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Effect of Nonstoichiometry on the Structure and Microwave Dielectric Properties of $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ and $Ba(Zn_{1/2+x}W_{1/2}O_{3-x/2}$

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Abstract—We have synthesized $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}\varepsilon$ and $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ barium tungstates with different deviations from cation stoichiometry ($x = 0.01$–0.05, $y = 0.01$—0.05), determined the phase composition of ceramics fabricated from the tungstates, and investigated their electrical properties. Even slight deviations from cation stoichiometry in $Ba(Zn_{1/2}W_{1/2})O_3$ lead to the formation of the scheelite phase $BaWO_4$, and its content increases with heat-treatment temperature. Barium or zinc deficiency in the systems studied improves the sintering behavior of $Ba(Zn_{1/2}W_{1/2})O_3$ and increases the degree of 1 : 1 B-site cation ordering, which in turn ensures an increase in microwave quality factor, Q.

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INTRODUCTION

$Ba(Zn_{1/2}W_{1/2})O_3$ has the cubic perovskite structure, in which oxygen octahedra share corners to form a three-dimensional framework [1]. This structure is characterized by 1 : 1 ordering of the cations that reside in the oxygen octahedra, that is, the formation of a superstructure in which layers of W^{6+} cations alternate with those of Zn^{2+} cations. It is known that the accommodation of ions of different sizes in the same crystallographic site is usually accompanied by the development of local lattice distortions [2], which act as additional centers of electromagnetic energy scattering. Ordering (superstructure formation) processes lead to partial isolation of deformation factors (cation segregation in different crystallographic planes) and, as a consequence, to a reduction in local lattice strain [2, 3]. Structural ordering has a significant effect on the absorption of electromagnetic energy in the microwave range and is, therefore, of practical interest for engineering high-efficiency dielectrics with low microwave losses ($\tan\delta$), or a high microwave quality factor ($Q = 1/\tan\delta$), in the centimeter and millimeter ranges.

As shown earlier, slight changes in chemical composition (deviations from cation stoichiometry) contribute to cation ordering processes in MNb_2O_6 columbites and $Ba(M_{1/3}Nb_{2/3})O_3$ perovskites with M = Co, Zn, and Mg, and considerably increase their quality factor (by 50–100%) [4, 5]. There are grounds to assume that deviations from stoichiometry will have an advantageous effect on the structure and properties of $Ba(Zn_{1/2}W_{1/2})O_3$.

It is worth noting that stoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$ has a rather high quality factor [6]. In addition, there is evidence that heterovalent B-site cation substitutions influence the microwave dielectric properties of $Ba(Zn_{1/2}W_{1/2})O_3$ [7, 8]. At the same time, the effect of partial cation nonstoichiometry on the phase composition and properties of polycrystalline $Ba(Zn_{1/2}W_{1/2})O_3$ has not been studied.

The purpose of this work was to study the effect of partial cation nonstoichiometry on the structure, phase composition, and microwave dielectric properties of the zinc-containing barium tungstates $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ and $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$.

EXPERIMENTAL

Barium- and zinc-deficient materials, $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ with $x = 0.01$–0.05 and $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ with $y = 0.01$–0.05, were prepared by solid-state reactions. The starting reagents used were extra-pure-grade ZnO, $BaCO_3$, and WO_3. Appropriate starting mixtures were homogenized by grinding with bidistilled water for 6–8 h in a vibratory mill. After drying at 150–200°C, the mixtures were heat-treated in alundum crucibles at 1150 and 1250°C for 4 h. To prepare ceramic samples, the heat-treated material was comminuted by vibration milling, an aqueous 5% solution of polyvinyl alcohol was added, and the powder was pressed into pellets, which were then sintered at 1360°C for 4 h. The phase composition of the synthesized materials was determined by X-ray diffraction (XRD) on a DRON-3M powder diffractometer with CuK_α radiation. The degree of 1 : 1 B-site cation ordering was eval-

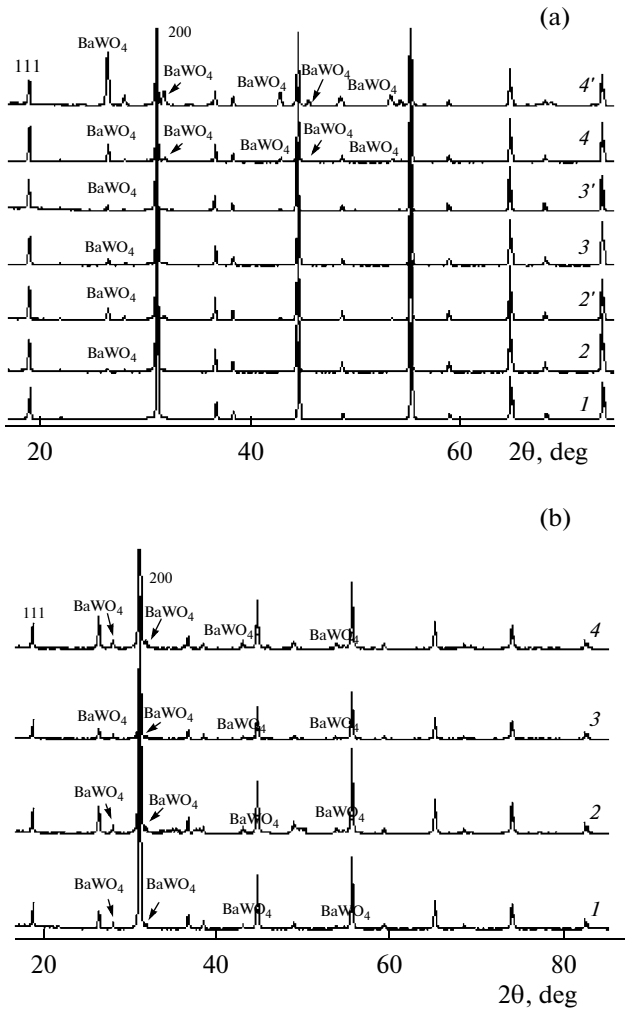

Fig. 1. XRD patterns of (a) $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ barium tungstate powders synthesized at (*1*–*4*) 1150 and (*2*′–*4*′) 1250°C and (b) ceramic samples prepared from the powders: $x = (1)$ 0, (*2*, *2*′) 0.01, (*3*, *3*) 0.02, (*4*, *4*) 0.05.

uated from the relationship between the observed ($(I_{111}/I_{200})_{obs}$) and calculated ($(I_{111}/I_{200})_{calc}$) intensities of the (1/2, 1/2, 1/2) superlattice reflection and (100) fundamental reflection: $S = (I_{111}/I_{200})_{obs}/(I_{111}/I_{200})_{calc}$. The microwave dielectric properties (ε, Q, and TCε) of our samples were studied using an Agilent N5230A PNA-L network analyzer.

RESULTS AND DISCUSSION

$Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ synthesis. XRD examination showed that the barium-deficient zinc-containing barium tungstates $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ ($x = 0.01$–0.05) prepared by firing at 1150 and 1250°C for 4 h contained, in addition to the perovskite phase $Ba(Zn_{1/2}W_{1/2})O_3$, crystalline $BaWO_4$ with a tetragonal scheelite structure as an additional phase (Fig. 1a). With increasing synthesis temperature (from 1150 to 1250°C) or deviation from stoichiometry (x), the $BaWO_4$ content of the powders increases (Fig. 1a). It is worth noting that this phase does not form in stoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$ synthesized under such conditions. Recent work by Jancar et al. [9] has shown that $BaWO_4$ is one of the two intermediate phases ($BaWO_4$ and $Ba_3W_2O_9$) in $Ba(Zn_{1/2}W_{1/2})O_3$ synthesis. According to their results, $Ba(Zn_{1/2}W_{1/2})O_3$ forms through the reaction of $BaWO_4$ and $Ba_3W_2O_9$ with zinc oxide at temperatures from 700 to 1000°C. The formation of $BaWO_4$ in $Ba(Zn_{1/2}W_{1/2})O_3$ materials sintered at temperatures above 1300°C was attributed to high-temperature ZnO sublimation followed by thermal decomposition of the $Ba(Zn_{1/2}W_{1/2})O_3$ perovskite. It seems likely that the temperature of $Ba(Zn_{1/2}W_{1/2})O_3$ decomposition in the $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ system is lower, which leads to $BaWO_4$ formation at lower (1150–1250°C) temperatures. For this reason, raising the synthesis temperature of $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ leads to an undesirable increase in $BaWO_4$ content, as evidenced by the present experimental data (Fig. 1a). Ceramic materials were prepared by sintering the synthesized $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ powders at 1360°C for 4 h. XRD examination of the ceramics showed that all of the tungstate samples, including stoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$, contained $BaWO_4$ as an additional phase (Fig. 1b). The $BaWO_4$ content of the ceramics was higher than that of the respective powders (Fig. 1), which is attributable to ZnO losses during sintering.

$Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ synthesis. XRD examination showed that, in contrast to $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$, the zinc-deficient zinc-containing barium tungstate powders, $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ ($y \geq 0$), prepared by firing at 1150°C for 4 h contained no $BaWO_4$ (Fig. 2a), indicating that the perovskite phase did not decompose at this synthesis temperature. The synthesized materials were single-phase. At the same time, sintering at a higher temperature of 1360°C led to the formation of $BaWO_4$ (Fig. 2b). According to Jancar et al. [9], $BaWO_4$ forms through the thermal decomposition of the $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ perovskite. Note that the $BaWO_4$ content of the sintered $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ samples is essentially independent of the deviation from stoichiometry (Fig. 2b). Thus, the present results demonstrate that, in contrast to the $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ system, where the thermal decomposition temperature decreases considerably with increasing barium deficiency, the decomposition temperature of the $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ materials remains unchanged.

Structural properties of nonstoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$. In the two systems studied, we observed the formation of cubic perovskite $Ba(Zn_{1/2}W_{1/2})O_3$ with strong (1/2, 1/2, 1/2) superlattice reflections (Figs. 1, 2), indicating a high degree of 1 : 1 B-site cation ordering. Regardless of the $BaWO_4$ content in the perovskite matrix, the measured density (ρ_{meas}) of the nonstoichiometric ceramics ($Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ and $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$) was 95–98% of theoretical density (ρ_{theor}) (table). At the same time, stoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$ had a lower den-

sity (89% of theoretical density). This indicates that slight deviations from stoichiometry markedly improve the sinterability of the polycrystalline material. Note that such behavior was also reported for nonstoichiometric ordered $Ba(Mg_{1/3}Nb_{2/3})O_3$ [5]. The crystallographic parameters of nonstoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$ are only weakly dependent on the deviation from stoichiometry (table). The unit-cell volume remained unchanged to within the present experimental uncertainty ($a = 8.121$ Å, $V = 535.57$ Å). At the same time, slight deviations from stoichiometry in both systems led to an increase in the degree of 1 : 1 order (table). In particular, the highest S value was reached at $x = 0.02$ in the $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ system and at $y = 0.01$ in $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$.

Dielectric properties of nonstoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$. We studied the microwave dielectric properties of the synthesized materials (table). The $Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ and $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ tungstates have rather low relative dielectric permittivity, $\varepsilon = 19$–24. Deviations from stoichiometry have little effect on their permittivity, with a small tendency for ε to increase. The temperature coefficient of the resonant frequency (TCF), related to the temperature coefficient of permittivity (TCε) by $TCF = -TC\varepsilon/2 - \alpha$ (where α is the linear thermal expansion coefficient), ranged from −35 to −40 ppm/K, independent of the chemical composition of the material and $BaWO_4$ content. The TCF of $BaWO_4$ is −70 ppm/K [10], but because of the low content of this phase in our ceramic samples it had little or no effect on the temperature dependences of parameters of $Ba(Zn_{1/2}W_{1/2})O_3$. At the same time, the quality factor Q, or the Qf product (where f is frequency), which is often referred to as the microwave quality factor, increases with deviation from stoichiometry in the two systems studied. The Qf product reaches high values regardless of the $BaWO_4$ content (table). Given that the Qf of $BaWO_4$ is 50 000–60 000 GHz [10], it is reasonable to expect that the presence of this phase in the $Ba(Zn_{1/2}W_{1/2})O_3$ perovskite matrix would not impair the dielectric properties of the materials, as observed. Moreover, the higher Q of the nonstoichiometric tungstates may be due to a slight increase in the density of the ceramic and in the degree of 1 : 1 order in $Ba(Zn_{1/2}W_{1/2})O_3$. The rather low quality factor of the ceramics (e.g., Qf = 14000 GHz in stoichiometric $Ba(Zn_{1/2}W_{1/2})O_3$) is probably due to the lower degree of 1 : 1 order ($S = 73\%$) and the low relative density (89%) of the ceramic.

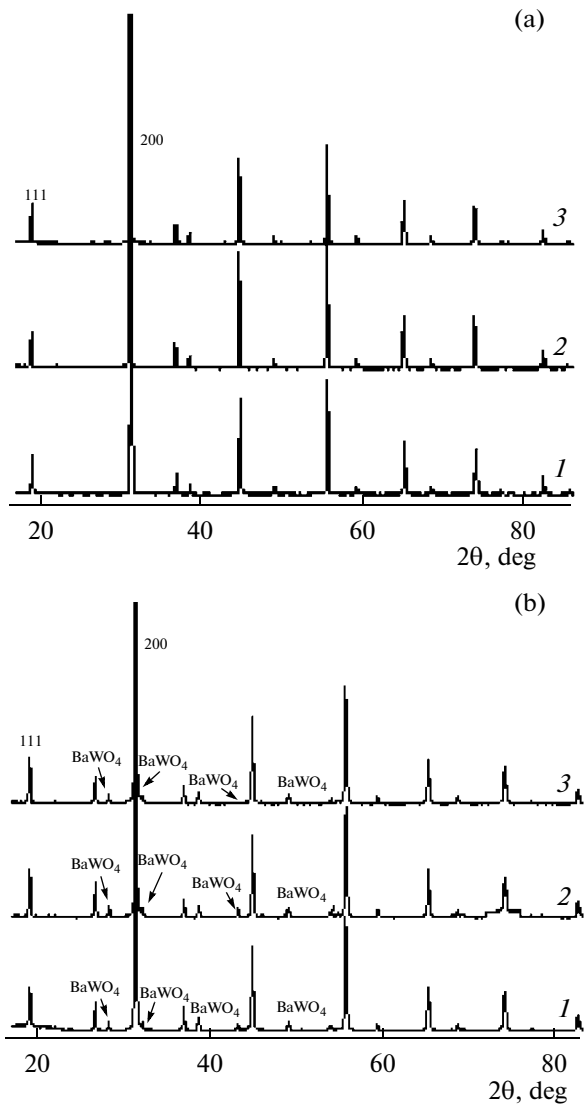

Fig. 2. XRD patterns of (a) $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ barium tungstate powders synthesized at 1150°C and (b) ceramic samples prepared from the powders: $y =$ (*1*) 0, (*2*) 0.01, (*3*) 0.05.

Structural parameters, degree of ordering (S), and dielectric properties of $Ba(Zn_{1/2}W_{1/2})O_3$ tungstates

Composition	a, Å	V, Å	ρ_{theor}, g/cm^3	ρ_{meas}, g/cm^3	S, %	ε	TCF, ppm/K	Qf, GHz
$Ba(Zn_{1/2}W_{1/2})O_3$	8.121	535.57	6.97	6.15	73	19	–35	14000
$Ba_{0.99}(Zn_{1/2}W_{1/2})O_{2.99}$	8.121	535.57	6.94	6.69	70	23	–35	22000
$Ba_{0.98}(Zn_{1/2}W_{1/2})O_{2.98}$	8.121	535.57	6.91	6.62	92	24	–40	31000
$Ba_{0.95}(Zn_{1/2}W_{1/2})O_{2.95}$	8.121	535.57	6.82	6.68	78	21	–40	25000
$Ba(Zn_{0.49}W_{0.5})O_{2.995}$	8.121	535.57	6.96	6.65	86	20	–35	40000
$Ba(Zn_{0.45}W_{0.5})O_{2.9975}$	8.121	535.57	6.90	6.72	82	22.5	–40	32000

CONCLUSIONS

$Ba_{1-x}(Zn_{1/2}W_{1/2})O_{3-x}$ and $Ba(Zn_{1/2-y}W_{1/2})O_{3-y/2}$ zinc-containing barium tungstates with different deviations from cation stoichiometry were prepared by solid-state reactions. The deviation from stoichiometry has a significant effect on the phase composition and electrical properties of the materials. Their dielectric properties are potentially attractive for designing components of centimeter- and millimeter-range communication systems.

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