

High-Temperature Decomposition of B-Site-Ordered Perovskite Ba(Zn_{1/2}W_{1/2})O₃

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The reactions during high-temperature decomposition of $Ba(Zn_{1/2}W_{1/2})O_3$ double perovskite, a potential microwave dielectric material, were studied by using X-ray diffraction, electron microscopy, and Knudsen effusion combined with mass spectrometry. The results show that above 1200°C, the perovskite decomposes due to the sublimation of ZnO, which results in the formation of BaWO₄, Ba₂WO₅, and amorphous BaO-rich phases. The simultaneous presence of BaWO₄ and Ba₂WO₅ causes the formation of a liquid phase above 1320°C, which in the case of ceramics results in a progressive deterioration of the microstructure. As a consequence, the dielectric losses of Ba(Zn_{1/2}W_{1/2}) O₃-based ceramics strongly depend on the processing parameters.

I. Introduction

THE history of ordered perovskites dates back to the early 1950s, when Steward and Rooksby reported that A₃WO₆type alkaline-earth tungstates exhibit a crystal structure similar to that of (NH₄)FeF₆.¹ In such a crystal structure, oxygen-coordinated octahedral positions are shared by alkaline-earth and tungsten cations in a 1:1 ratio, which can be represented as $A(A_{1/2}W_{1/2})O_3$. The octahedrally coordinated cations are ordered so that successive crystal planes, in the direction of cubic close packing, are solely occupied either by an alkaline-earth or a tungsten cation. Such an arrangement yields a cubic symmetry that belongs to the Fm-3m space group. Perovskites exhibiting this structural type are nowadays often referred to as "double perovskites." Later, other varieties of octahedral cation ordering in the perovskite structure were synthesized, a concise description of which was given by Galasso et al. in the 1960s.² Some 20 years later, it was realized that some of these ordered perovskites exhibit extremely low dielectric losses at microwave frequencies, which attracted the attention of the dielectric materials research community. Ceramics based on the 1:2 ordered $Ba(Zn_{1/3})$ $Ta_{2/3}O_3$ were among the first to be identified as possible candidates for use as dielectric resonators in microwave devices.³ Apart from their low dielectric losses (high Q-value), these Ba(Zn_{1/3}Ta_{2/3})O₃ ceramics exhibit a temperature-stable resonant frequency with a near-zero temperature coefficient of resonant frequency ($\tau_f \sim 0$ ppm/K), which has led to their commercialization. By the end of the 1990s, this material was being widely utilized as a dielectric resonator in the base stations of wireless telecommunications systems. Unfortunately, however, the production of Ba(Zn_{1/3}Ta_{2/3})O₃-based ceramics requires high temperatures and long processing times and, furthermore, the price of Ta has increased since the turn of the millennium. This, of course, has spurred the search for alternative materials, and the focus of the research turned to the Nb-analog Ba(Zn_{1/3}Nb_{2/3})O₃. Compared with Ba(Zn_{1/3}Ta_{2/3})O₃, the Nb-analog exhibits higher dielectric losses (lower *Q*-value) and a lower temperature stability of the resonant frequency, with $\tau_f \sim +30$ ppm/K. The obvious way to compensate for this non-zero temperature dependence of the resonant frequency of Ba(Zn_{1/3}Nb_{2/3})O₃ is to synthesize solid solutions with compounds that exhibit a negative value of τ_f . Hence, with the key issue being the cation order, which is a prerequisite for the high *Q*-values, candidate materials were sought among the ordered perovskites.⁴⁻⁶ We have identified Ba(Zn_{1/2}W_{1/2})O₆ as a possible candidate.

The literature data on Ba(Zn_{1/2}W_{1/2})O₆ appears to be somewhat contradictory. While the values for the dielectric constant ($\varepsilon_r \sim 28$) reported show good agreement, there is a considerable difference in the reported *Q*-values.^{7–9} According to the Kyocera patent,⁷ ceramics based on Ba(Zn_{1/2}W_{1/2})O₆ exhibit a $Q \times f$ value of 82 000 GHz, whereas Zhao *et al.*⁸ reported a value of 36 000 GHz. Khalyavin *et al.*,⁹ on the other hand, measured a $Q \times f$ of 22 000 GHz, albeit with the presence of secondary phases in the ceramics. To complicate matters further, in a recently published paper, Prakash *et al.*¹⁰ claim that the crystal structure of Ba(Zn_{1/2} W_{1/2})O₃ synthesized by solid-state reaction is monoclinic, while in all the other literature reports, Ba(Zn_{1/2}W_{1/2})O₃ belongs to the *Fm-3m* space group with cubic symmetry. With these inconsistencies in mind, we decided to perform a detailed investigation of the crystal structure and chemistry of Ba(Zn_{1/2}W_{1/2})O₃.

II. Experimental Procedure

The samples were prepared by solid-state reaction using stoichiometric amounts of reagent powders of BaCO₃ (99.95%, Alfa Aesar, Ward Hill, MA), ZnO (99.9%, Alfa Aesar), and WO₃ (99.99%, Alfa Aesar). After weighing, the powders were homogenized under ethanol in a planetary ball mill using 10 mm yttriastabilized zirconia balls. The homogenized powders were then dried, uniaxially pressed into disk-shaped samples, and calcined in an atmosphere of air. The calcination temperature was increased stepwise from 600° to 1200°C, and after each calcination step, the samples were hand ground in an agate mortar and ballmilled under ethanol for 2 h. The phase composition after each calcination step was determined by X-ray powder diffraction, carried out with a Bruker AXS D4 Endavor (Bruker, Karlsruhe, Germany). The data were collected using CuKa radiation in the 2θ range from 10° to 70° with a step of 0.04° . For the purpose of crystal-structure refinement, the X-ray spectrum was collected with a PANalytical X'Pert PRO in a configuration with a Johannson monochromator (PANalytical X'pert PRO, Almelo, the Netherlands) to remove the CuK α_2 radiation. The 2 θ range was from 5° to 140° with a 0.016° step and 15 s/step. The TOPAS software package was used for the Rietveld refinement.

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The microstructural analyses were performed with a JEOL JXA 840A (Tokyo, Japan) scanning electron microscope (SEM) and a JEOL JEM 2010F transmission electron microscope (TEM). For the transmission electron microscopy, the samples were mechanically thinned down to 100 μ m, dimple ground to 20 μ m, and then ion-milled to electron transparency using Ar plasma at 4 kV.

The vapor pressure of Zn was determined by Knudsen effusion mass spectrometry (KEMS). This is a combination of the standard Knudsen effusion method and mass spectrometry.¹¹ The latter is used to identify and measure the vapor pressure of the molecular species that are in equilibrium with the condensed sample within the Knudsen cell. This is accomplished by allowing the effusing molecules to pass the ion source, become ionized, and finally be analyzed in terms of their masses and abundance. The vapor pressure of the *i*-th species in the cell can thus be obtained from the following equation:

$$p_i = C_i \times \sum_j I_{ij}^+ \times T \tag{1}$$

where p_i is the pressure of the *i*-th molecular species in equilibrium, *T* is the temperature of the cell, $\sum_j I_{ij}$ is the sum of all the ion abundances "*j*" belonging to the molecular species *i*, and C_i is the sensitivity constant of the mass spectrometer for the molecular species *i*. In general, its value must be determined with a separate experiment using various techniques. In the present work, we used silver as an internal standard. The pressure of the species of interest (in this case Zn) at each temperature was obtained by using the following equation:

$$p_{\rm Zn} = \frac{\sum\limits_{j({\rm Zn})} I_{\rm Zn}^+}{\sum\limits_{j({\rm Ag})} I_{\rm Ag}^+} \times \frac{\sigma_{\rm Ag}}{\sigma_{\rm Zn}} \times p_{\rm Ag}$$
(2)

where σ_{Ag} and σ_{Zn} represent the ionization cross sections of silver and zinc, respectively and p_{Ag} is the saturation vapor pressure of silver at the measurement temperature. Approximately 100 mg of powdered sample was loaded together with a similar amount of silver into the alumina Knudsen cell with an orifice diameter of 0.5 mm. The cell was then placed in the evaporator of a low-resolution 60° Nier-type mass spectrometer. After evacuation to 10E-4 Pa, the sample was degassed by heating at 5°C/min up to 600°C. During the heating, some CO₂ was released from the sample. Finally, the temperature was slowly increased until ions of Zn⁺ began to appear. At 900°C, for instance, the abundances of Zn⁺ and Ag⁺ were measured as 955 and 16 800 counts/s, respectively. The measurements were then repeated for each 20° up to 1000°C. The details of the setup can be found elsewhere.¹²

The microwave dielectric properties of the sintered ceramic discs were measured with a HP 8719C network analyzer (Palo Alto, CA) using the cavity reflection method. The ceramic disks, with a diameter-to-height ratio of approximately 0.4, were placed in the gold-plated metal cavity, with a diameter of 50 mm and a height of 30 mm. The permittivities of the ceramic samples were calculated from the TE₀₁₈ resonance frequency using the Itoh–Rudokas model,¹³ and the *Q*-value was determined at the same resonance by analyzing the *S*₁₁ parameter, as proposed by Kajfez and Hwan.¹⁴ For the purpose of determining the temperature coefficient of resonant frequency, we placed the test cavities in the temperature-controlled chamber and the resonant frequency was measured in the temperature range between 20° and 60°C.

III. Results and Discussion

The X-ray diffraction pattern of the reaction mixture after calcination at 600°C (Fig. 1) indicates the presence of the scheelite-type compound BaWO₄ in addition to the reagent powders. After firing at 700°C, the concentration of the BaWO₄ increases, while the majority of the WO₃ appears to be consumed. Firing at 800°C results in the formation of the perovskite Ba $(Zn_{1/2}W_{1/2})O_3$ and Ba₃W₂O₉, while the reagents BaCO₃ and ZnO are still present in the reaction mixture. After 900°C, the concentrations of BaWO₄ and Ba₃W₂O₉ decrease, and after firing at 1000°C the perovskite is, according to the X-ray diffraction data, the only crystalline phase present in the reaction mixture.

An examination of the X-ray patterns shown in Fig. 1 further suggests that the formation of BaWO₄ proceeds with a faster kinetics compared with the formation of the other intermediate phases. Furthermore, it appears that once formed, the BaWO₄ reacts only slowly to form Ba $(Zn_{1/2}W_{1/2})O_3$. Figure 2 shows the X-ray diffraction patterns of the reaction mixture after firing at 1000° and 1100°C, where the mixture was only hand-ground in an agate mortar between the firings instead of being ball-milled,



Fig. 1. (a) The XRD patterns collected from the reaction mixture after calcination at different temperatures between 600° and 1000°C (W–WO₃, BC–BaCO₃, BW–BaWO₄, B₃W₂–Ba₃W₂O₉, BZW–Ba(Zn_{1/2}W_{1/2}O₃), (b) XRD pattern of the single-phase Ba(Zn_{1/2}W_{1/2})O₃ after calcination at 1000°C, indexed according to the face-centered double-perovskite unit cell.



Table I. Atomic Positional, Isotropic Displacement and, Site-Occupation Parameters for Ba(Zn_{1/2}W_{1/2})O₃

	-				,
Atom	x	у	Ζ	<i>B</i> (Å)	Occupation
Ba	0.2500	0.2500	0.2500	0.3	1
Zn1	0.5000	0.5000	0.5000	0.4	0.9877 (21)
W1	0.0000	0.0000	0.0000	0.3	0.98778 (21)
0	0.23806 (29)	0.0000	0.0000	0.9	1
Zn2	0.0000	0.0000	0.0000	0.3	0.0123 (21)
W2	0.5000	0.5000	0.5000	0.3	0.0123 (21)
D	(9/) = 7.517				

 $R_{wp}(\%) = 7.517.$



Fig.2. Part of the XRD pattern from the reaction mixture after calcination at 1000° and 1100°C. The mixture was only hand-ground between the firings (BW-BaWO₄).

as described in the experimental section. In both patterns, the (112) and (004) reflections ($2\theta \sim 26.5$ and 28.0) of the tetragonal scheelite-type BaWO₄ are clearly visible. This means that there should also be BaO- and ZnO-rich phase(s) present in the reaction mixture; however, we could not detect them by X-ray diffraction. The reflections of the ZnO-rich phase are probably lost in the background and the BaO-rich phase could be in the amorphous state, as we will show later. The presence of BaWO₄ in the A(B_{1/2}W_{1/2})O₃ (A = Sr or Ba and B = Zn, Fe, Co, or Ni) was also observed by Fresia *et al.*,¹⁵ who were also, based on our literature survey, the first to synthesize this type of perovskite. They reported that they could not find a way to prevent its formation nor could they remove it from the system. We found, as the X-ray patterns in Fig. 1 indicate, that single-phase $Ba(Zn_{1/2})$ ${}_{2}W_{1/2}O_{3}$ can be prepared in the solid state by applying several calcination steps in the temperature range from 600° to 1000°C with intermediate ball milling (see Section II). This suggests that mechanical activation and an increase in the surface area of the

reacting powders are crucial for removing the scheelite-type BaWO₄ phase from the system. The crystal-structure refinement of the prepared single-phase $Ba(Zn_{1/2}W_{1/2})O_3$ confirmed the *Fm-3m* cubic symmetry, with a lattice parameter a = 8.123 Å, and furthermore, revealed that B-site cations are fully ordered in a 1:1 arrangement. The details are provided in Fig. 3 and Table I.

With the purpose of investigating the high-temperature chemistry of Ba(Zn_{1/2}W_{1/2})O₃, the single-phase powder synthesized was subjected to annealing at temperatures above 1000°C. After 10 h at 1300°C, the X-ray pattern again showed the presence of a scheelite-type BaWO₄ (Fig. 4), which indicated the decomposition of the perovskite matrix. Additional annealing at 1400°C increased the amount of BaWO4 and, in addition, caused the formation of the Ba₂WO₅ phase (Fig. 4). The decomposition of perovskites containing tungsten on the B-site has been observed before. Fuentes *et al.*,¹⁶ for example, found that heating the Ba(Sm_{2/3}W_{1/3})O₃ powder above 1300°C results in the formation of Sm_2O_3 and an unidentified phase, whereas Khalyavin et al. found that Ba(Zn_{1/2}W_{1/2})O₃ decomposes above 1200°C, forming BaWO₄ and at least, one more unidentified phase. It is also known that the decomposition of Zn-containing ordered perovskites can occur as a result of ZnO volatilization.¹⁷⁻¹⁹ We performed several experiments, with the aim to understand the cause and the mechanism of the Ba $(Zn_{1/2}W_{1/2})O_3$'s decomposition. First, we sintered compacted powder samples within a ZnO muffle. The X-ray spectra that resulted from such firings are



Fig. 3. Final Rietveld plot of Ba(Zn_{1/2}W_{1/2})O₃ prepared by solid-state reaction at temperatures up to 1000°C. The blue pattern is observed, the red is calculated, and the gray represents the difference. Blue bars mark the peak positions.





Fig. 4. Part of the XRD pattern collected from the single-phase $Ba(Zn_{1/2}W_{1/2}O_3 \text{ after firing at } 1300^\circ \text{ and } 1400^\circ \text{C} \text{ for } 10 \text{ h} (BW-BaWO_4, B_2W_5-Ba_2WO_5).$

shown in Fig. 5. A comparison of Figs. 4 and 5 reveals that the ZnO muffle suppresses the formation of the $BaWO_4$ and Ba_2WO_5 phases. A microstructural analysis of the sample sintered in the ZnO muffle at 1350°C confirms the absence of Ba–tungstates; however, small ZnO-rich secondary-phase inclusions can be found (Fig. 6).

The sample sintered in the muffle of ZnO at 1350°C was used for further high-temperature experiments. The polished surface of the sample was first exposed to 1350°C in an atmosphere of air for 5 min. As expected, grooves were created at the grain boundaries, which is usually the aim of a thermal-etching process. However, apart from revealing the grain boundaries, the 5-min annealing at 1350°C also resulted in the formation of precipitates, with sizes up to approximately 5 µm, along the grain boundaries (Fig. 7(a)). An X-ray diffraction analysis of the surface combined with semi-quantitative EDS showed that the precipitates are scheelite-type BaWO₄. The sample was then further annealed in the air at the same temperature, and after 10 h, the surface was re-polished and analyzed. The microstructure was now very different, as can be observed from the backscattered electron images shown in Figs. 7(b) and (c). Among the perovskite matrix grains and along the grain boundaries, there are regions that resemble a two-phase eutectic microstructure. The combination of X-ray and EDS analyses indicates that the slightly darker phase within the eutectic-like microstructure corresponds to Ba₂WO₅ and the brighter one corresponds to BaWO₄. Furthermore, the back-scattered electron imaging re-



Fig. 5. Part of the XRD pattern collected from the single-phase $Ba(Zn_{1/2}W_{1/2})O_3$ after firing at 1300° and 1400°C within the ZnO muffle.



Fig. 6. Scanning electron microscope image of the polished surface of the Ba $(Zn_{1/2}W_{1/2})O_3$ ceramic sample sintered at 1350°C in the ZnO muffle (Z–ZnO-rich inclusions).

veals an approximately 30-µm-thick layer of Ba_2WO_5 on the surface of the sample (Fig. 7(d)). Additionally, as is clear from Fig. 8, the TEM analysis revealed the presence of an amorphous BaO-rich phase at the triple points.

These findings imply that the decomposition of the perovskite $Ba(Zn_{1/2}W_{1/2})O_3$, heated in the air, could be connected with the sublimation of ZnO. To verify whether or not the sublimation of ZnO occurs, we performed KEMS. This method is based on a mass-spectrometric identification and quantification of the gaseous species that are in equilibrium with the solid sample within the Knudsen effusion cell (see Section II).

It is known that at elevated temperatures ZnO undergoes a dissociative sublimation according to

$$\operatorname{ZnO}(s) \leftrightarrow \operatorname{Zn}(g) + 1/2\operatorname{O}_2(g)$$
 (3)

The identification of Zn in the gaseous phase therefore serves as an indication of the loss of ZnO from the material. The KEMS analysis, performed in the temperature range between 900° and 1000°C, revealed an equilibrium pressure of Zn(g) over Ba($Zn_{1/2}W_{1/2}$)O₃, which is slightly lower than that over pure ZnO (Fig. 9). Plotting the data presented in Fig. 9 in the logarithmic form allows us to make a linear extrapolation, which yields the following dependency of the equilibrium pressure of Zn on the temperature.

Over pure ZnO... ln
$$p_{Zn/ZnO}$$

= -37 459 × 1/T + 28.07 (Pa) (4)

Over Ba
$$(Zn_{1/2}W_{1/2})O_3 \dots \ln p_{Zn/Ba}(Zn_{1/2}W_{1/2})O_3$$

= -41 980 × 1/T + 30.62 (Pa) (5)

In terms of equilibrium thermodynamics, the sublimation of ZnO can be treated as a partial effect of the perovskite decomposition, which can be expressed by Eq. (1). Therefore, the difference between the partial pressure of Zn over pure ZnO and over the perovskite can be regarded as a consequence of the different ZnO activity. Using basic equilibrium–thermodynamic relations, and keeping in mind that $a_{ZnO} = 1$ for the case of pure ZnO, it follows that

$$a_{\rm ZnO/Ba(Zn_{1/2}W_{1/2})O_3} = \left(\frac{p_{\rm Zn}}{p_{\rm Zn}^*}\right)^{\frac{3}{2}}$$
(6)

where $a_{ZnO/BaZn_{1/2}W_{1/2}O_3}$ is the activity of ZnO in the Ba(Zn_{1/2}W_{1/2}) O₃, and p_{Zn} and p_{Zn}^* are the partial pressures of Zn over pure ZnO and over Ba(Zn_{1/2}W_{1/2})O₃, respectively.

From Eqs. (4)–(6), we can calculate that the activity of the ZnO in the perovskite is 1 for temperatures above 1500°C. This implies that



Fig.7. Scanning electron microscope images of the $Ba(Zn_{1/2}W_{1/2})O_3$ ceramic sample sintered at 1350°C in the ZnO muffle and annealed in air at 1350°C: (a) 5 min and (b)–(d) 10 h (BW–BaWO₄, B₂W₅–Ba₂WO₅).

with respect to the sublimation of ZnO, the perovskite $Ba(Zn_{1/2}$ $W_{1/2}O_3$ behaves as pure ZnO at temperatures above 1500°C.

It follows from Eqs. (4) and (5) that at 1350°C the equilibrium partial pressure of Zn over pure ZnO is $p_{Zn/ZnO} \sim 147$ Pa and



Fig. 8. Bright-field transmission electron microscope image of the triple point within the $Ba(Zn_{1/2}W_{1/2})O_3$ ceramic sample sintered at 1350°C in the ZnO muffle and annealed in air at 1350°C for 10 h (B–BaO-rich amorphous phase).

that over perovskite Ba(Zn_{1/2}W_{1/2})O₃, it is $p_{Zn/Ba(Zn_{1/2}W_{1/2})O_3} \sim 116$ Pa. It should, however, be noted that the KEMS experiment was conducted in vacuum, where the partial pressure of oxygen is negligible. For the case of exposing the perovskite to elevated temperatures in an atmosphere of air, p_{Zn} can be calculated from equilibrium–thermodynamic relations:

$$K_{\rm d} = \frac{a_{\rm Zn} a_{\rm O_2}^{1/2}}{a_{\rm ZnO}} \Rightarrow a_{\rm Zn} = \frac{K_{\rm d} a_{\rm ZnO}}{a_{\rm O}^{1/2}} \Rightarrow p_{\rm Zn} = \frac{K_{\rm d} a_{\rm ZnO}}{p_{\rm O}^{1/2}}$$
(7)

where K_d is the dissociation constant for the reaction described by Eq. (1), and a_{Zn} , a_{O_2} and a_{ZnO} are the activities of Zn(g),



Fig. 9. Vapor pressure of Zn over pure ZnO and over the perovskite $Ba(Zn_{1/2}W_{1/2})O_3$. (A, vapor pressure over pure ZnO, calculated from data obtained from the IVTANTHERMO database; B, measured vapor pressure over perovskite $Ba(Zn_{1/2}W_{1/2})O_3$; C, extrapolated curve).

Table II. The Dissociation Constant (K_d) for the Reaction Described by Eq. (1) Obtained from the IVTANTHERMO Database²⁰

<i>T</i> (°C)	K _d	$\alpha_{ZnO/Ba(Zn_{1/2}W_{1/2})O_3}$	<i>p</i> _{Zn in air} (Pa)
1200	9.16×10^{-7}	0.46	0.10
1250	3.21×10^{-6}	0.53	0.37
1300	1.29×10^{-5}	0.61	1.72
1350	3.09×10^{-5}	0.70	4.72
1400	1.05×10^{-4}	0.79	18.1

The activity of ZnO in the perovskite $Ba(Zn_{1/2}W_{1/2})O_3 (a_{ZnO/Ba(Zn_{1/2}W_{1/2})O_3})$ was calculated using Eq. (4); and the partial pressure of Zn in air was calculated using Eq. (5) for different temperatures.

 $O_2(g)$, and ZnO(s), respectively, p_{O2} is the partial pressure of oxygen. The dissociation constant can be found in the IV-TANTHERMO database,²⁰ whereas the activity of ZnO(s) for the case of Ba($Zn_{1/2}W_{1/2})O_3$ can be calculated using Eq. (5) and the data obtained with the KEMS experiment. The results of such calculations performed for the different temperatures are shown in Table II.

These findings confirm the loss of ZnO during the thermal processing of $Ba(Zn_{1/2}W_{1/2})O_3$, which results in the decomposition of the perovskite phase.

The sublimation of ZnO is a well-known problem that interferes with the processing of ceramics based on Zn-containing ordered perovskites. Apart from causing the formation of secondary phases, the loss of ZnO also affects the sintering kinetics.1 In the case of 1:2 ordered perovskites, such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$, the loss of ZnO causes a B-site deficiency and ultimately results in the formation of hexagonal perovskite phases, such as an eight-layered $Ba_8ZnTa_6O_{24}{}^{18,21}$ and a five-layered $Ba_5Nb_4O_{15}{}^{6,22}$ The crystal structure of these phases can be understood as a polytypic B-site-deficient hexagonal perovskite with B-site vacancies ordered between two hexagonally stacked BaO₃ layers. Such an arrangement results in the so-called shifted perovskite structures.²³ It can be argued that the formation of such structures upon the sublimation of ZnO is a result of the ordering of the B-site vacancies that are formed due to the loss of Zn.

The described experimental results indicate that in the case of $Ba(Zn_{1/2}W_{1/2})O_3$, however, the loss of ZnO results in a different decomposition of the perovskite phase. It appears that the decomposition starts with the formation of the scheelite-type $BaWO_4$, which is accompanied by the formation of a BaO-rich amorphous phase that segregates at the triple points of the matrix.

Any further loss of ZnO is accompanied by the formation of Ba_2WO_5 , as can be seen from the X-ray spectra shown in Fig. 4. As Ba_2WO_5 is a stable compound at $1350^{\circ}C$,²⁴ the $BaWO_4$ and the amorphous BaO-rich phase must be transient phases that form for kinetic reasons. We suggest that the following sequences of chemical reactions occur during the decomposition of $Ba(Zn_{1/2}W_{1/2})O_3$:

$$2\operatorname{Ba}(\operatorname{Zn}_{1/2}W_{1/2})\operatorname{O}_3 \to \operatorname{BaWO}_4 + \operatorname{BaO}\ (am) + \operatorname{Zn}(g) + 1/2\operatorname{O}_2(g) \quad (8)$$

$$BaWO_4 + BaO (am) \rightarrow Ba_2WO_5$$
(9)

where BaO (am) refers to the BaO-rich amorphous phase.

From the experiments performed, we cannot conclude whether an additional decomposition reaction in parallel with Eq. (8), which leads directly to Ba₂WO₅, occurs

$$2\text{Ba}(\text{Zn}_{1/2}\text{W}_{1/2})\text{O}_3 \rightarrow \text{Ba}_2\text{WO}_5 + \text{Zn}(g) + 1/2\text{O}_2(g)$$
 (10)

In any case, both $BaWO_4$ and Ba_2WO_5 are present in the system during the decomposition of $Ba(Zn_{1/2}W_{1/2})O_3$, which results in the formation of a liquid phase at temperatures above

Table III. Dielectric Constant (ϵ_r), Quality Factor ($Q \times f$), and Temperature Coefficient of Resonant Frequency (τ_f) of Ba(Zn_{1/2}W_{1/2})O₃-Based Ceramics Sintered at 1350°C

$T_{\rm s} = 1350^{\circ}{\rm C}$	ε _r	$Q \times f$ (GHz)	$\tau_f (ppm/K)$
Air—2 h	26	65000	-34
Air—6 h	27	22 000	-34
ZnO muffle—2 h	28	30 000	-36

 1320° C.²⁴ In the case of ceramics, such a liquid phase can be found along the grain boundaries and between the decomposing perovskite grains (Figs. 7(b) and (c)).

The loss of ZnO, thus, causes a deterioration of the microstructure, which progresses with an increase in the retention time at elevated temperatures. Consequently, the dielectric properties of the Ba($Zn_{1/2}W_{1/2}$)O₃-based ceramics strongly depend on the sintering time, as can be seen from Table III.

The measured microwave dielectric properties, shown in Table III, imply that the dielectric losses of the $Ba(Zn_{1/2}W_{1/2})O_3$ perovskite ceramics increase with an increase in the sintering time, which can be attributed to the decomposition of the perovskite matrix that occurs due to the loss of ZnO. Furthermore, it can be seen from Table III that the use of the ZnO muffle during sintering, which suppresses the sublimation of ZnO, adversely affects the *Q*-value of the ceramics. This can be explained by the presence of low-*Q* ZnO-rich inclusions in the microstructure of the ceramics that form during the sintering in a Zn-rich atmosphere (Fig. 6).

From this, we can conclude that the inconsistencies regarding the *Q*-value of $Ba(Zn_{1/2}W_{1/2})O_3$ -based ceramics found in the literature are due to different levels of decomposition of the perovskite matrix.

IV. Conclusions

A double-perovskite $Ba(Zn_{1/2}W_{1/2})O_3$ with face-centered-cubic *Fm-3m* symmetry can be synthesized in the solid state at temperatures below 1000°C, the 1:1 B-site cation order is established during the formation of the perovskite phase without any additional high-temperature annealing. The sublimation of ZnO, which becomes appreciable at temperatures above 1200°C, however, causes the decomposition of the perovskite phase. During the decomposition, the BaWO₄ and Ba₂WO₅ binary phases are formed, which results in the formation of a liquid phase at temperatures above 1320°C. In the case of ceramics, such a liquid phase deteriorates the microstructure and increases the dielectric losses. Control of the processing temperature and time is therefore of crucial importance for obtaining high-*Q* microwave dielectrics based on the perovskite Ba(Zn_{1/2}W_{1/2})O₃.

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