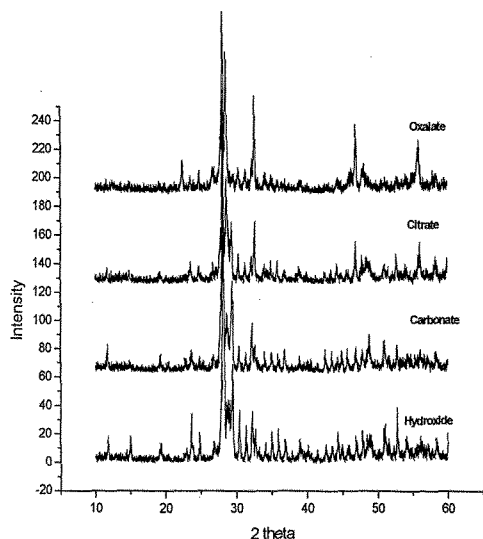


Fig.1 XRD patterns of thermally decomposed products heated at 700°C.

According to similar micromorphology, most of the obtained powders demonstrate similar sintering behavior. Adding 0.5% V_2O_5 to niobate powders leads to the fast sintering at 820°C though at 800°C the densification proceeds substantially slower (Fig.2A). Using the mixture of V_2O_5 and CuO as sintering aid results in further reducing T_s down to 780°C (Fig.2B).

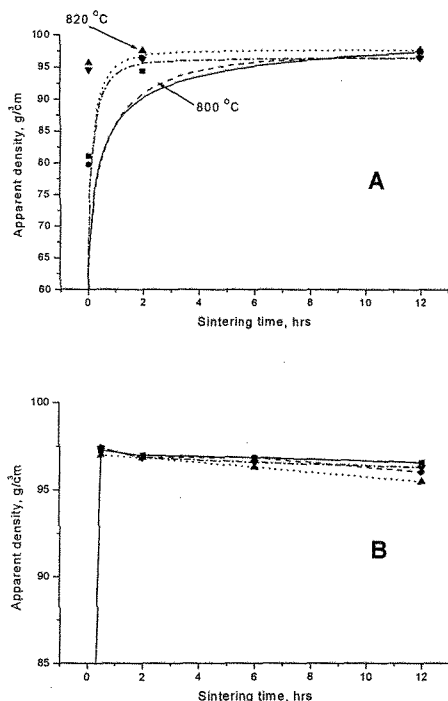


Fig.2. Densification of $BiNbO_4$ green bodies with different sintering aids: A) 0.5% V_2O_5 ; B) 0.5% V_2O_5 + 0.3% CuO, $T_s = 780$ °C.

The character of sintering curves at $T_s=780$ °C is rather typical for low temperature sintering processes

[5]: most part of the densification occurs during approaching T_s and at first several minutes of isothermal processing. At the same time continuous annealing at 780°C leads to the considerable dedensification for all samples, often associated with exaggerated grain growth (Fig.2B).

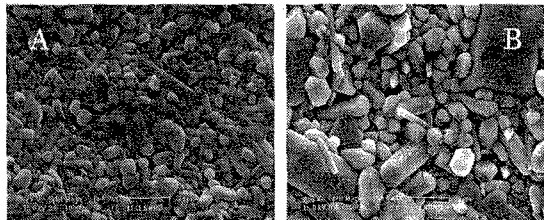
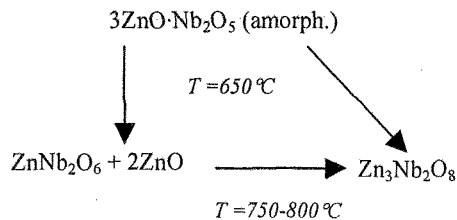


Fig.3. SEM micrographs of $BiNbO_4$ ceramics sintered at 780°C for: A) 5 min.; B) 12 hrs.

Recently obtained data[6] demonstrated that further reducing sintering temperature down to 700°C by modifying of powder processing techniques. At the same time the functional parameters of obtained materials are rather moderate: dielectric permittivity values ($\epsilon = 46-47$) correspond to the usual level of $BiNbO_4$ ceramics, while dielectric losses are higher ($Q \cdot f = 2,500 \sim 7,000$ at $f = 6.5$ GHz). SEM analysis of ceramics shows that the last feature can be related to rather slow grain growth in this ceramics during sintering and poor grain orientation, while continuous annealing promotes undesirable exaggerated grain growth (Fig.3B), usually accompanied by significant decrease of $Q \cdot f$.

3.2 $Zn_3Nb_2O_8$.

Similarly to $BiNbO_4$, thermal decomposition of $Zn_3Nb_2O_8$ precursors leads to the amorphous products. Essential feature of the phase formation process during further annealing is the competition between direct crystallization of orthorhombic $Zn_3Nb_2O_8$ from amorphous state and fast formation of $ZnNb_2O_6$ columbite followed by slow solid state reaction leading to $Zn_3Nb_2O_8$.



The $Zn_3Nb_2O_8/ZnNb_2O_6$ ratio in thermal decomposition products demonstrates strong dependence on the chemical prehistory and on thermal processing conditions. Taking into account that sinterability of $ZnNb_2O_6$ is considerably lower than that of $Zn_3Nb_2O_8$, the influence of phase composition of thermolysis products on its densification rate looks decisive.

Analysis of particle size evolution during powder annealing, necessary for the completion of $Zn_3Nb_2O_8$ formation and/or crystallization, shows that processing at 600–650°C leads to the preserving initial nanocrystalline micromorphology of the powder (Fig. 4A, B).

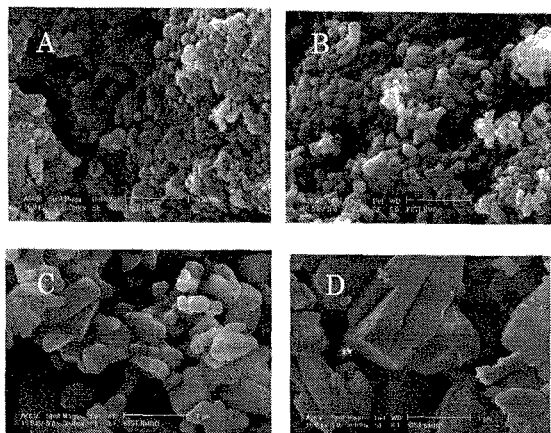


Fig.4 SEM micrographs of thermal decomposition products of $Zn_3Nb_2O_8$ precursors (coprecipitated hydroxides) at A) 600°C; B) 650°C; C) 700°C; D) 800°C.

Meanwhile, increasing the temperature to 700°C and higher is accompanied by rather fast and relatively uniform grain growth (Fig.4 C, D). This feature of $Zn_3Nb_2O_8$ is rather different with $BiNbO_4$ powders, demonstrated rather slow morphological evolution. The grain morphology and grain packing character of $Zn_3Nb_2O_8$ are influenced also by the chemical prehistory of the powder.

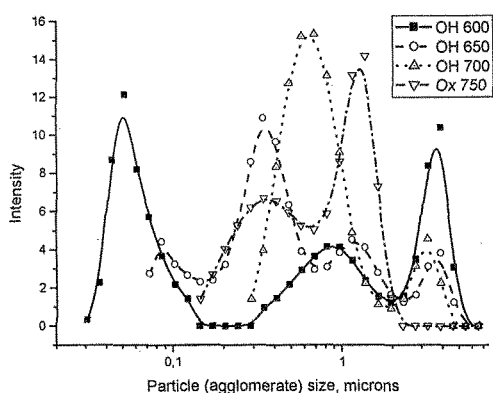


Fig.5. Particle size distributions for products of thermal decomposition at various temperatures. OH - hydroxide precursor; OX- oxalate precursor.

The processes in the aggregate structure of zinc niobate powders correlate quite well with grain size evolution observed by SEM. Substantial part of grains in the powder, obtained from hydroxide precursor at 600°C, is non-agglomerated, demonstrating large contribution of nanocrystalline particles (Fig.5). Increasing the decomposition temperatures results in progressive shift of the distribution maxima to higher values, reflecting, along with growing grain size, enhancement of strength of agglomerates. Appearance of relatively hard agglomerates is observed also in the powders obtained from oxalate precursor. In this case the strength of agglomerates can be caused both by higher decomposition temperature due to complicated

crystallization processes and by genesis of these powders from frozen solutions with its tough spatial salt framework.

The sinterability of $Zn_3Nb_2O_8$ powders demonstrates obvious correlations with chemical prehistory of the powders and its thermal processing conditions though sometimes this correlation looks rather unusual. Indeed, nanocrystalline grain size and soft agglomeration of powder, annealed at 600°C, don't lead to the highest densification rate. The best sinterability of $Zn_3Nb_2O_8$ powder shows at the sample of OH-650°C (Fig.6).

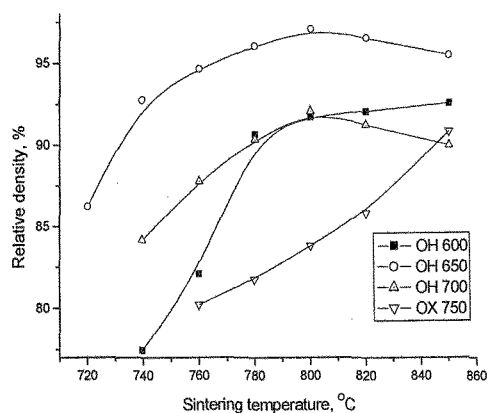


Fig.6. Sintering curves for $Zn_3Nb_2O_8$ powders with different thermal and chemical prehistories.

Probably, the crystallization of $Zn_3Nb_2O_8$ in the poorly crystalline OH-600 powder promotes intergrain necks formation and, hence, complicated effect on the densification. According to agglomerate size analysis data (Fig.5), the powder, processed at 600°C, contains also the largest fraction of coarse agglomerates and this may cause complicating low temperature sintering. Sintering rate decrease accompanying the increase of thermal decomposition temperature from 650°C to 700°C should be attributed to substantial growth of grains and agglomerates at this temperature. The poorest sinterability in the powder with oxalate prehistory can be

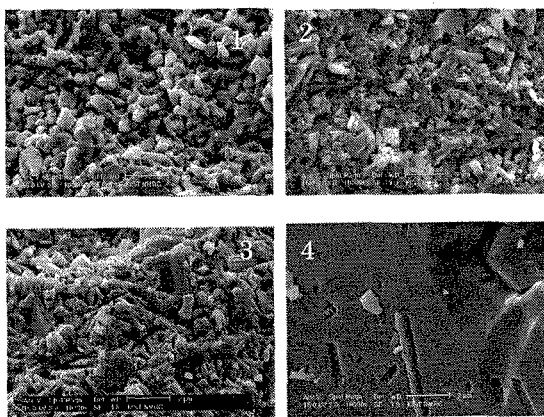


Fig.7. SEM micrographs of $Zn_3Nb_2O_8$ ceramics isothermally sintered at $T_s = 780^\circ\text{C}$ for 1) 1min.; 2) 10 min.; 3) 2 hrs; 4) 20 hrs.

referred to its enhanced agglomeration, so that at the same level of grain size its sintering rate is substantially lower.

Similarly to BiNbO_4 , continuous thermal processing of $\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics at $T \geq 800\text{ }^{\circ}\text{C}$ is accompanied by exaggerated grain growth and severe dedensification of obtained ceramics. Apart from BiNbO_4 , the processes of primary crystallization in $\text{Zn}_3\text{Nb}_2\text{O}_8$ occur also rather intensively, resulting in the formation closely packed arrays of elongated faceted grains (Fig.7).

Along with enhanced sinterability, $\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics obtained from freeze dried precursors demonstrate also rather good microwave dielectric properties. As for BiNbO_4 , dielectric permittivity of dense ceramics displays little or no correlation with sintering temperature or chemical prehistory remaining at the level of $\epsilon = 20\sim 21$ typical for this compound. Changes of microwave dielectric losses of $\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics during sintering correlate quite well with evolution of microstructure: short sintering time results in rather small Q-f values while continuous sintering also results in decrease of quality factor. Similarly, the sintering at $T > 800\text{ }^{\circ}\text{C}$ results in reduced Q-f values due to growing contribution of exaggerated grain growth processes (Fig.8). At the same time the sintering of powders with optimum micromorphology for 4~8 hours at $740\sim 780\text{ }^{\circ}\text{C}$ allows to achieve Q-f values $> 35,000$, that exceeds the quality factor values for a number of industrially produced MW dielectrics.

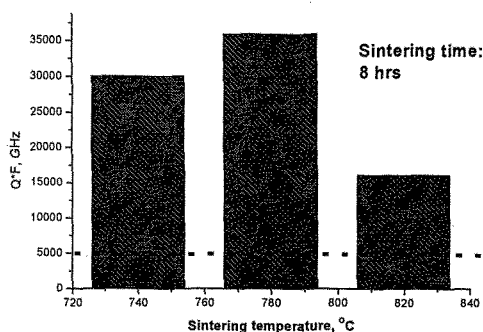


Fig.8. Quality product (Q·f, $f = 11\sim 12\text{ GHz}$) values for $\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics sintered at different temperatures.

4. CONCLUSIONS

1. Application of precursor powders, obtained by chemical synthesis methods, allows to produce microwave dielectric ceramics with high quality factor by low temperature sintering at $T < 750\text{ }^{\circ}\text{C}$.

2. Sinterability of complex niobium oxides demonstrates strong dependence on the phase composition and crystallinity of the powder precursor and rather moderate correlation with powder micromorphology.

3. Different level of microwave losses of BiNbO_4 and $\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics, obtained from finely dispersed precursors, can be attributed to the different intensity of grain growth processes during sintering.

5. ACKNOWLEDGEMENTS

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