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Effect of Nonstoichiometry on the Structure and Microwave Dielectric Properties of Cobalt Metaniobate

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Abstract—The formation of cobalt metaniobate, $CoNb_2O_6$, with the columbite structure has been studied, and possible ways of optimizing solid-state synthesis conditions have been examined. Single-phase $CoNb_{2-y}O_{6-2.5y}$ has been obtained in the composition range $0 \le y \le 0.05$. The microstructure and microwave dielectric properties of $Co_{1-x}Nb_2O_{6-x}$ materials have been investigated. The results indicate that the electrical Q of the nonstoichiometric materials drops sharply for $x > 0$ because of the presence of Nb_2O_5 as an impurity phase. For $x < 0$, Q gradually decreases with increasing Co content, which is caused by the rise in lattice strain and presence of $Co_4Nb_2O_9$ impurity.

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INTRODUCTION

Materials with low microwave losses (high electrical quality factor, $Q = 1/\tan\delta$) are of key importance in designing filters and generators for advanced communication systems. The use of such materials in microwave devices makes it possible to enhance the sensitivity and selectivity of communication lines and, hence, to insure high efficiency and reliability of information transfer [1, 2]. In connection with this, the search and characterization of high-Q microwave dielectrics is of great current interest, especially in the context of the ever higher frequencies used in modern communication systems, up to 20–30 GHz in VSAT networks and 30–40 GHz in LMDS systems.

Among the known microwave dielectrics, of particular interest are $M^{2+}Nb_2O_6$ columbites, which are also reaction intermediates in the synthesis of $A^{2+}(M^{2+}_{1/3}Nb_{2/3})O_3$ perovskites [3–5]. In $ZnNb_2O_6$- and $MgNb_2O_6$-based materials with dielectric permittivities $\varepsilon = 23$ and 20, respectively, the 10-GHz Qf product is 83000 and 94000 [6–8]. In contrast to magnesium- and zinc-containing niobates, the data reported in the literature as to the dielectric properties of the cobalt niobate $CoNb_2O_6$ are contradictory. In particular, according to Lee et al. [6], $CoNb_2O_6$ has a rather low electrical Q ($Qf = 11000$), whereas Pullar et al. [8] achieved notably higher Q values: $Qf = 40000$. Previous work [4, 5] has shown that the ability to prepare single-phase $M_2{+}Nb_2O_6$ metaniobates is highly dependent on synthesis conditions. In the case of $MgNb_2O_6$, reaction intermediates, in particular $Mg_4Nb_2O_9$, were present in the final product even after long-term heat treatment at high temperatures (>1100°C) [5], which made it impossible to prepare materials with good properties [4, 5]. In contrast to $MgNb_2O_6$, data on $CoNb_2O_6$ formation are not available in the literature.

Available data suggest that the presence of reaction intermediates may have a significant effect on the dielectric properties of the synthesized material, in particular on its electrical Q. One would also expect the nature and concentration of impurity phases in $Co_{1-x}Nb_2O_{6-x}$ to depend on the Nb : Co ratio. The objective of this work was to investigate the phase changes involved in the solid-state synthesis of the cobalt niobate with the columbite structure and to assess the effect of metal nonstoichiometry on the phase composition, microstructure, and electrical properties of $Co_{1-x}Nb_2O_{6-x}$ materials.

EXPERIMENTAL

Cobalt metaniobate was prepared by solid-state reactions, using extrapure-grade Co_3O_4 (99.95% purity) and Nb_2O_5 (99.9%) as starting chemicals. Appropriate amounts of these oxides were mixed by grinding with water in a vibratory mill for 4 h. After drying, the powders were pressed into disks, which were then heat-treated for 4 h at temperatures of up to 1400°C. To obtain polycrystalline materials, the start-

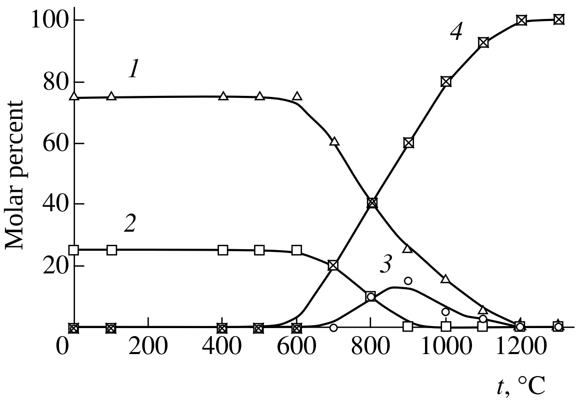

Fig. 1. Phase composition of Co_3O_4 + $3Nb_2O_5$ samples heat-treated for 1 h at different temperatures: (*1*) Nb_2O_5, (*2*) Co_3O_4, (*3*) $Co_4Nb_2O_9$, (*4*) $CoNb_2O_6$.

ing mixtures were preheat-treated at 1100–1200°C, ground in a vibratory mill, and pressed. The compacts were then sintered at 1350–1400°C in air for 2–8 h. To examine the effect of nonstoichiometry on the structure and properties of $Co_{1-x}Nb_2O_{6-x}$, we synthesized materials with different Nb : Co ratios, varying x from –0.05 to 0.05 in steps of 0.005, which corresponded to Nb : Co ratios from 1.9 to 2.1. The phase composition and structural parameters of heat-treated samples were determined by x-ray diffraction (XRD) on a DRON-3U powder diffractometer (CuK_α radiation). The microstructure and chemical composition of crystalline phases were determined by scanning electron microscopy (SEM) on a JEOL JXA 840A equipped with an energy-dispersive x-ray (EDX) spectrometer (Tracor Northern Series II x-ray microanalyzer system). The dielectric properties of the synthesized materials were studied at a frequency of 8–10 GHz by a dielectric resonator method using an Agilent N5230A PNA-L network analyzer.

RESULTS AND DISCUSSION

$Co_{1-x}Nb_2O_{6-x}$ formation. According to XRD results, $CoNb_2O_6$ formation began near 550°C and reached completion in the range 1100–1150°C (Fig. 1). In the temperature range 700–900°C, two cobalt niobates, $CoNb_2O_6$ and $Co_4Nb_2O_9$, were formed concurrently:

$$2Co_3O_4 + 6Nb_2O_5 \longrightarrow 6CoNb_2O_6 + O_2, \quad (1)$$

$$4Co_3O_4 + 3Nb_2O_5 \longrightarrow 3Co_4Nb_2O_9 + 2O_2. \quad (2)$$

At higher temperatures (900–1150°C), $CoNb_2O_6$ was formed through the reaction between the intermediate phase $Co_4Nb_2O_9$ and residual Nb_2O_5:

$$Co_4Nb_2O_9 + 3Nb_2O_5 \longrightarrow 4CoNb_2O_6. \quad (3)$$

The observed sequence and nature of phase changes indicate that the formation of phase-pure $CoNb_2O_6$ is a multistep process (Fig. 1). In the temperature range 1100–1150°C, increasing the heat-treatment time to 6–10 h causes the XRD peaks from Nb_2O_5 and $Co_4Nb_2O_9$ to disappear. At the same time, it cannot be ruled out based on XRD data that the final product contained trace levels (≤1–2 wt %) of these phases.

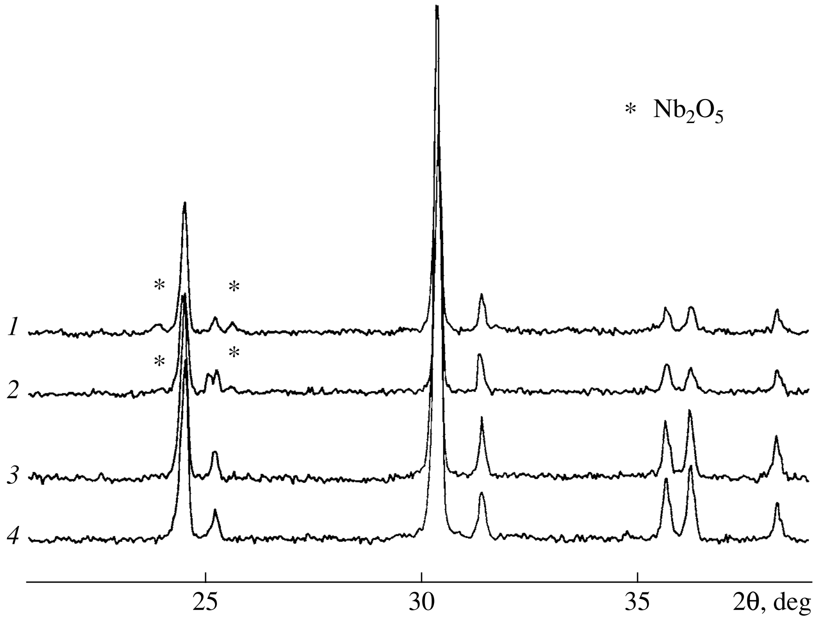

Fig. 2. XRD patterns of polycrystalline $Co_{1-x}Nb_2O_{6-x}$ samples with x = (*1*) 0.05, (*2*) 0.03, (*3*) –0.03, and (*4*) –0.05 heat-treated at 1150°C for (*1*, *2*) 1 and (*3*, *4*) 6 h.

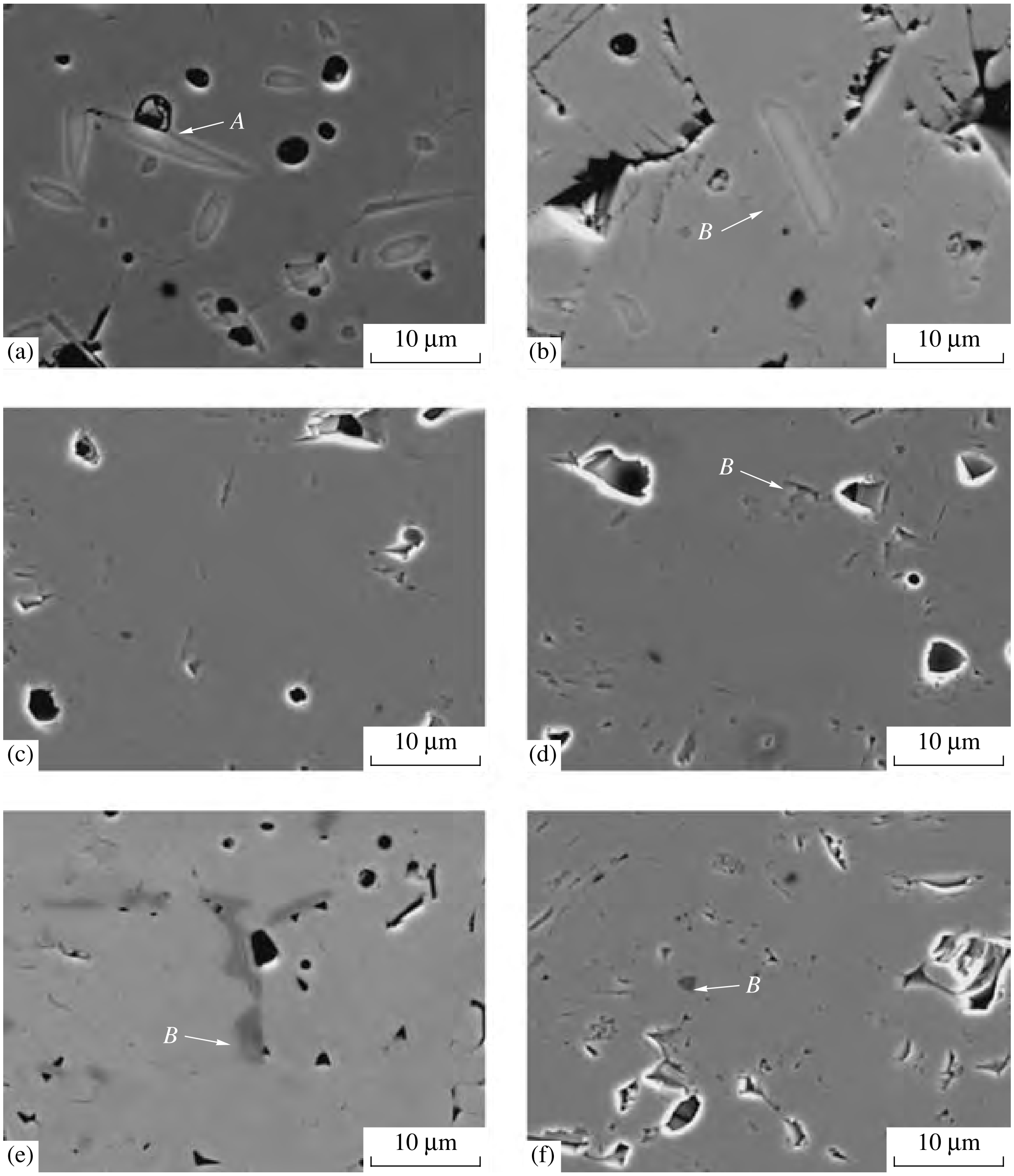

Fig. 3. SEM micrographs of polished sections of polycrystalline $Co_{1-x}Nb_2O_{6-x}$ samples with x = (a) 0.05, (b) 0.03, (c) 0, (d) –0.03, and (e, f) –0.05 sintered at 1150°C for (a–d, f) 1 and (e) 6 h; (*A*) Nb_2O_5, (*B*) $Co_4Nb_2O_9$.

Effect of nonstoichiometry on the phase composition and structure of $Co_{1-x}Nb_2O_{6-x}$. The columbite structure of $Co^{2+}Nb_2^{5+}O_6$ contains infinite zigzag chains of edge-shared oxygen octahedra [9]. In this structure, the oxygen octahedra can be occupied by Co^{2+} and Nb^{5+} ions in different ratios [9]. It is reasonable to expect that both the size of the Co^{2+} ion and the Nb : Co ratio in the unit cell influence the crystallographic distortion of the columbite structure and, hence, the phase composition and electrical properties of the material.

According to XRD results, the $Co_{1-x}Nb_2O_{6-x}$ samples with $x > 0$ consisted of two crystalline phases: the major phase $CoNb_2O_6$ and trace levels of Nb_2O_5. The Nb_2O_5 content was found to increase with increasing x (Fig. 2, scans *1*, *2*). The same was evidenced by microstructural analysis of polished sections of appropriate ceramic samples (Figs. 3a, 3b). Note that, at $x > 0$, the Nb : Co ratio in the major phase evaluated from EDX spectra depends little on x (Fig. 4).

For $x < 0$ (Nb : Co < 2 in the starting mixture), single-phase materials were obtained in the composition

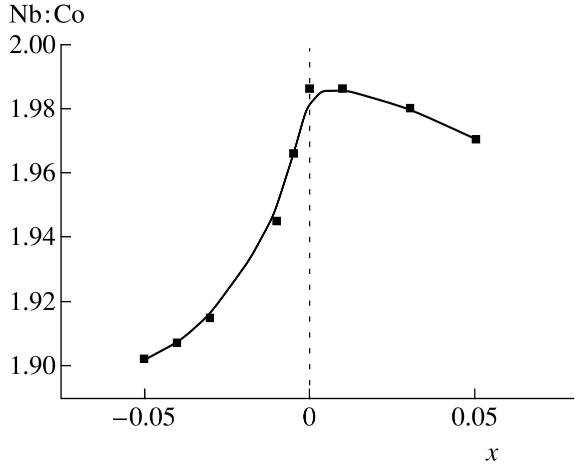

Fig. 4. Experimentally determined Nb : Co ratio in the major phase of $Co_{1-x}Nb_2O_{6-x}$ samples as a function of x.

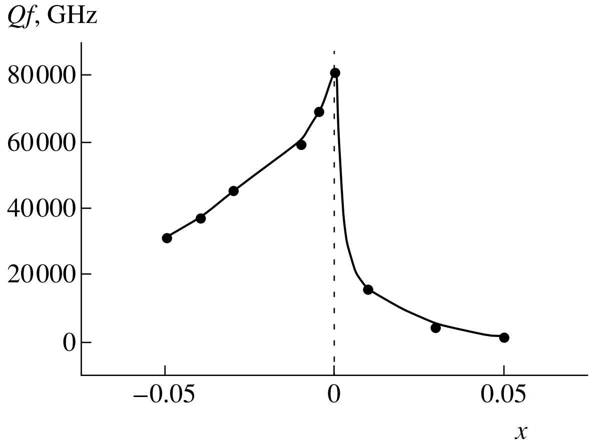

Fig. 5. Qf product as a function of x for $Co_{1-x}Nb_2O_{6-x}$ samples at a frequency of about 10 GHz.

range $-0.03 \le x \le 0$. At more negative x values ($-0.05 \le x < -0.03$), the major phase $CoNb_2O_6$ contained trace levels of a more Co-rich crystalline phase. Microinclusions of the additional phase were on the order of 0.5–1.0 μm in size (Figs. 3d, 3f), so that their chemical composition could not be accurately determined by EDX microanalysis. The phase changes observed during the synthesis of the columbite phase (Fig. 1) suggest however that the composition of the additional phase was $Co_4Nb_2O_9$. The content of the additional phase increases very little as x becomes more negative (Figs. 3d–3f). At the same time, reducing the sintering time to 1–2 h increases the size and concentration of $Co_4Nb_2O_9$ microinclusions (Fig. 3e). For $x < 0$, the Nb : Co ratio in the major phase decreases monotonically with increasing Co content (Fig. 4). Note that, in spite of the rather low EDX microanalysis accuracy in determining the Nb and Co contents of the major phase, our results provide conclusive evidence that the Nb : Co ratio in the sintered materials decreases monotonically with increasing Co content. XRD and microstructural analysis data (Figs. 2, 3) indicate that $CoNb_{2-y}O_{6-2.5y}$ ($y = 2x/(x-1)$) is single-phase in the composition range $0 \le y \le 0.058$. As the Nb : Co ratio in the starting mixture decreases (y increases), we observe a slight shift of XRD peaks to higher 2θ angles (Fig. 2), indicating a reduction in unit-cell volume.

Given that the grain size in the materials studied was independent of chemical composition, the observed broadening of XRD peaks attests to a rise in lattice strain in the columbite phase $CoNb_{2-y}O_{6-2.5y}$, which is probably associated with structural distortions in the niobium-deficient materials.

Microwave dielectric properties of $Co_{1-x}Nb_2O_{6-x}$. The dielectric properties of $Co_{1-x}Nb_2O_{6-x}$ materials are presented in the table. Our results indicate that, in the composition range studied, the Nb : Co ratio has little or no effect on the dielectric permittivity ε of our samples, which lies within the range ε = 20–21. The temperature coefficient of permittivity (TCP) varies insignificantly (at about 155×10^{-6} K^{-1}) for $x > 0$ (Nb : Co > 2) and decreases slightly with increasing niobium deficiency ($x < 0$): from 155×10^{-6} K^{-1} in stoichiometric $CoNb_2O_6$ to 130×10^{-6} K^{-1} in $CoNb_{1.9}O_{5.75}$

Phase composition and 10-GHz dielectric properties of $Co_{1-x}Nb_2O_{6-x}$ materials

x	Phase composition	ε	TCP × 10^{-6}, K^{-1}	Qf, GHz
0.05	$CoNb_2O_6$, Nb_2O_5	19.9	150	800
0.03	$CoNb_2O_6$, Nb_2O_5	19.8	155	2500
0.01	$CoNb_2O_6$, Nb_2O_5	20.0	160	3500
0	$CoNb_2O_6$	20.5	155	82000
–0.01	$CoNb_2O_6$	20.7	152	59000
–0.03	$CoNb_2O_6$	20.2	135	49000
–0.04	$CoNb_2O_6$, $Co_4Nb_2O_9$	20.0	135	37000
–0.05	$CoNb_2O_6$, $Co_4Nb_2O_9$	20.0	130	34000

($x = -0.05$). At the same time, electrical Q (hereafter, represented by the Qf product, where f is the measurement frequency) depends significantly on x (Fig. 5). All of the samples with $x > 0$ have rather low quality factors ($Qf < 20\,000$), presumably because they contain Nb_2O_5. For $x < 0$, Q decreases steadily with decreasing Nb : Co ratio (Fig. 5). The highest electrical Q ($Qf = 82\,000$) is offered by stoichiometric $CoNb_2O_6$. Note that the Q of our materials is at least twice that reported by Lee et al. [6] and Pullar et al. [8]. Analysis of the present results indicates that the electrical Q of our materials is determined, for the most part, by two factors: the presence of Nb_2O_5 at $x > 0$, which markedly reduces Q, and the rise in lattice strain and presence of $Co_4Nb_2O_9$ at $x < 0$, which gradually reduce Q.

CONCLUSIONS

We studied the formation of cobalt metaniobate, $CoNb_2O_6$, with the columbite structure and obtained single-phase $CoNb_{2-y}O_{6-2.5y}$ in the composition range $0 \le y \le 0.05$. The electrical Q of $Co_{1-x}Nb_2O_{6-x}$ materials drops sharply for $x > 0$ because they contain Nb_2O_5 as an impurity phase. For $x < 0$, Q decreases only gradually with decreasing Nb : Co ratio.

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