Disorder-Assisted Atypical Temperature-Dependent Dielectric Behavior of $A_6B_2O_{17}$ ($A = Zr$, Hf; $B = Nb, Ta$) Phases

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Abstract: We report on temperature-dependent dielectric behavior of disordered ternary $A_6B_2O_{17}$ ($A = Zr$, Hf; $B = Nb, Ta$)-form oxides as assessed through modified temperature resonant post Hakki-Coleman measurements. Permittivity measurements through this approach generally agree with dielectric measurements of $A_6B_2O_{17}$ bulk ceramics and thin films measured through a standard Hakki-Coleman technique. Coefficients for the temperature dependence of permittivity for ternary $A_6B_2O_{17}$ phases are strongly positive, suggesting contributions to polarizability arising from long-range mechanisms associated with structural disorder. These observations support the working theory of material functionality deriving from entropy embodied as chemical diversity and structural disorder in $A_6B_2O_{17}$ phases.

1. Introduction

The $A_6B_2O_{17}$ ($A = Zr$, Hf; $B = Nb, Ta$) phases have captured the ceramics community’s interest due to their complex structure which tolerates substantial atomic disorder and chemical diversity (Figure 1) [1–4]. Foundational reports [2–4] demonstrate the entropic contribution to structural stability and pave the way for novel property studies. While substantial attention is fixed on $A_6B_2O_{17}$ high-temperature thermal and chemical transport and mechanical properties [5–7], new reports highlight opportunities for these phases as electronic materials [8,9]. Microwave frequency dielectric properties suggest promise for electroceramic applications, but characterization has hitherto been limited to room temperature performance.
As discussed by Harrop [10], materials tend to exhibit temperature-dependent permittivity behavior underpinned by fundamental differences in structure and bonding. Therefore, permittivity temperature coefficient measurements form a phenomenological basis for classifying materials. Comparisons between materials with dissimilar dielectric behavior will highlight any unique property effects derived from chemistry and structure. The recent focus on entropic contributions to material structure and performance gives heightened importance to fundamental property studies for disordered systems [11–13]. Characterizing the temperature-dependence of permittivity in $A_6B_2O_{17}$ represents an important opportunity for entropy-assisted electroceramics engineering. We report on temperature-dependent bulk dielectric properties of ternary $A_6B_2O_{17}$ phases and contextualize their performance relative to similar crystalline ionic inorganics; we discuss connections between structural disorder and dielectric properties.

2. Experimental Methods

Bulk ceramics are synthesized via solid state reactive sintering as described in the literature [4]. Briefly, stoichiometric amounts of as-received oxide powders (ZrO$_2$, TOSOH, 99.87%; Nb$_2$O$_5$, Sigma Aldrich, 99.99%; Ta$_2$O$_5$, Sigma Aldrich, 99.5%) are ball milled in methanol (Fisher Scientific, Grade: Certified ACS Reagent) using yttrium-stabilized zirconia media for 30 hours, followed by air drying at 100 °C to drive off methanol for at least 2 hours. Powders are compacted via uniaxial pressing in a 0.5-inch steel die to form ~1g green bodies and are subsequently sintered in air at 1500 °C for 12 hours. Reacted pellets are examined with X-ray diffraction (Panalytical Empyrean, Bragg-Brentano geometry, Cu kα λ = 1.54 Å) to
confirm $A_6B_2O_{17}$ phase formation. Approximate density measurements are made using calipers to confirm small volume fraction porosity for reliable dielectric measurements.

Permittivity and dielectric loss were characterized for a ceramic, cylindrical resonator using the TE$_{011}$ mode whereas the temperature coefficient of permittivity was determined from a resonant post inside of a cavity using the similar TE$_{018}$ mode. For the temperature-dependent measurements, samples are individually placed on a Styrofoam substrate inside a silver-painted fused silica cylindrical cavity to prevent thermal expansion. A metallic plate screwed into the sample cavity provides boundary conditions for measuring the TE$_{018}$ mode. The sample cavity is connected via coaxial cables to a vector network analyzer which records sample resonant peaks at the TE$_{018}$ mode from which permittivity is calculated (see Supplementary Materials). The sample cavity sits on a hot plate which is adjusted for elevated temperature measurements at 50 °C, 75 °C, and 100 °C. An additional (empty) sample cavity is situated on the hot plate adjacent to the active sample cavity; this empty cavity is connected to an isolated thermocouple which provides accurate temperature monitoring. A schematic of this setup is available in the Supplementary Materials.

3. Results and Discussion

X-ray diffraction results (Figure 2) confirm near-complete reactions in $A_6B_2O_{17}$ ternary ceramics under the given thermal budget, similar to other literature reports [4]. Except Hf$_6$Ta$_2$O$_{17}$, all pellets are dense (> 95% $\rho_{\text{Theoretical}}$) with a minimal anticipated contribution to permittivity from porosity; Hf$_6$Ta$_2$O$_{17}$ has proven difficult to densify under these sintering conditions, though other reports observe densification at higher temperatures [6]. We report the electrical results for under-dense Hf$_6$Ta$_2$O$_{17}$ and note a similar phenomenological behavior as the companion phases but lower measured permittivity due to large contributions from porosity.

Figure 3 shows permittivity measurements and resonant frequencies as a function of temperature for each ternary $A_6B_2O_{17}$ permutation. Overall, permittivity values are similar to measurements for Zr$_6$Nb$_2$O$_{17}$ and Zr$_6$Ta$_2$O$_{17}$ using a standard Hakki-Coleman approach [9].
Measured permittivities are strongly linear with temperature across the tested range. Based on prior classifications by Harrop [10] and $A_6B_2O_{17}$ room-temperature dielectric properties [9] as measured through a Hakki-Coleman approach [14], we anticipate a large negative temperature coefficient of permittivity (approximately -500) typical of an ionic paraelectric. Surprisingly, we observe a strongly positive temperature coefficient for each ternary $A_6B_2O_{17}$ permutation (Table 1).

To contextualize and validate these results, we measured temperature coefficients for similar known oxides including TiO$_2$ and CaTiO$_3$. We select these materials as comparison metrics because they are high-$k$ dielectrics with similar ionic bonding character to $A_6B_2O_{17}$ (see Supplementary Materials). As ionic paraelectrics, they should have large negative temperature

**Figure 3.** Dielectric permittivity and resonant frequency measurements for $A_6B_2O_{17}$ samples as a function of temperature.
coefficients, similar to (albeit larger than) expected values for the \( A_6B_2O_{17} \) phases. Additionally, measurements for ordered structures like TiO\(_2\) and CaTiO\(_3\) could highlight dielectric anomalies associated with a disordered structure as in \( A_6B_2O_{17} \). TiO\(_2\) and CaTiO\(_3\) measurements (Table 1) are generally consistent with literature reports for each oxide and fall within expected ranges for paraelectrics based on Harrop’s classifications [10]. While TiO\(_2\) and CaTiO\(_3\) possess large relative permittivities and similar ionic bonding character to \( A_6B_2O_{17} \) (see Supplementary Materials), both exhibit large negative temperature coefficients typical of ionic paraelectrics; this data contrasts with \( A_6B_2O_{17} \) results.

Both Harrop’s report [10] and Bosman and Havinga’s study on cubic ionic compounds [15] show that most conventional solid-state high-\( k \) materials should exhibit a negative temperature coefficient of permittivity (Figure 4). The large positive temperature coefficients exhibited by \( A_6B_2O_{17} \) phases are therefore uncharacteristic of high-\( k \) ionic inorganics. This dissimilarity is underscored by contrasting results for \( A_6B_2O_{17} \) and both TiO\(_2\) and CaTiO\(_3\). The unique \( A_6B_2O_{17} \) response must arise from an intrinsic polarization mechanism associated with the chemistry and structure. Isolating the precise mechanism driving this behavior in \( A_6B_2O_{17} \) is challenging, not least because it likely derives from structural factors which are not relevant in materials examined by prior reports [10,15]. However, comparisons between ordered and disordered structures

<table>
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<th>Slope of ( \epsilon_r ) vs ( T ) [1/°C]</th>
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<th>TC( \epsilon_r ) [ppm/°C]</th>
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</tr>
<tr>
<td>CaTiO(_3) (perovskite)</td>
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<td>-1446</td>
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</table>

Table 1. Dielectric permittivity and temperature coefficient measurements for each \( A_6B_2O_{17} \) permutation as well as crystalline inorganic reference samples.

Figure 4. Reproduction of the temperature coefficient plot by Harrop [10] with \( A_6B_2O_{17} \) superimposed. \( A_6B_2O_{17} \) phases exhibit temperature-dependent dielectric behavior which is atypical of ionic inorganics in this regime.
give us a basis for assessing unique property behaviors in $A_6B_2O_{17}$. We propose that the disordered $A_6B_2O_{17}$ structure gives rise to long-range polarization mechanisms which change the temperature-dependent dielectric response. However, regardless of the exact mechanism at play, these results demonstrate that the unique characteristics of $A_6B_2O_{17}$ phases are not relegated simply to structure. As highlighted by Harrop [10], materials that exhibit anomalous temperature-dependent permittivity often display other unique, frequently nonlinear, electronic properties. This opens the door to electronic property exploration in $A_6B_2O_{17}$ phases and other novel oxides with a focus on disorder-assisted materials design for new functional electroceramics.

4. Conclusions

We report a strong positive temperature dependence of dielectric permittivity in $A_6B_2O_{17}$ ($A = Zr, Hf; B = Nb, Ta$) disordered oxides. This anomalous behavior contrasts with similar ionic inorganics such as TiO$_2$ and CaTiO$_3$, which adopt strongly negative temperature coefficients. This suggests long-range mechanistic contributions to polarizability likely associated with the $A_6B_2O_{17}$ disordered structure. $A_6B_2O_{17}$ show increasing promise for electroceramics applications and merit continued investigation.

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