Available online at www.sciencedirect.com

Journal of the European Ceramic Society 27 (2007) 2933–2936

www.elsevier.com/locate/jeurceramsoc

The effect of non-stoichiometry on the microstructure and microwave dielectric properties of the columbites $A^{2+}Nb_2O_6$

Anatolii Belous[a,*], Oleg Ovchar[a], Bostjan Jancar[b], Jana Bezjak[b]

[a] V.I.Vernadskii Institute of General and Inorganic Chemistry NAS of Ukraine, 32/24 Palladin Avenue, 03680 Kyiv-142, Ukraine
[b] Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Abstract

Both the microstructure and microwave dielectric properties of sintered columbites with the composition $A^{2+}{}_{1+x}Nb_2O_6$ (A^{2+} = Mg, Zn, Co) were analysed. The slight changes in the Nb/A ratio in studied systems have been found to noticeably affect the microwave quality factor (Q) of the ceramics. Regardless of the A^{2+} ion the dependencies of a Q-factor magnitude on chemical composition demonstrate rather a non-linear trend. Very low products $Q \times f$ measured for all studied systems at $x < 0$ can be attributed to the presence of secondary phase Nb_2O_5. At $x \geq 0$ the $Q \times f$ magnitude passes through the maxima subject to the A^{2+} ion. The highest products $Q \times f \geq 110{,}000$ GHz have been found in the Mg and Zn-containing columbites at $x = 0.03$ and 0.01, respectively, whereas in the case of Co-containing analogues the maximum $Q \times f = 82{,}000$ GHz corresponds to stoichiometric composition.

Keywords: Sintering; Electron microscopy; Dielectric properties; Niobates; Functional applications

1. Introduction

Binary niobates $A^{2+}{}_{1+x}Nb_2O_6$ with the columbite stucture exhibit, in some cases, excellent dielectric properties at microwave frequencies.[1–3] Moreover, these compounds are generally used as precursor phases for the synthesis of high-Q perovskites $Ba(A_{1/3}{}^{2+}Nb_{2/3})O_3$.[4] Recently, the $Q \times f$ products as high as 80,000–90,000 GHz have been reported for Mg and Zn-containing columbites.[1–3] However, the microwave dielectric properties of the columbites are to a large extent sensible to their preparation.[2,5] Moreover, the synthesis of single-phase columbites is often difficult because of the formation of corundum-like crystal phases $A_4Nb_2O_9$, and requires prolonged heating.[5] To avoid the formation of undesired phase in $MgNb_2O_6$ the use of an excess of MgO is effective.[5,6] At the same time there are still no sufficient data related to the effect of chemical composition on the dielectric properties of columbites.

Therefore, the aim of the work was to study the effect of a slight deviation from stoichiometric composition $A^{2+}Nb_2O_6$, where A^{2+} is Mg, Zn, Co, on the phase composition, microstructure and microwave dielectric properties of the ceramic materials.

2. Experimental procedure

The ceramics with the composition $A^{2+}{}_{1+x}Nb_2O_6$, where A^{2+} = Mg, Zn, Co were produced by the conventional mixed-oxide route. The sintering was performed in both air (8 h) and oxygen atmosphere (10 atm and 4 h) at the temperatures around 1300 °C (A^{2+} = Zn) and 1400 °C (A^{2+} = Mg, Co). The starting reagents were extra pure MgO, ZnO, Co_3O_4 (99.95%) and Nb_2O_5 (99.9%). The phase composition and crystal lattice parameters of sintered ceramics were examined by means of X-ray diffraction analysis (XRD) on the diffractometer DRON-3M (Cu Kα, radiation). Microstructural analysis of the ceramic samples was prformed by means of scanning electron microscopy (JEOL, JSM 5800, Tokyo, Japan) using energy dispersive X-ray spectroscopy (EDX) and the LINK software package (ISIS 3000, Oxford Instruments, Bucks, UK). The dielectric characteristics of the materials ε, Q, and τ_f at frequencies around 10 GHz were examined using a cavity reflection method on the Network Analyser PNA-L Agilent N5230A.

3. Results and discussion

3.1. The system $Mg_{1+x}Nb_2O_6$

The formation of $MgNb_2O_6$ starts at 700 °C. Within the temperature range of 700–1100 °C this process is accompanied by

---

* Corresponding author. Tel.: +380 44 424 2211; fax: +380 44 424 2211.
E-mail address: belous@ionc.kar.net (A. Belous).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.11.017

Table 1
Microwave dielectric properties of sintered columbites

x	Phase composition	ε	τ_f (ppm/C)	$Q \times f$ (GHz)
The system $Mg_{1+x}Nb_2O_6$				
−0.03	$MgNb_2O_6$, Nb_2O_5	19.9	−56	600
−0.01	$MgNb_2O_6$, Nb_2O_5	19.8	−59	1,400
0	$MgNb_2O_6$	19.4	−55	58,000
0.005	$MgNb_2O_6$	19.9	−60	65,000
0.01	$MgNb_2O_6$	19.9	−58	108,000
0.01*	$MgNb_2O_6$	19.3	−60	101,000
0.03	$MgNb_2O_6$, $Mg_4Nb_2O_9$	21.0	−60	121,000
0.03*	$MgNb_2O_6$, $Mg_4Nb_2O_9$	20.5	−62	112,000
The system $Co_{1+x}Nb_2O_6$				
−0.03	$CoNb_2O_6$, Nb_2O_5	20.2	−72	3,500
0	$CoNb_2O_6$	20.5	−70	81,000
0*	$CoNb_2O_6$, Co-reach phase	20.0	−64	64,000
0.01	$CoNb_2O_6$	20.9	−65	59,000
0.04	$CoNb_2O_6$, Co-rich phase	22.0	−67	37,000
0.04*	$CoNb_2O_6$, Co-rich phase	21.2	−65	40,000
The system $Zn_{1+x}Nb_2O_6$				
−0.01	$ZnNb_2O_6$, Nb_2O_5	22.5	−65	8,000
0	$ZnNb_2O_6$	23.0	−68	81,000
0*	$ZnNb_2O_6$	22.2	−72	65,000
0.01	$ZnNb_2O_6$, Zn-rich phase	20.9	−74	120,000
0.03	$ZnNb_2O_6$, Zn-rich phase	20.9	−74	92,000

The materials sintered in oxygen atmosphere are marked by asterisk.

the formation $Mg_4Nb_2O_9$ with the corundum-type structure. At the temperatures higher than 1100 °C, the latter interacts with the residual Nb_2O_5. Therefore, the formation of $MgNb_2O_6$ is a multistage process. Increasing the soaking time up to 6–10 h at the calcinations temperature above 1100 °C results in the formation of a single-phase product according to the X-ray phase analysis data.

Examination of X-ray diffraction patterns collected on polycrystalline $Mg_{1+x}Nb_2O_6$ materials for $x < 0$ denotes the presence of the secondary phase Nb_2O_5 in the material. These data are confirmed also by the electron microscopy. Within the range of $0 \le x < 0.03$ a single-phase product is formed. This indicates a possibility of the formation of a narrow homogeneity region $Mg_{1+x}Nb_2O_6$ which exists at $0 \le x < 0.03$. This can be expressed also as $MgNb_{2-y}O_6$ (where $y = 2x/(x - 1)$) to denote the niobium deficiency. At higher x values ($x > 0.03$) the secondary phase corresponding to $Mg_4Nb_2O_9$ is formed. It is known that this phase has the corundum-like structure and demonstrates extremely high values of the Q-factor at microwave frequencies.[7]

The microwave dielectric properties of the columbites $Mg_{1+x}Nb_2O_6$ are summarized in Table 1. Within the studied concentration range, a slight deviation from stoichiometry does not practically influence the dielectric constant (ε), which varies between 19 and 20. The temperature coefficient τ_f is within the range of −55 to −60 ppm/C for all of studied compositions. At the same time, the presence of residual Nb_2O_5 at $x < 0$ is accompanied by a significant reduction of the product $Q \times f$: the higher the amount of secondary Nb_2O_5 is the lower is the product $Q \times f$. In the stoichiometric $MgNb_2O_6$ ($x = 0$) the measured product $Q \times f$ is lower compared to that reported elsewhere.[1,2] This may be associated with the effect of starting reagents on sintering temperature which was much higher (about 100 °C) in this study. In the case of the positive x the magnitude of the product $Q \times f$ increases almost linearly by 200–300% with increasing x (Fig. 1, curve 1), and reaches $Q \times f = 120{,}000$ GHz at $x = 0.03$. It should be noted that at $x = 0.03$ – when the highest $Q \times f$ magnitude is observed – the materials already contain a slight amount of secondary phase $Mg_4Nb_2O_9$ with the permittivity $\varepsilon = 12$ and very high Q-factor ($Q \times f = 210{,}000$ GHz).[7] However, a negligible contamination of high-Q $Mg_4Nb_2O_9$ may not significantly deteriorate the Q-factor of the columbite $Mg_{1+x}Nb_2O_6$. It should be noted that sintering at 10 atm oxygen pressure does not result in any noticeable changes in the magnitude of the product $Q \times f$.

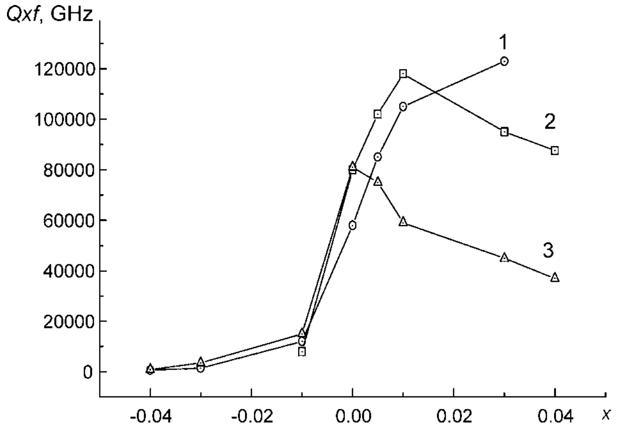

Fig. 1. The product $Q \times f$ for the columbites $A_{1-x}Nb_2O_6$, where A = Mg (1), Zn (2), and Co (3), as a function of x. The samples were sintered in air for 8 h at 1400 °C (1 and 3) and 1300 °C (2).

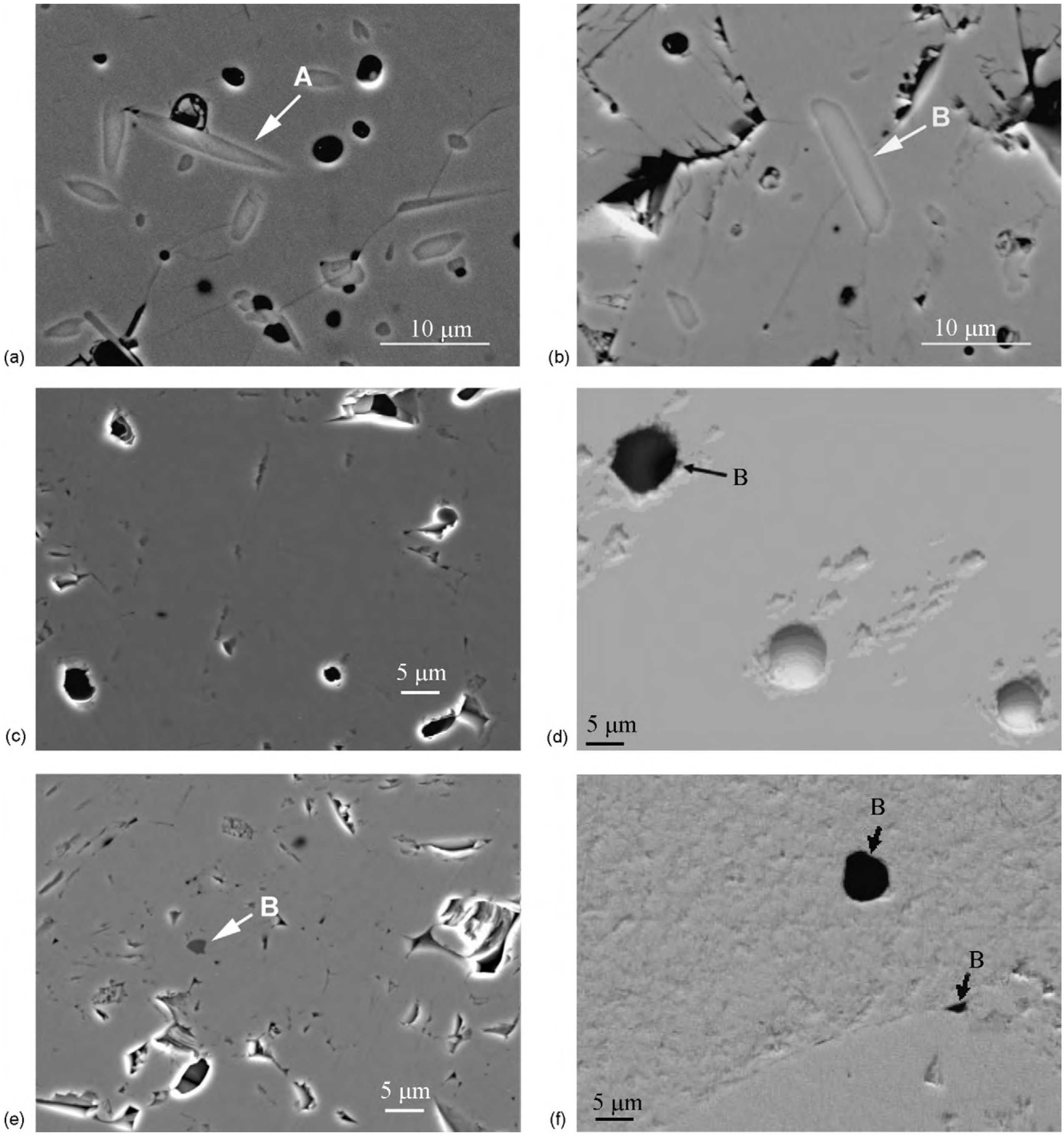

Fig. 2. Typical SEM microphotographs collected on sintered columbites $Co_{1+x}Nb_2O_6$ for $x = -0.03$ (a), $x = -0.01$ (b), $x = 0$ (c and d), and $x = 0.04$ (e and f). A: Nb_2O_5; B: Co-rich phase. Photographs a, b, c and e, developed form the samples sintered in air whereas d and f correspond to sintering at 10 atm oxygen pressure.

3.2. *The system $Co_{1+x}Nb_2O_6$*

$CoNb_2O_6$ starts to form at 600 °C that is about by 100 °C lower than $MgNb_2O_6$. The formation mechanism for this columbite is quite similar to that described for $MgNb_2O_6$. The only difference is that all of the reactions take place at lower temperatures. Because of this feature – in contrast to Mg-containing analogues – a single-phase Co-columbite can be easily obtained even after short-term firing for 2–4 h at 1050–1100 °C.

Similarly to the Mg-columbites non-stoichiometric columbites $Co_{1+x}Nb_2O_6$ with a slight Co deficiency ($x < 0$) always contain secondary phase Nb_2O_5 (Fig. 2a and b). In the case of $x > 0$ (niobium deficiency) a homogeneity region $Co_{1+x}Nb_2O_6$ ($CoNb_{2-y}O_6$) is observed at $0 \leq x < 0.01$ which is more narrow compared to that found in Mg-containing columbites. When $x \geq 0.01$ the small inclusions of a secondary Co-rich phase appear in the columbite matrix (Fig. 2d–f).

It should also be noted that within the homogeneity region of $Co_{1+x}Nb_2O_6$ ($0 \leq x < 0.01$) a slight broadening of the X-ray peaks was observed on the XRD diffraction patterns collected from sintered samples. Taking into consideration that the grain size in studied materials did not change, the observed broadening of X-ray peaks may be assumed to an increase in the internal strains of the columbite lattice. From Table 1 it is evident that the values of both ε and τ_f vary only slightly within studied ranges of x. At the same time, the magnitude of the product $Q \times f$ depends strongly on x (Fig. 1, curve 3). The analysis of obtained results indicates that the product $Q \times f$ is mainly determined by two factors: (1) at $x < 0$ it is affected by the presence of Nb_2O_5, leading to a noticeably sharp decrease in Q; (2) at $x > 0$ it is affected at once by an increase in the internal lattice strains and by the presence of an extra Co-rich phase, that results in a much smoother decrease in Q. Due to the above two reasons at $x = 0$, the magnitude of the Q-factor reaches maximum values ($Q \times f > 80{,}000$ GHz) which are about two times higher than those reported elsewhere.[1,2] It should be also noted that in this study the sintering temperature of Co-containing columbites was by 100 °C higher compared to that previously reported.[1,2]

3.3. The system $Zn_{1+x}Nb_2O_6$

In contrast to the other studied columbites $ZnNb_2O_6$ is formed by the direct interaction between zinc and niobium oxides without formation of any secondary inrtermediate phases. The temperature ranges of this process are much lower comparing to those of Mg and Co-containing columbites: $ZnNb_2O_6$ starts to form at 500 °C whereas at 800 °C studied mixtures contain only single-phase columbite.

Similarly to other columbite members non-stoichiometric $Zn_{1+x}Nb_2O_6$ always contain secondary phase Nb_2O_5 when $x < 0$. In the case of $x > 0$ (niobium deficiency) a single-phase composition is observed at $0 \leq x \leq 0.005$. When $x \geq 0.005$ new secondary phase, which is rich in zinc, is formed. Microstructural analysis of the columbites $Zn_{1+x}Nb_2O_6$ indicates that the increase in the zinc content in the nominal composition is accompanied by a reduced porosity of sintered material.

The magnitude of the $Q \times f$ product of the columbites $Zn_{1+x}Nb_2O_6$ passes through the maximum at $x = 0.01$ (Fig. 1, curve 2) whereas it demonstrates rather weak dependence on x in the case when sintering was performed under 10 atm of the oxygen pressure (Table 1). Observed discrepancy may be associated with the suppressed lattice imperfections in the oxygen atmosphere caused by the zinc evaporation which should be significantly less in the latter case. The evaporation of zinc may probably also promote the sintering process of $Zn_{1+x}Nb_2O_6$ by increasing their densification, and as a consequence result into increasing magnitude of the $Q \times f$ product. At the same time, a further decrease in the Q-factor at $x \geq 0.01$ may be associated with the presence of secondary Zn-rich phase. As a result in the system $Zn_{1+x}Nb_2O_6$ the highest magnitude of the $Q \times f = 120\,000$ GHz was obtained at $x = 0.01$ when the minimum porosity was observed.

4. Conclusions

The microstructure, phase composition and the microwave quality factor of the columbites $A^{2+}{}_{1-x}Nb_2O_6$ (where A^{2+} = Mg, Zn, Co) are to a large extent effected by a deviation from stoichiometric composition. As a consequence, the magnitude of the $Q \times f$ product of the columbites varies non-linearly with x reaching maximum values in stoichiometric Co-containing materials, and in Nb-defficient both Mg and Zn-containing analogues.

Acknowledgements

This work was partially supported by the NATO Grant under the NATO SfP project 980881: “Dielectric Resonators” of the NATO “Science for Peace” Program.

References

1. Lee, H. J., Hong, K. S., Kim, S. J. and Kim, I. T., Dielectric properties of MNb_2O_6 compounds (where M: Ca, Mn, Co, Ni, or Zn). *Mater. Res. Bull.*, 1997, **32**(7), 847–855.
2. Pullar, R. C., Breeze, J. D. and Alford, N. McN., Characterization and microwave dielectric properties of $M^{2+}Nb_2O_6$ ceramics. *J. Am. Ceram. Soc.*, 2005, **88**(9), 2466–2471.
3. Zhang, Y. C., Yue, Z. X., Gui, Z. and Li, L. T., Microwave dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics. *Mater. Lett.*, 2003, **57**, 4531–4534.
4. Kolodiazhnyi, T., Petric, A., Belous, A., V’yunov, O. and Yanchevskij, O., Synthesis and dielectric properties of barium tantalates and niobates with complex perovskite structure. *J. Mater. Res.*, 2002, **17**(12), 3182–3189.
5. Ananta, A., Brydson, R. and Thomas, N. W., Synthesis, formation and characterization of $MgNb_2O_6$ powder in a columbitelike phase. *J. Eur. Ceram. Soc.*, 1999, **19**(3), 355–362.
6. Sreedhar, K. and Mitra, A., Formation of lead magnesium niobate perovskite from $MgNb_2O_6$ and $Pb_3Nb_2O_8$ precursors. *Mater. Res. Bull.*, 1997, **32**, 1643–1649.
7. Ogawa, H., Kan, A., Ishihara, S. and Higashida, Y., Crystal structure of corundum type $Mg_4(Nb_{2-x}Ta_x)O_9$ microwave dielectric ceramics with low dielectric loss. *J. Eur. Ceram. Soc.*, 2003, **23**, 2485–2488.