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# Synthesis and Properties of Columbite-Structure $Mg_{1-x}Nb_2O_{6-x}$

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**Abstract**—The formation of the columbite-structure magnesium niobate $MgNb_2O_6$ is a multistep process. Single-phase material can only be obtained through long-term high-temperature heat treatment. Deviations from stoichiometry have a significant effect on the microwave quality factor $Q$ of the material: magnesium-deficient ceramics contain small amounts of $Nb_2O_5$ and have relatively low $Q$ values, whereas an excess of magnesium leads to the formation of $Mg_4Nb_2O_9$ (alpha-alumina structure) as an impurity phase, thereby drastically increasing the electrical $Q$.

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## INTRODUCTION

Advances in wireless communication systems are highly dependent upon improvements in microwave dielectric materials. In particular, centimeter and millimeter wave wireless applications require high-$Q$ materials that would be less expensive than the known high-$Q$ perovskite-structure barium-tantalate-based microwave dielectrics [1–3] and would not need high sintering temperatures. The columbite-structure magnesium niobate $MgNb_2O_6$ offers high dielectric performance in the microwave region [4–7]. Owing to its high microwave quality factor ($Q$), magnesium niobate is of interest for a variety of practical applications. In addition, this compound is widely used as a precursor in the synthesis of the high-$Q$ dielectric material $Ba(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$-based ferroelectric relaxors [8, 9].

The synthesis of phase-pure magnesium niobate with the columbite structure presents a number of problems. Using solid-state synthesis, Ananta et al. [5] obtained x-ray pure $MgNb_2O_6$ with the columbite structure by heat treatment at 1150°C for 4 h. Heat treatment at higher or lower temperatures led to the formation of $Mg_4Nb_2O_9$ as an impurity phase. Moreover, microstructural examination showed that even the samples that were phase-pure by x-ray diffraction (XRD) contained impurity phases [5]: in addition to $MgNb_2O_6$, trace levels of $Mg_4Nb_2O_9$ (alpha-alumina structure) were present. Phase-pure columbite-structure niobates were prepared earlier by solution-phase reactions [10], a molten-salt process [11], and oxalate route [12]. Phase-pure columbite niobates are difficult to obtain for several reasons, in particular, because the formation of $MgNb_2O_6$ is typically accompanied by that of $Mg_4Nb_2O_9$ [5]. Note that the Mg–Nb–O system contains four ternary compounds: $MgNb_2O_6$, $Mg_4Nb_2O_9$, $Mg_5Nb_4O_{15}$, and $Mg_{1/3}Nb_{11(1/3)}O_{29}$ [13, 14]. At room temperature, however, only $MgNb_2O_6$ and $Mg_4Nb_2O_9$ are stable [15]. For this reason, phase-pure $MgNb_2O_6$ can be prepared by solid-state reactions only if the sample is heat-treated for a long time (20–24 h) [5, 16].

$MgNb_2O_6$ ceramics offer high microwave quality factors ($Qf$ = 79600 GHz) [6], which can be raised further by prolonged (50 h) heat treatment ($Qf$ = 95900 GHz) [7].

The properties of multiphase systems are known to be sensitive to even slight deviations from stoichiometry. Data on the effect of nonstoichiometry on the properties of $MgNb_2O_6$ are not available in the literature.

The objective of this work was to study the effect of small deviations from stoichiometry on the phase composition, microstructure, and microwave dielectric properties of columbite-structure magnesium niobate ceramics.

## EXPERIMENTAL

Samples for this investigation were prepared by solid-state reactions in appropriate mixtures of analytical-grade MgO and $Nb_2O_5$ (or nanoparticulate niobium oxide prepared by solution-phase reaction). The mixtures were homogenized by ball milling with bidistilled

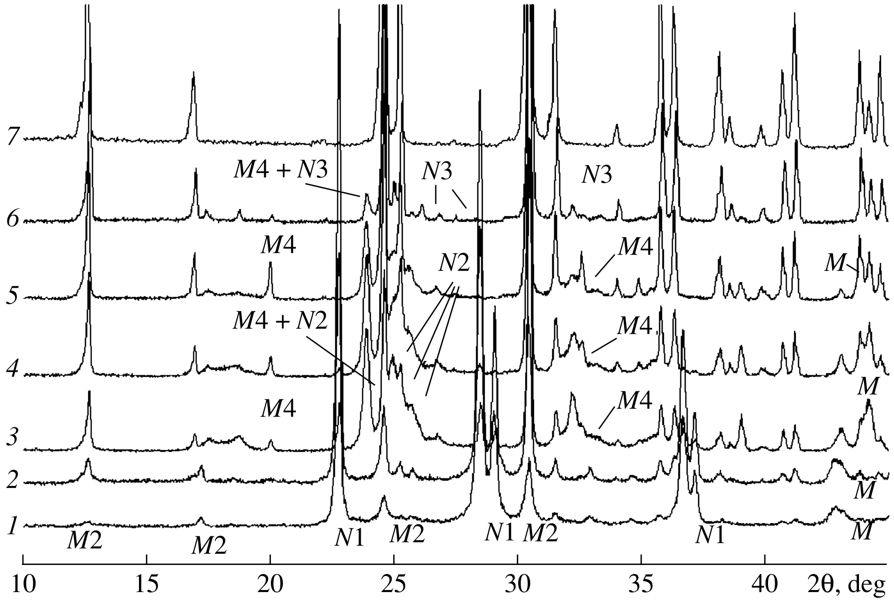

**Fig. 1.** Phase composition of $MgO–Nb_2O_5$ samples (precipitated $Nb_2O_5$) heat-treated for 1 h at different temperatures: (*1*) 700, (*2*) 800, (*3*) 900, (*4*) 1000, (*5*) 1100, (*6*) 1200, and (*7*) 1400°C; *N*1–*N*3 = $Nb_2O_5$ (PDF, nos. 27-1003 (*N*1), 26-0885 (*N*1), 72-1121 (*N*2), and 37-1468 (*N*3)), *M* = MgO (PDF, no. 45-0946), *M*2 = $MgNb_2O_6$, *M*4 = $Mg_4Nb_2O_9$ (PDF, no. 38-1459).

water. After boiling down and drying at 100–150°C, the mixtures were screened through a nylon-6 sieve. To study phase changes during synthesis, the dried mixtures were pressed at 50 MPa, and the green compacts were fired at temperatures of up to 1400°C. Next, the samples were ground, and their phase composition was determined by XRD (DRON-3M powder diffractometer, Cu$K_\alpha$ radiation, step-scan mode with a step size $\Delta(2\theta) = 0.02°$ and a counting time of 10 s per data point). As external standards, we used $SiO_2$ ($2\theta$ calibration) and $Al_2O_3$ (NIST SRM 1976 intensity standard [17]). The phases present were identified using JCPDS Powder Diffraction File data. Ceramic samples were prepared by sintering at temperatures from 1350 to 1400°C for 2–8 h.

The microstructure and chemical composition of the synthesized 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). In dielectric measurements in the microwave region, we used an Agilent N5230A PNA-L network analyzer.

## RESULTS AND DISCUSSION

To optimize the sintering temperature, we studied phase changes in $Mg_{1-x}Nb_2O_{6-x}$ samples with $x$ = 0.03, 0.01, 0, –0.01, and –0.03.

XRD data indicate that, independent of whether we use off-the-shelf niobium oxide or the material synthesized via precipitation from solution, $MgNb_2O_6$ formation in the mixtures studied begins above 700°C (Figs. 1, 2). After heat treatment at 700°C, the mixtures consisted predominantly of $Nb_2O_5$ and MgO. The strongest reflection from MgO, 200, was located at $2\theta = 43°$, whereas the observed temperature variations of the intensity and position of the peaks from $Nb_2O_5$ attested to a number of phase changes. In niobium oxide synthesis through precipitation from solution, the calcination temperature has a significant effect on the crystal structure of the resulting oxide. As the heat-treatment temperature is raised, the first to form is the low-temperature phase (*N*1) of niobium oxide (PDF, no. 27-1003). Near 700°C, the low-temperature phase (*N*1) transforms into $\beta$-$Nb_2O_5$(*N*2, PDF, no. 26-885). At 900°C, $\beta$-$Nb_2O_5$ transforms into the high-temperature phase (*N*3) (Fig. 1, scan *3*). In our syntheses with the precipitated niobium oxide, at a short calcination time (1 h) phase-pure $MgNb_2O_6$ was obtained at high temperatures (≃1400°C). The off-the-shelf niobium oxide consisted of $\beta$-$Nb_2O_5$(*N*2) (Fig. 2). After heat treatment at temperatures above 900°C, we observed diffraction peaks from both the *N*2 and *N*3 oxides. The intensity of the peaks from $MgNb_2O_6$ increased steadily with heat-treatment temperature. However, even after calcination at 1100°C for 1 h, the sample contained significant amounts of unreacted oxides. At temperatures above 1200°C, the peaks from MgO completely disappeared, but the samples contained small amounts of niobium oxide. Phase-pure $MgNb_2O_6$ was obtained at 1400°C (1 h).

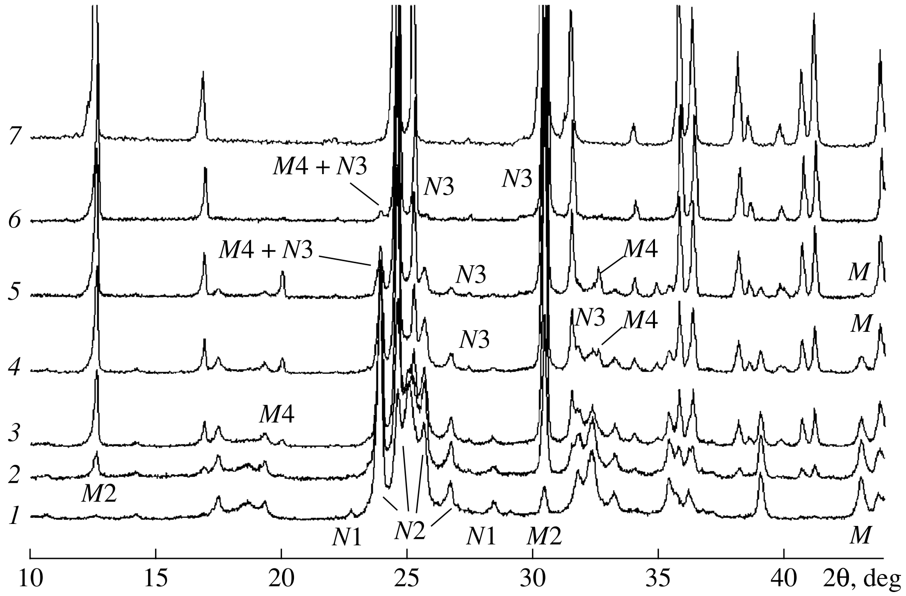

**Fig. 2.** Phase composition of MgO–$Nb_2O_5$ samples (off-the-shelf $Nb_2O_5$) heat-treated for 1 h at different temperatures: (*1*) 700, (*2*) 800, (*3*) 900, (*4*) 1000, (*5*) 1100, (*6*) 1200, and (*7*) 1400°C; *N*1–*N*3 = $Nb_2O_5$ (PDF, nos. 27-1003 (*N*1), 26-0885 (*N*1), 72-1121 (*N*2), and 37-1468 (*N*3)), *M* = MgO (PDF, no. 45-0946), *M*2 = $MgNb_2O_6$, *M*4 = $Mg_4Nb_2O_9$ (PDF, no. 38-1459).

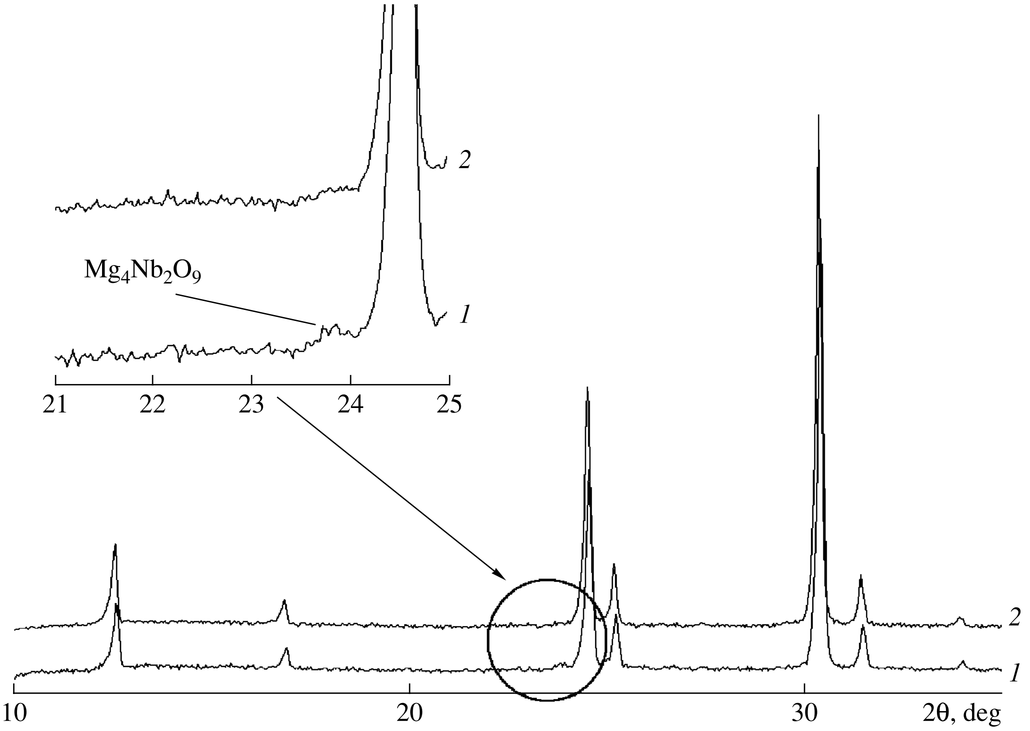

**Fig. 3.** XRD patterns of powder samples calcined at 1150°C for (*1*) 1 and (*2*) 6 h.

Diffraction peaks from $Mg_4Nb_2O_9$ were present at calcination temperatures from 900 to 1200°C. Analysis of our XRD data indicated that $MgNb_2O_6$ and $Mg_4Nb_2O_9$ formed by parallel reactions. After heat treatment at 1200°C, the product consisted of $MgNb_2O_6$ and small amounts of $Mg_4Nb_2O_9$ and $Nb_2O_5$, no matter which starting reagents had been used. Our results suggest that magnesium niobate for-

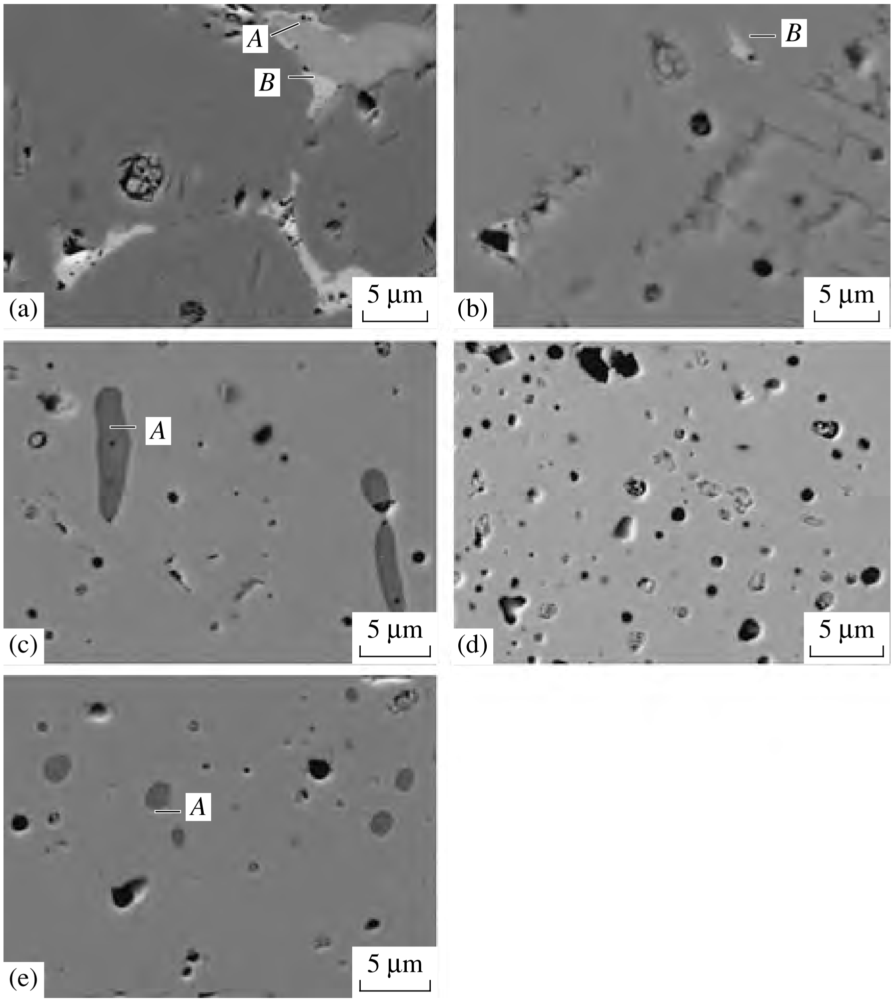

**Fig. 4.** SEM micrographs of $Mg_{1-x}Nb_2O_{6-x}$ samples with $x$ = (a) 0.03, (b, d) 0, and (c, e) –0.03 sintered for (a–c) 2 and (d, e) 6 h; $A = Mg_4Nb_2O_9$, $B = Nb_2O_5$.

mation can be represented by the schemes

$$MgO + Nb_2O_5 \xrightarrow{700\text{–}1100°C} MgNb_2O_6, \quad (1)$$

$$4MgO + Nb_2O_5 \xrightarrow{900\text{–}1100°C} Mg_4Nb_2O_9, \quad (2)$$

$$Mg_4Nb_2O_9 + 3Nb_2O_5 \xrightarrow{1100\text{–}1400°C} 4MgNb_2O_6. \quad (3)$$

Phase-pure $MgNb_2O_6$ can be obtained either by raising the heat-treatment temperature to 1400°C (Figs. 1, 2) or by increasing the heat-treatment time at relatively low temperatures (Fig. 3). The XRD pattern of the powder synthesized at 1150°C in 1 h showed reflections from $Mg_4Nb_2O_9$ (Fig. 3). Increasing the heat-treatment time to 6 h, we obtained phase-pure $MgNb_2O_6$ (Fig. 3).

The XRD patterns of the $Mg_{1-x}Nb_2O_{6-x}$ samples with $x > 0$ indicated the presence of $Nb_2O_5$ as a minority phase. In the range $-0.03 \le x < 0$, we obtained XRD single-phase material. Electron-microscopic examination showed however that, over the entire composition range studied, the samples contained an impurity phase: $Nb_2O_5$ at $x > 0$ and $Mg_4Nb_2O_9$ at $-0.03 \le x < 0$ (Fig. 4). Increasing the sintering time notably reduced the content of the impurity phase, but only at the stoichiomet-

10-GHz dielectric properties of $Mg_{1-x}Nb_2O_{6-x}$ ceramics

| $x$ | $f_{res}$, GHz | $Qf$, GHz | ε | TCF, ppm/°C |
|---|---|---|---|---|
| 0.03 | 9.28 | 1400 | 20.8 | –56 |
| 0.01 | 9.56 | 12000 | 19.7 | –56 |
| 0 | 9.76 | 40000 | 18.5 | –56 |
| –0.01 | 9.60 | 107000 | 18.5 | –59 |
| –0.03 | 9.55 | 128000 | 21.5 | –62 |

Note: TCF = temperature coefficient of resonant frequency.

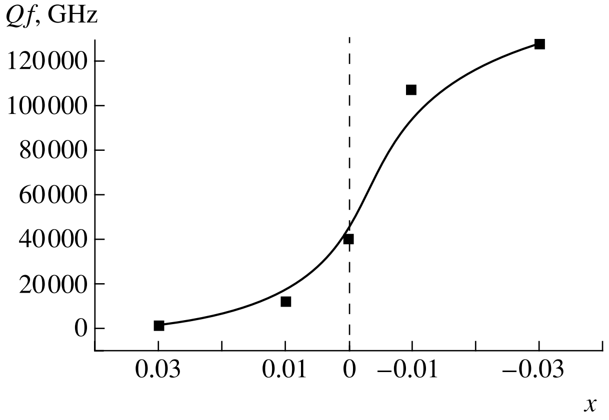

**Fig. 5.** Composition dependence of the $Qf$ product ($f \simeq 10$ GHz) for $Mg_{1-x}Nb_2O_{6-x}$ ceramics.

ric composition ($x = 0$) was single-phase material obtained (Fig. 4).

The microwave dielectric properties of the $Mg_{1-x}Nb_2O_{6-x}$ samples are summarized in the table and in Fig. 5. In the composition range studied, the dielectric permittivity ε of the ceramics varies from 18.5 to 21.5. The presence of $Nb_2O_5$ ($x > 0$) drastically reduces the electrical $Q$. At the same time, in the composition range $-0.03 \le x < 0$ the $Qf$ product rises, reaching 128000 GHz. Note that, in the range $-0.03 \le x < 0$, where our samples have high $Q$ values, they contain $Mg_4Nb_2O_9$ (alpha-alumina structure) as an impurity phase. This phase has a relatively low permittivity, $\varepsilon = 12$, and very large microwave quality factor, $Qf = 210000$ GHz [18]. It seems likely that it is the presence of small amounts of the high-$Q$ phase $Mg_4Nb_2O_9$ (alpha-alumina structure) in the columbite-structure magnesium niobate which is responsible for the high electrical $Q$ of the two-phase $Mg_{1-x}Nb_2O_{6-x}$ ceramics with $-0.03 \le x < 0$.

## CONCLUSIONS

The present results demonstrate that the formation of the columbite-structure magnesium niobate $MgNb_2O_6$ through solid-state reactions is a multistep process and that the purity and particle size of the starting reagents have little effect on the phase changes involved in $MgNb_2O_6$ synthesis. Deviations from stoichiometry in the $Mg_{1-x}Nb_2O_{6-x}$ system lead to the formation of impurity phases: $Nb_2O_5$ at $x > 0$ and $Mg_4Nb_2O_9$ at $-0.03 \le x < 0$. The presence of $Nb_2O_5$ reduces the microwave quality factor of the ceramics, whereas $Mg_4Nb_2O_9$ drastically increases it. The content of the impurity phases decreases with increasing heat-treatment time, but single-phase ceramics were only obtained at the stoichiometric composition ($x = 0$).

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