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$Ba_8ZnTa_6O_{24}$: A New High *Q* Dielectric Perovskite

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The hexagonal perovskite, $Ba_8ZnTa_6O_{24}$, was prepared in single-phase form and was found to be a stable secondary phase, formed as a result of the loss of ZnO from $Ba(Zn_{1/3}Ta_{2/3})O_3$ microwave dielectrics. The experimental and calculated X-ray patterns of $Ba_8ZnTa_6O_{24}$ indicate it is isostructural with $Ba_8Ta_6NiO_{24}$ with an 8H $(cchc)_2$ close-packed BaO_3 stacking sequence and the lattice parameters, $a = 10.0825(14)$, $c = 19.0587(38)$Å. High-density ceramics of $Ba_8ZnTa_6O_{24}$ could be prepared at temperatures considerably lower (1400°C) than those used to sinter pure $Ba(Zn_{1/3}Ta_{2/3})O_3$, and exhibit very good microwave dielectric properties with $\varepsilon = 30.5$, $Q_f = 62\,300$, and $\tau_f = +36$ ppm/°C at 8.9 GHz.

I. Introduction

CERAMIC dielectric resonators based on the complex perovskite $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) have been extensively studied due to their exceptionally high-quality factors in the microwave region. Since the first report of their outstanding dielectric performance, many investigations have been conducted on the effect of different processing schemes and chemical additives on the crystal chemistry, microstructure, and properties of BZT-based ceramics.[1–9] Through this work, it has become clear that the microwave properties respond to alterations in the chemical ordering of Zn and Ta, and to the volatilization of ZnO during the high-temperature calcination and sintering treatments. While the effect of changes in temperature and bulk chemistry on the cation order are now relatively well understood, there is still considerable disagreement on the nature and role of the impurity phases formed as a result of the volatilization of ZnO. This communication reports the synthesis, structure, and dielectric properties of the hexagonal perovskite $Ba_8ZnTa_6O_{24}$, which is shown to be a stable secondary phase in Zn-deficient samples of BZT. It is also shown that ceramic samples of $Ba_8ZnTa_6O_{24}$ can be sintered to high density at temperatures and times considerably lower than BZT and exhibit excellent *Q* factors.

It is widely accepted that the chemical ordering of Zn and Ta and the volatilization of ZnO are critical in mediating the dielectric properties of BZT ceramics. Although there is general agreement on how the chemical order responds to different thermal treatments and chemical substituents, there is still considerable debate on how the loss of ZnO affects the phase stability and properties of BZT ceramics. Since the first report on the observation of ZnO-deficient surface phases during sintering,[3] several investigations have reported that the processing of BZT-based systems at high temperature is accompanied by the formation of secondary phases.[7–9] For example, a variety of different phases along the $BaO–Ta_2O_5$ binary (e.g., $BaTa_2O_6$, $Ba_5Ta_4O_{15}$, and $Ba_3Ta_2O_8$) have been reported to form as a result of the loss of ZnO.[7–9] Unambiguous identification of the impurity phases is complicated by their relatively low-volume fractions, and the close proximity of some of their diffraction peaks to those of the major BZT phase. In each of the references cited above the strongest peaks associated with the secondary phases lie in the region of $2\theta = \sim 29°–32°$; it is in this region that BZT has its strongest diffraction peak. The similarity in the diffraction patterns of some of the impurities and BZT arises from the close crystal chemical relationship between their structures. For example, $BaTa_2O_6$, which exists as more than one polymorph, has a tungsten bronze-type structure, and $Ba_5Ta_4O_{15}$ is comprised of blocks of cubic-stacked BaO_3 perovskite-type layers separated by single BaO_3 layers in hexagonal packing ("ccchh" packing).

In contrast to the large number of reports citing different possible impurities along the $BaO–Ta_2O_5$ binary section, Zn-deficient ternary phases in the $BaO–ZnO–Ta_2O_5$ system have received very little attention. One ternary phase, $Ba_8ZnTa_6O_{24}$, was mentioned by Tolmer and Desgardin[8] in a study of the effect of different raw materials, temperature, and atmosphere on the phase stability, ZnO loss, and dielectric properties of BZT. However, in that work, the formation of $Ba_8ZnTa_6O_{24}$ during the loss of ZnO from BZT was rejected in favor of the formation of $BaTa_2O_6$. The only other discussion of $Ba_8ZnTa_6O_{24}$ has come recently from the groups of Hill (Transtech Inc.) and Ibberson (University of Liverpool), who first mentioned its formation during the course of our own studies (M. Hill, R.M. Ibberson, personal communications, 2002).

Although $Ba_8ZnTa_6O_{24}$ has been mentioned in the literature, it has not been prepared in bulk form, and its structure and microwave dielectric properties have not been examined. The previous identification[8] of this phase suggested that it is isotypic with the eight-layered hexagonal perovskite, $Ba_4LiTa_3O_{12}$ ($Ba_8Li_2Ta_6O_{24}$).[10] A closely related nickel-containing perovskite, $Ba_8NiTa_6O_{24}$, has also been reported in the literature.[11] Structure refinement of that compound revealed an 8H $(cchc)_2$ close-packed sequence of BaO_3 layers identical to that of $Ba_4LiTa_3O_{12}$; however, an ordered arrangement of Ta, Ni, and vacancies in the pairs of face-shared octahedra results in a different cell repeat ($a_{Ni} = a_{Li}\sqrt{3}$) in the (0001) basal plane. In this paper, we report the formation of single-phase samples of $Ba_8ZnTa_6O_{24}$. The diffraction patterns of this compound were found to be consistent with the impurity peaks observed in previously published patterns of Zn-deficient BZT, and support a structure identical to that of its nickel counterpart, $Ba_8NiTa_6O_{24}$. The sintering characteristics and microwave dielectric properties are also investigated, and the phase is shown to have a high *Q* value.

II. Experimental Procedure

Samples of $Ba_8ZnTa_6O_{24}$ were prepared by standard solid-state techniques using dried powders of $BaCO_3$ (99.9%, Cerac, Inc., Milwaukee, WI), ZnO (99.995%, Cerac), and Ta_2O_5 (99.99%, Cerac). After weighing and mixing, the samples were ball milled in ethanol. The dried powders were calcined at 1000°C for about 16 h to remove CO_2 and ball milled again. Uniaxially pressed (4 MPa) pellets of the ball-milled powder were heated to 1350°C

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for about 24 h with intermediate grinding. After checking for phase purity using X-ray diffraction, the finely ground powders were isostatically pressed at 550 MPa and sintered at 1400°C for 1 h. For the two-stage sintering methods, the semi-sintered pellets were crushed, lightly ground under acetone, re-pressed at 550 MPa, and re-sintered at 1400°C for 0.5–1 h.

X-ray diffraction patterns were collected using Cu$K\alpha$ radiation generated at 45 kV and 30 mA (Model DMAX-B diffractometer, Rigaku Co., Tokyo, Japan). Lattice parameters were calculated by least-squares refinement of powder X-ray diffraction data collected using silicon powder as an internal standard. Polished and thermally etched sintered pellets were examined using a scanning electron microscope (Model 6300FV, JEOL, Tokyo, Japan). The relative permittivity (ε_r) and dielectric loss tangent (tan δ) were measured in the 100 Hz to 1 MHz frequency range from −100° to 100°C using the parallel plate method (Model HP 4284A Precision LCR Meter, Hewlett-Packard, Palo Alto, CA) in an environmental chamber (Model 9920, Delta Design, San Diego, CA). The temperature coefficient of the relative capacitance (τ_c) was calculated from −20° to 80°C by linear fits of the capacitance data. Microwave measurements were performed using standard cavity transmission methods using a network analyzer (Model 8720 ES, Agilent Technologies, Palo Alto, CA). The temperature coefficient of resonant frequency (τ_f) was determined in the temperature range 25°–75°C by inserting the test cavities into a temperature-controlled chamber.

III. Results and Discussion

An X-ray diffraction pattern collected from a single-phase sample of $Ba_8ZnTa_6O_{24}$ is shown in Fig. 1. This sample was obtained by heating the powders at 1350°C for 24 h (with an intermediate ball mill) after a pre-calcine at 1000°C for 16 h. All of the peaks in the pattern can be indexed using a hexagonal cell with $a = 10.0825(14)$, $c = 19.0587(38)$ Å. The X-ray pattern of $Ba_8ZnTa_6O_{24}$ is very similar to that of the corresponding Ni compound, $Ba_8NiTa_6O_{24}$, which has a hexagonal perovskite structure (space group $P6_3cm$) based on an 8H $(cchc)_2$ close-packed arrangement of BaO_3 layers.[11] The introduction of the hexagonal layer interrupts the usual network of corner-shared octahedra that characterize a cubic perovskite through the formation of a single layer with face sharing; see Fig. 2(a). The previous structure refinements of the $Ba_8Ta_6NiO_{24}$ structure revealed the existence of two different pairs of face-shared octahedra. In one face-shared pair, the octahedra are occupied by Ta and a vacancy, respectively; in the second, one octahedron is partially occupied (85%) by Ta, with the other containing 75% Ni, 15% Ta, and 10% vacancies.[11] The ordering of these two pairs is shown in Fig. 2(b). The atomic positions and site occupancies for $Ba_8NiTa_6O_{24}$ were used to simulate the X-ray pattern of $Ba_8ZnTa_6O_{24}$, which was found to give excellent agreement with the experimental data. A comparison of the calculated and experimental powder patterns is shown in Fig. 1. The diffraction pattern of $Ba_8ZnTa_6O_{24}$ also gives an excellent match to the impurity peaks observed in previously published patterns of the ZnO-deficient surface of BZT (e.g., in Fig. 6, in Desu and O'Bryan,[3] and Fig. 4 in Webb *et al.*[9]) and it is likely that this phase, rather than the proposed binary Ba–Ta–O phases, was formed in those investigations.

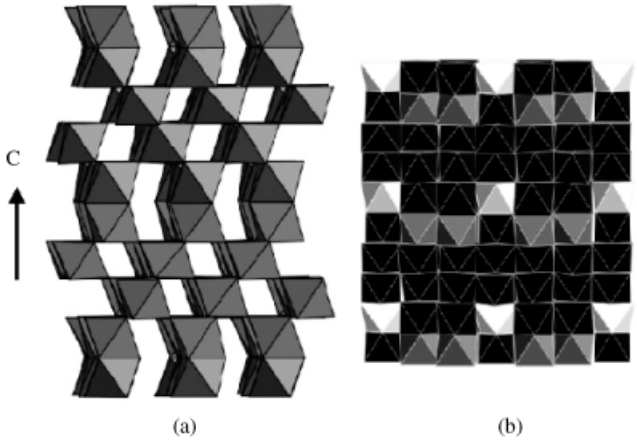

Fig. 2. Structure models of $Ba_8ZnTa_6O_{24}$ (after Abakumov *et al.*[11]) projected along: (a) [110] to highlight the corner and face-shared octahedra and (b) [110] to highlight the ordering of Ta, Ni, and vacancies in the face-shared octahedra (Ta = black, vacancy = white, Zn-rich = gray). In both the figures, Ba atoms are omitted for clarity.

In the initial stages of the synthesis of $Ba_8ZnTa_6O_{24}$, the first formed phase assemblage consists of a metastable mixture of BZT and $Ba_5Ta_4O_{15}$, and after the first calcine at 1350°C, only minimal amounts of $Ba_8ZnTa_6O_{24}$ are observed. It was noted that once the $Ba_8ZnTa_6O_{24}$ phase begins to form during the 1350°C heat treatment, the pellets showed significant shrinkage, suggesting it might have a fairly low sintering temperature. The densification of pure $Ba_8ZnTa_6O_{24}$ was investigated first on isostatically pressed pellets heated to 1400°C. At this temperature, the initial densification was quite rapid; however, the final densities (after ~12 h) were only ~85% of their theoretical value.

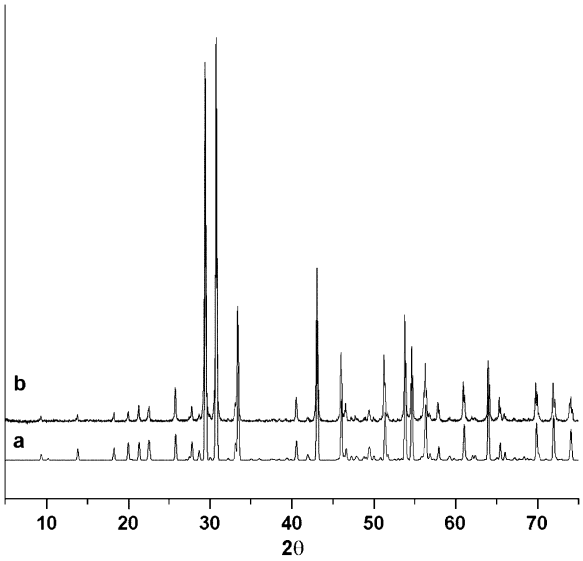

Fig. 1. Powder X-ray diffraction pattern of $Ba_8ZnTa_6O_{24}$: lower scan (a) calculated using positions reported for $Ba_8NiTa_6O_{24}$[11] and upper scan (b) experimental pattern.

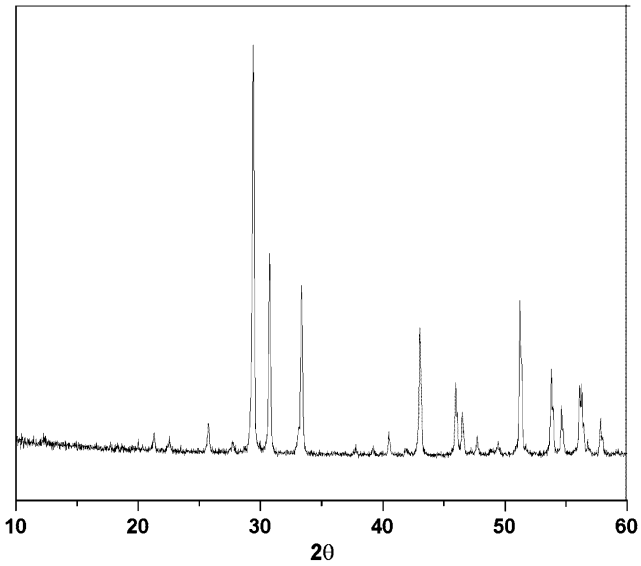

Fig. 3. Powder X-ray diffraction pattern collected from the surface of a polished pellet of $Ba_8ZnTa_6O_{24}$.

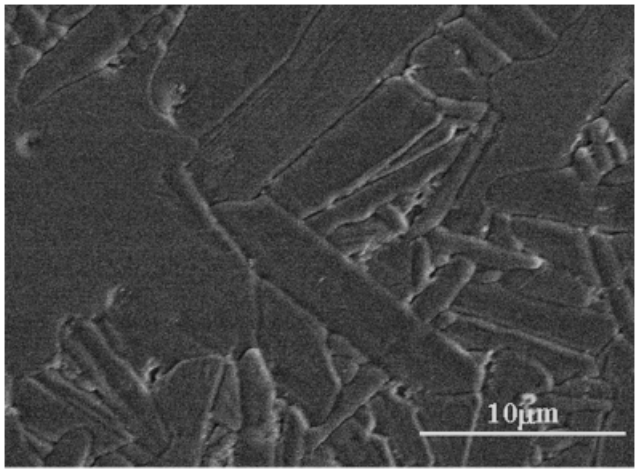

Fig. 4. SEM micrograph of $Ba_8ZnTa_6O_{24}$ after the two-stage sintering process.

Surprisingly, no significant improvement in the density was observed in pellets sintered at higher temperatures (up to 1500°C). The poor densities did not seem to be associated with any loss of ZnO (as gauged by measurement of the mass of the pellets) or with the formation of additional impurity phases, and the X-ray pattern of the polished pellet surface (Fig. 3) was similar to that collected from the single-phase powder. However, some differences were noted in the relative intensities of some of the reflections from the pellet surface; in particular, those associated with (h00) showed significant reductions in intensity, consistent with some degree of preferential crystallographic orientation in the sintered compacts. SEM micrographs of the pellet surface also revealed a large degree of dispersion in the grain size.

To overcome the limited densification, which is most likely associated with the preferential orientation and exaggerated growth of the hexagonal platelets with a (001) orientation, a two-stage sintering technique was utilized. In this method, the low-density-sintered compacts were powdered and lightly ground by hand, re-compacted, isostatically pressed, and reheated to the original sintering temperature for 1/2–1 h. Using this method, densities $\geq 94\%$ theoretical were routinely obtained. The microstructure of the ceramics after the two-stage sintering is shown in Fig. 4. The surface exhibits minimal porosity and is comprised of "bar" and platelet-shaped grains, with sizes up to ~ 10 μm.

Dielectric measurements were made on the dense, single-phase pellets obtained from the two-stage sintering method. Measurements at low frequency yielded a dielectric constant of 30.3 at 1 MHz and 25°C; when corrected for the density of the pellets (94% of theoretical), this yields $\varepsilon = 32.2$. The capacitance exhibited a small linear decrease with temperature over the range investigated ($-100°$ to $+100°$C), and the temperature coefficient of the capacitance was calculated to be -75 ppm/°C. At this frequency, the losses were too low to be determined reliably. Measurements at microwave frequencies showed a strong and very narrow resonance peak consistent with a very high Q value. At 8.874 GHz, the measured Q was 7025, yielding a Q_f of 62 300. The value of the dielectric constant ($\varepsilon = 30.51$) at this frequency was in good agreement with the lower frequency data. The temperature coefficient of resonant frequency, measured from 20° to 75°C, was $+36$ ppm/°C. The very good Q values and excellent sintering properties of $Ba_8ZnTa_6O_{24}$ suggest that it could have useful applications; however, solid solution or second-phase additives will need to be identified to reduce the temperature coefficient to an acceptable value.

Experiments were also conducted on sintered composites of $Ba_8ZnTa_6O_{24}$ and BZT to investigate their phase compatibility at high temperature. The absence of any new phases in the resultant XRD patterns demonstrated that these two phases form stable two-phase mixtures. These experiments also indicated that the addition of $Ba_8ZnTa_6O_{24}$ might be beneficial in lowering the sintering temperature of BZT. The sintering characteristics of these composite systems, and the dielectric properties of other compounds with this eight-layer hexagonal perovskite structure, will be the subject of a future publication.

IV. Conclusions

Single-phase samples of $Ba_8ZnTa_6O_{24}$ were prepared and found to be isostructural with $Ba_8Ta_6NiO_{24}$, a structure based on an $8H(cchc)_2$ close-packed arrangement of BaO_3 layers. The X-ray pattern of $Ba_8ZnTa_6O_{24}$, which can be indexed with $a = 10.0825(14)$ and $c = 19.0587(38)$, gives an excellent fit with the impurity phases previously reported to form on the surface of Zn-deficient samples of $Ba(Zn_{1/3}Ta_{2/3})O_3$. The phase compatibility of $Ba_8ZnTa_6O_{24}$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ was confirmed through high-temperature annealing. Dense ceramic samples of $Ba_8ZnTa_6O_{24}$, formed at 1400°C via a two-stage sintering process, have excellent microwave dielectric properties with $\varepsilon = 30.5$, and $Q_f = 62\,300$ at 8.9 GHz; however, additives will be needed to lower the temperature coefficient $\tau_f = +36$ ppm/°C.

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