Dielectric Relaxation and Magnetic Structure of A-Site-Ordered Perovskite Oxide Semiconductor CaCu₃Fe₂Ta₂O₁₂

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ABSTRACT: A new perovskite oxide semiconductor, CaCu₃Fe₂Ta₂O₁₂, was synthesized through a high-pressure and high-temperature approach. The compound possesses an Im̅₃ space group, where it crystallizes to an A-site-ordered but B-site partial ordered quadruple perovskite structure. Spin ordering occurs around 150 K owing to the antiferromagnetic coupling between Fe³⁺ spins and ferromagnetic coupling between Cu²⁺ spins. The room-temperature dielectric permittivity of CaCu₃Fe₂Ta₂O₁₂ was measured to be approximately 2500 at 1 kHz. More importantly, isothermal frequency-dielectric spectroscopy demonstrates the existence of two dielectric relaxations. Debye-like relaxation is attributed to charge carriers trapped among the oxygen vacancies at low temperatures and Maxwell−Wagner polarization relaxation at high temperatures. CaCu₃Fe₂Ta₂O₁₂ is a new magnetic semiconductor, where A-site ordering is intercorrelated with second-order Jahn−Teller distortion. These findings offer opportunities to design novel perovskite oxides with attractive magnetic and dielectric properties.

INTRODUCTION

Oxides with perovskite or perovskite-related structures are extensively investigated due to the interesting physical properties. Perovskite oxides have the general formula ABO₃, where A site and B site are generally occupied by relatively large-size cations and transition-metal ions, respectively. The structure of ABO₃ consists of the corner-sharing BO₆ octahedral framework where A cations occupy the 12-fold coordinated octahedral interstice. By appropriate substitution for the A site, not only the ordered superstructures are generally stabilized, but also the ordered arrangements of the A cations offer possibilities to design compounds with novel physical properties.

Interesting examples include the A-site-ordered perovskite oxides AA′₃B₄O₁₂, where A = alkali, alkaline earth, lanthanide ions; A′ = Cu, Mn; B = Ti, Fe, Cr, Ru, Mn, Co. This family of compounds with the perovskite structures presents a particular ordering between the A cations and A′ cations. In particular, the Jahn−Teller Cu²⁺ cation could favor the square-planar site, which rationalizes the unusual modification of ACu₃B₄O₁₂ perovskites. A great deal of interesting and unexpected properties has been found for these perovskites, such as giant magnetoresistance in low magnetic fields of CaCu₃Mn₄O₁₂, ferromagnetism of CaCu₃Ge₄O₁₂ and CaCu₃Sn₄O₁₂, heavy-fermion-like behavior of CaCu₃Ru₄O₁₂, and charge disproportionation of CaCu₃Fe₄O₁₂. Meanwhile, CaCu₃Ti₂O₁₂ (CCTO) has received considerable attention, owing to quite high dielectric permittivity (ε’ > 10,000) with very low temperature dependence (above 100 K). The microscopic origin of the unusual dielectric behavior of CCTO may be explained in terms of the dielectric relaxation models, such as internal barrier layer capacitors (IBLC) and Maxwell−Wagner (MW) relaxation. Based on these dielectric relaxation models, it is easy to get insight into the origin of large dielectric permittivity and dielectric relaxation mechanism. Therefore, the introduction of dielectric relaxation models into the A-site-ordered perovskite oxides offers opportunities for understanding the attractive and unusual dielectric behavior in magnetic materials. In addition, for
A$_2$BB$’$O$_6$ double perovskites, B-site cation arrangements play imperative roles in the dielectric properties. Thus, by the introduction of the B-site cations into the A-site-ordered perovskite oxides, the special-ordered arrangements of B-site cations offer possibilities to find new compounds with intriguing dielectric performances. In addition, most A-site-ordered perovskite investigations are restricted in an insulator, and limited work has been reported for oxide semiconductors with magnetic characteristics. The coupling between semiconductors and magnetic semiconductors provides us with multiple degrees of freedom for controlling novel physical properties, and this can be used for optoelectronic devices and energy applications. However, the challenge is that the compounds cannot be prepared in an atmospheric environment. Here, based on a successfully synthesized A-site-ordered oxide semiconductor CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ through a high-pressure combined with high-temperature approach, we investigated its crystal structure and dielectric and magnetic performances. More importantly, we propose two relaxation models to fully understand the unusual dielectric behavior of the magnetic compound.

### EXPERIMENTAL SECTION

#### Sample Preparation.

A polycrystalline compound of quadruple perovskite CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ was obtained through a high-pressure and high-temperature approach using a hexahedron anvil press (Gülin Guive Machinery Co., Ltd.). The crystal structure of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ is A-site-ordered and B-site partial ordered (Figure 1a). The ionic radius of Fe$^{4+}$ and Ta$^{4+}$ is 0.645 (coordination VI) and 0.64 (coordination VI) angstrom, respectively. The starting materials, dried CaCO$_3$, CuO, Fe$_2$O$_3$, and Ta$_2$O$_5$, were mixed using stoichiometric proportions and then calcined at 850 °C for 4 h. The products were then finely ground and sealed in a Mo/Nb capsule. High-temperature and high-pressure treatments were performed simultaneously at 7 GPa and 1000 °C for 20 min followed by quenching and decompression processes. The large-size sample with a volume of about 2000 mm$^3$ was obtained from the Mo/Nb capsule.

#### Crystal Structure Determination.

We carried out crystal structure characterization of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ by synchrotron X-ray diffraction (SXRD). The strong scattering contrast between Fe and Ta helps us to study the cation ordering degree of the material. In order to minimize absorption, the sample was mounted into 0.5 mm glass capillaries. SXRD data was recorded on a Mythen-1 detector using the ALBA synchrotron with the MSPD beamline $^{18}$ of wavelength $\lambda = 0.4134$ (Å) (Cerdanyola del Valles, Spain). Neutron powder diffraction (NPD) patterns were recorded on a SPODI powder diffractometer with a wavelength of 1.548 Å (Garching, Germany).$^{19}$ Rietveld refinements of the SXRD and NPD data using the Fullprof software package.$^{20}$ High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were measured using a JEM-2100 (JEOL, Tokyo, Japan).

#### Physical Measurements.

The physical property measurement system (PPMS, Quantum Design) was used to record the magnetic properties of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$. UV-3600 (SHIMADZU, Japan) was used to measure UV-vis diffuse reflectance spectra. The dielectric properties of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ were performed using a precision impedance analyzer (Agilent 4294A, USA).

#### RESULTS AND DISCUSSION

The global instability index (GII) can be obtained from structural-stability prediction program SPuDS.$^{21}$ With GII = 0.036 for CaCu$_3$Fe$_2$Ta$_2$O$_{12}$, this compound was not successfully synthesized under ambient conditions. Therefore, we synthesized the CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ polycrystalline sample through a high-pressure combined with high-temperature method and the photograph of the large-size specimen is shown in the inset of Figure 1d. The SXRD pattern demonstrated the compound to be a cubic perovskite phase with a trace of impurity, as shown in the inset of Figure 1d. Rietveld refinement results for SXRD data and the bond valence sum (BVS) result of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ are listed in Table 1. Furthermore, the refinement result reveals that the compound possesses an A-site-ordered perovskite structure with the space group Im$ar{3}$ (no. 204); metal, M; oxygen, O; metal–oxygen bond lengths, M–O; bond valence sum, BVS; residuals $R_{wp}$ = 0.18, $R_p$ = 0.16.

### Table 1. Rietveld Refinement Results for SXRD Data and BVS Result of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ at 300 K$^a$

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>$U_{iso}$ (100Å$^2$)</th>
<th>G</th>
<th>M–O (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2a</td>
<td>0.7499(5)</td>
<td>1.0</td>
<td>2.631 (3) × 12</td>
<td>2.04</td>
</tr>
<tr>
<td>Cu</td>
<td>6d</td>
<td>0.5294(1)</td>
<td>1.0</td>
<td>1.983 (2) × 4</td>
<td>1.95</td>
</tr>
<tr>
<td>Fe/Ta</td>
<td>8c</td>
<td>0.2640(1)</td>
<td>1.0</td>
<td>2.001 (5) × 6</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>24h</td>
<td>0.5692(1)</td>
<td>0.984</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Space group: Im$ar{3}$ (no. 204); metal, M; oxygen, O; metal–oxygen bond lengths, M–O; bond valence sum, BVS; residuals $R_{wp}$ = 0.18, $R_p$ = 0.16.

Figure 1. (a) Crystal structure of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$, (b) SAED pattern and (c) corresponding HRTEM image of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ along the [110] zone axis. (d) SXRD pattern and the Rietveld refinement profile of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$. The observed, calculated, and difference patterns and positions of the Bragg reflection are shown by black forks, red line, blue line, and green ticks, respectively. The insets show a large-size specimen placed on a calibrated scale and the dihedral angle pattern at a low-angle region. The pink nbla symbol indicates impurity in the sample.
1b, note that no clear diffraction spots with $h + k + l = \text{odd}$ reflections can be observed in the SAED pattern of the sample, such as the 111 spot, indicating that Fe and Ta cations are in a random arrangement at the B-site. For the HRTEM image in Figure 1c, the characteristic spacings of the (002) and (220) lattice planes are 0.37 and 0.27 nm, respectively, which is in agreement with the refined lattice parameters. All of these results are well matched, which confirms that $\text{CaCu}_3\text{Fe}_2\text{Ta}_2\text{O}_{12}$ belongs to the cubic structure with the space group $\text{Im} \bar{3}$, where only Ca and Cu ordering occurs at the A-site, as shown in Figure 1a.

The compound crystallizes in an $\text{Im} \bar{3}$ space group, and the possible space groups in perovskite oxides with the general formula $\text{A}_2\text{A}'_3\text{B}_2\text{B}'_2\text{O}_{12}$ are summarized in Table 4. Surprisingly, short Cu–O bond lengths of 1.983(2) Å were found in $\text{CaCu}_3\text{Fe}_2\text{Ta}_2\text{O}_{12}$, showing a square-planar coordination of oxygen with distortion at the A'-site. Thus, this results in considerable tilting of the FeO$_6$ and TaO$_6$ octahedra. Based on the BVS method,$^{24}$ the valence states of A-site cations (Ca and Cu) can be estimated by metal–oxygen bond lengths, but the reliable valence states of B-site cations (Fe and Ta) are not accurately calculated due to the Fe/Ta disorder in $\text{CaCu}_3\text{Fe}_2\text{Ta}_2\text{O}_{12}$, as shown in Table 1.

We also analyzed the NPD patterns by the Rietveld method to further confirm the crystal and magnetic structures of $\text{CaCu}_3\text{Fe}_2\text{Ta}_2\text{O}_{12}$, as shown in Figure 2. The parameters of the
The refined structure are listed in Tables 2 and 3. The crystal structure of an AA′BiB′2O12 perovskite was refined through a starting model derived by SPUuDs.25 As shown in Figure 2a,b, patterns of 4 and 300 K have no significant difference, indicating that the compound crystallizes in the Im3 space group. The h + k + l = odd reflection is absent in the NPD patterns, such as the 111 reflection. This suggests a disordered arrangement of Fe and Ta cations at the B-site, which is consistent with the results obtained from SXRD and SAED. Nevertheless, a B-site-ordered diffraction peak from the space group Pn̅3, such as 221, in NPD was observed, as shown in the insets of Figure 2a,b indicating the random distribution of Fe and Ta cations in most of the regions in CaCu3Fe2Ta2O12 and a small account of local B-site ordering regions. The preparation of CaCu3Fe2Ta2O12 by a high-pressure synthesis method, in which the quenching process is commonly used, will easily introduce a certain degree of ion disorder into the compound. The average Fe/Ta = 0.382 and 0.332 mm s^{-1} quadrupole splitting was observed, revealing the non-cubic distortion near 0 mm s^{-1}.

Figure 3. Mössbauer spectrum of CaCu3Fe2Ta2O12 at 300 K. The black dots represent the observed spectrum, and the red solid line represents the fitting curve. The inset shows the Mössbauer spectrum near 0 mm s^{-1}.

Sn atoms are both in a random arrangement at the A-site and B-site, respectively, leading to local electric field gradient at the Fe site. Meanwhile, it gave the same explanation, where local structural distortions in disordered CaFeTaO6 generate the large splitting of the spectrum caused by the significant charge difference between Fe^{3+} and Ta^{5+}. Therefore, Mössbauer spectrum reveals that the CaCu3Fe2Ta2O12 perovskite displays a partially ordered arrangement of Fe and Ta cations, and this arrangement is essentially disordered.

From the temperature-dependent magnetic susceptibility data shown in Figure 4a, measured with a 10 kOe external field, a clear paramagnetic state with linear inverse magnetic susceptibility cannot be observed up to 350 K. The inverse magnetic susceptibility significantly decreases with decreasing temperature from the highest temperature down to approximately 150 K, which could associate with the not perfect disorder and the presence of local B-site cation ordering in CaCu3Fe2Ta2O12. Below 150 K, spin ordering is indicated and the measured magnetization exhibits smaller values as compared to a pure Curie–Weiss ∼1/1T type behavior of a paramagnetic substance theoretically extrapolated to lower temperatures. There exists nonmagnetic Ta^{5+} (5d0) ion in CaCu3Fe2Ta2O12; therefore, observation of low-temperature magnetization is attributed to A-site Cu^{2+} contributing as S = 1/2 with 1 μB and B-site Fe^{3+} as S = 5/2 with 5 μB to the ordered moment at low temperatures. Note that the observed magnetization is 0.39 μB/μ at 10 kOe and at 5 K without saturation, as presented in Figure 4b. The observed magnetization matches very well that obtained from the net magnetic moment from neutron diffraction. Therefore, the antiferromagnetic coupling between Fe^{3+} spins and ferromagnetic coupling between Cu^{2+} spins give rise to a net magnetic moment as indicated from these measurements to some extent.

The observed value of magnetization is consistent with the B-site-disordered CaCu3FeNb2O12 perovskite.22 The transition temperature (T_N) and magnetic moment in perovskite oxides with the general formula AA′BiB′2O12 are summarized in Table 4. For the double perovskite SrFeTaO6 the spin-glass transition temperature (25 K) is significantly lower than the magnetic transition temperature of CaCu3Fe2Ta2O12 (150 K) due to only the Fe^{3+}–Fe^{3+} interaction in SrFeTaO6. Meanwhile, the magnetic transition temperature of CaCu3Fe2Ta2O12 (150 K) is also higher than for other A-site-ordered perovskites with the magnetic A-site Cu^{2+} cation. For instance, it is 6 times larger than that of antiferromagnetic CaCuTa2O12 (25 K) and 15 times larger than that of ferromagnetic CaCuSn2O12 (10 K), in which only the A-site...
Cu\(^{2+}\) \((S = 1/2)\) spins contribute to the magnetic behavior.\(^{29,30}\)

Introducing the B-site Fe\(^{3+}\) ions in CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) provides an additional Fe\(^{3+}\)(↑)−Fe\(^{3+}\)(↓) antiferromagnetic coupling as strong as that of the A′-site Cu\(^{2+}\)(↑)−Cu\(^{2+}\)(↑) ferromagnetic coupling. Therefore, the much stronger Fe\(^{3+}\)(↑)−Fe\(^{3+}\)(↓) antiferromagnetic and Cu\(^{2+}\)(↑)−Cu\(^{2+}\)(↑) ferromagnetic exchange energies dominate the weaker Cu\(^{2+}\)−Fe\(^{3+}\) interaction and lead to CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) with a higher magnetic transition temperature (150 K) relative to that of the B-site nonmagnetic CaCu\(_3\)Ti\(_4\)O\(_{12}\) (25 K). In contrast, the magnetic transition temperature of CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) (150 K) is much less than that of LaFeO\(_3\) (740 K) with Fe\(^{3+}\)−Fe\(^{3+}\) interaction. As is well known, the magnetic transition temperature is strongly dependent on the B-site and B′-site cation ordering as well as on the superexchange interaction.\(^{31}\)

In LaFeO\(_3\), the larger overlap of electron orbitals gives rise to larger superexchange interactions that result in a higher magnetic transition temperature.\(^{32}\) In the B-site-disordered perovskite CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\), the significantly lower magnetic transition temperature is rationalized within the Fe\(^{3+}\)/Ta\(^{5+}\) vibronic superexchange interaction. Therefore, the B-site-disordered perovskite CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) has a much lower magnetic transition temperature relative to that of LaFeO\(_3\).

To further confirm the electronic property of CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\), we measured the UV−vis diffuse reflectance spectra in Figures S1a and S1b in the Supporting Information. The experimental result suggests that CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) is a semiconductor and the band gap is approximately 1.77 eV, which is consistent with the theoretical calculation.\(^{33}\)

Figure S1c displays the temperature-dependent resistance and electrical resistivity of the compound. Although CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) has high resistivity at room temperature, the feature is evidently consistent with a semiconducting behavior. Prominent electrical conductivity may be due to the existence of Fe-rich or Ta-rich clusters caused by the Fe/Ta cation disorder at the B-site. As shown in Figure S1d, the electrical conductivity of CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) increases as the temperature increases. The electrical transport can be described as a semiconducting behavior, and the electrical conductivity can be expressed as

\[
\sigma = \sigma_0 \exp\left(\frac{E_v}{k_B T}\right)
\]

Figure 4. (a) Temperature dependence of magnetic susceptibility and inverse susceptibility measured at 10 kOe of CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\). (b) Field dependence of magnetization of CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) at 5 K.

Table 4. Comparison of the Space Group, Transition Temperature \((T_N)\), Magnetic Moment, and Dielectric Permittivity in Perovskite Oxides with the General Formula A\('A\)'\(_3\)B\(_2B'\(_2\)O\(_{12}\)

<table>
<thead>
<tr>
<th>sample</th>
<th>A/B-site ordered</th>
<th>space group</th>
<th>(T_N) (K)</th>
<th>magnetic moment ((\mu_B/fu))</th>
<th>dielectric permittivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCu(_3)Fe(_2)Re(<em>2)O(</em>{12})</td>
<td>A- and B-site ordered</td>
<td>Pn(_3)</td>
<td>560</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>CaCu(_3)Fe(_2)Sb(<em>2)O(</em>{12})</td>
<td>A- and B-site ordered</td>
<td>Pn(_3)</td>
<td>170</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>CaCu(_3)Fe(_2)Nb(<em>2)O(</em>{12})</td>
<td>A- and B-site ordered</td>
<td>Pn(_3)</td>
<td>170</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>CaCu(_3)Fe(_2)Ni(<em>2)O(</em>{12})</td>
<td>A-site-ordered</td>
<td>Im(_3)</td>
<td>65</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>CaCu(_3)Cr(_2)Sb(<em>2)O(</em>{12})</td>
<td>A- and B-site ordered</td>
<td>Pn(_3)</td>
<td>60</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>CaCu(_3)Cr(_2)Ru(<em>2)O(</em>{12})</td>
<td>A-site-ordered</td>
<td>Im(_3)</td>
<td>140</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>CaCu(_3)Ga(_2)Sb(<em>2)O(</em>{12})</td>
<td>A- and B-site ordered</td>
<td>Pn(_3)</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCu(_3)Fe(_2)Ta(<em>2)O(</em>{12}) (this work)</td>
<td>A-site-ordered</td>
<td>Im(_3)</td>
<td>150</td>
<td>0.39</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure 5. Temperature dependence of (a) dielectric permittivity \(\varepsilon'_r\) and (b) dielectric loss tan \(\delta\) of CaCu\(_3\)Fe\(_2\)Ta\(_2\)O\(_{12}\) at both 1 and 10 kHz. The insets show an expanded view of the dielectric spectrum at a low-temperature region.
and the tan δ of CaCu3Fe2Ta2O12. The red solid curves indicate the fitting result based on eq 5 for ε′′. (c) Temperature dependence of the relaxation time of CaCu3Fe2Ta2O12. The data are linearly fitted based on eq 6.

Table 5. Parameters ε′, ε″, α, s, and τ Obtained from Fitting by the Modified Cole–Cole Relaxation of CaCu3Fe2Ta2O12 at Selected Temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ε′1</th>
<th>ε′2</th>
<th>ε″1</th>
<th>ε″2</th>
<th>α1</th>
<th>α2</th>
<th>s</th>
<th>τ1</th>
<th>τ2</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>1544</td>
<td>93.5</td>
<td>39.5</td>
<td>0.56</td>
<td>0.69</td>
<td>0.70</td>
<td>8.12 × 10⁻⁴</td>
<td>15.13</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>1601</td>
<td>95.5</td>
<td>39.5</td>
<td>0.55</td>
<td>0.59</td>
<td>0.68</td>
<td>6.32 × 10⁻³</td>
<td>0.052</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>1635</td>
<td>97.5</td>
<td>39.5</td>
<td>0.42</td>
<td>0.42</td>
<td>0.66</td>
<td>5.92 × 10⁻⁶</td>
<td>8.48 × 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>1646</td>
<td>99.5</td>
<td>39.5</td>
<td>0.37</td>
<td>0.39</td>
<td>0.63</td>
<td>3.67 × 10⁻⁷</td>
<td>4.27 × 10⁻⁵</td>
<td></td>
</tr>
</tbody>
</table>

where σ, k, T, and E are the pre-exponential factor, Boltzmann constant, absolute temperature, and conduction activation energy, respectively. The E is 0.70 eV by least-squares fit to the entire data. Note that the E is approximately half of the band gap. It indicates the thermally activated process of the intrinsic charge carriers.

Figure 5 highlights the temperature dependence of the dielectric properties of CaCu3Fe2Ta2O12. The both ε′ and tan δ of the sample are weakly temperature-dependent over a wide temperature range (below 200 K). The sample shows an intrinsic dielectric permittivity of ε′ ≈ 25 at low temperatures, which is a half of CCTO (intrinsic ε′ ≈ 60). Such a low dielectric response is attributed to suppression of cooperative switching in either the local electric polarization or the atomic displacements caused by lattice distortion due to the B-site-disordered arrangement. The intrinsic dielectric permittivity values in perovskite oxides with the general formula AA′B′B′′O12 are summarized in Table 4. At low temperatures, freezing of electric dipoles results in the dramatic decrease in ε′ value. However, the ε′ undergoes a step-like increase at a higher temperature due to the thermally activated process of the charge carriers. Moreover, two frequency dependencies of the loss factor are clearly observed between 100 and 300 K, corresponding to two dielectric relaxations marked as A and B, as shown in Figure 5b. Actually, both dielectric relaxations can be attributed to a thermally activated process, which originate from two independent mechanisms: (a) the relaxation A is related to polaron (the charge carriers trapped at the oxygen vacancies). This is expected to give rise to a Debye-like relaxation. Thus, the relaxation A is dominated by a Debye-like relaxation; (b) with further increasing the temperature, the thermally activated charge carriers accumulate on the grain boundaries in the samples that have different conductivities to screen the polarization discontinuity. This extrinsic source of dielectric relaxations is known as the MW relaxation. However, the influence of B-site disorder on the local potential fluctuation leads to a change in MW polarization in CaCu3Fe2Ta2O12, which gives rise to the significant enhancement of ε′ at high temperatures. Therefore, the relaxation B stems from the MW polarization modified by the B-site disorder.

Table 6. Parameters ε, ε′, ε″, α, s, and τ Obtained from Fitting by the Modified Cole–Cole Relaxation of CaCu3Fe2Ta2O12 at Selected Temperatures

As is well known, the preparation of perovskite oxide ceramics by a high temperature sintering method, such as SrTiO3 and BaTiO3, will also easily introduce intrinsic oxygen vacancies into ceramic samples due to traces of reduced Ti at high temperatures. However, the relaxation is not observed owing to the limited measurement window at low frequencies. The prominent increase in ε″ at low frequencies is attributed to enhancement of thermally activated conductivity. In many dielectric materials, the conductivity is related to the dielectric relaxation that has been observed at low frequencies. Therefore, it is imperative to establish the relationship between the dielectric relaxation behavior and defect compensation mechanisms based on the dielectric relaxation model for the diffuse dielectric anomaly associated with electrical conduction.
When the contribution of electrical conduction cannot be neglected in dielectric materials, the term of electrical conduction is generally added to the double Cole–Cole equations, as shown in eq 5.

$$\varepsilon^\prime = \varepsilon_\infty + \left( \frac{\varepsilon_1 - \varepsilon_\infty}{1 + (\omega\tau)^{-s_1}} \right) + \left( \frac{\varepsilon_2 - \varepsilon_1}{1 + (\omega\tau)^{-s_2}} \right) - \frac{j\sigma^*}{\varepsilon_0 \omega \tau}$$  

(5)

where $\varepsilon_1$ and $\varepsilon_2$ are the static dielectric permittivity of the relaxations A and B, respectively, $\varepsilon_\infty$, $\omega$, and $\tau$ represent the dielectric permittivity at very high frequencies, angular frequency, and relaxation time, respectively, $s$ ($0 < s < 1$) is a constant, and $\sigma^*$ represents the complex conductivity. This relationship reveals that the electrical conduction may contribute to $\varepsilon_1'$ and $\varepsilon_2'$. The fitting results of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ are shown in Figure 6a. Simultaneously, we obtain the fitting parameters of $\varepsilon_1$, $\varepsilon_\infty$, $\alpha$, $s$, and $\tau$ as summarized in Table S. The reduction in $\alpha$ with increasing temperature indicates that the low-temperature relaxation is close to the ideal Debye relaxation. In addition, a rapid decrease in $\tau$ with increasing temperature suggests a faster polarization process due to the enhancement in dipole density. To get insight into the two dielectric relaxation behaviors, the dielectric relaxations are described by the Arrhenius law

$$\tau = \tau_0 \exp\left( \frac{E_a}{k_B T} \right)$$  

(6)

where $\tau$ represents the relaxation time, $\tau_0$ and $k_B$ are constants, and $E_a$ indicates the activation energy. As shown in Figure 6c, a linear fitting $E_a = 0.185$ eV is for relaxation A and $E_a = 0.310$ eV for relaxation B. The activation energy of relaxation A, which is suitable for the activation energy of the polaron hopping, that is, charge carriers trapped at the oxygen vacancies. The dielectric relaxation A originates from the interfacial polarization, such as grain boundaries, which is called MW polarization. The discrepancy in $E_a$ arises from the slight contribution of the IBL effect to the dielectric response caused by the B-site disorder in CaCu$_3$Fe$_2$Ta$_2$O$_{12}$. CaCu$_3$Ti$_2$O$_{12}$ with giant dielectric response originates from semiconducting grains and insulating grain boundaries. In contrast, it is hard to form semiconducting grains and insulating grain boundaries in CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ due to the prominent electrical conductivity caused by the B-site disorder. Therefore, the IBL effect slightly contributes to the dielectric response in CaCu$_3$Fe$_2$Ta$_2$O$_{12}$ which is consistent with the observed dielectric permittivity from Figure 5. Note that favorable agreement between experimental and fitting data over a wide frequency range for $\varepsilon_1'$ strongly supports our model.

### CONCLUSIONS

A new A-site-ordered oxide semiconductor, CaCu$_3$Fe$_2$Ta$_2$O$_{12}$, was prepared through a high-pressure combined with high-pressure approach. Combining the SXRD, NPD and TEM data, we reveal that the compound possesses an $Im\bar{3}$ space group, where it crystallizes to an A-site-ordered but B-site partial ordered quadruple perovskite structure. The introduction of the Jahn–Teller Cu$^{3+}$ spin into the A site leads to spin ordering below 150 K. An antiferromagnetic ordering originates from the B-site Fe$^{3+}$ sublattice and a ferromagnetic ordering arises from the A'-site Cu$^{3+}$ sublattice. Interestingly, dielectric spectroscopy reveals two different relaxation behaviors. The low-temperature relaxation is dominated by a Debye-like relaxation, which is attributed to the charged carrier trapped among the oxygen vacancies, while the high-temperature relaxation arises from the MW polarization mechanism. These findings offer opportunities to design new perovskite oxides with attractive magnetic and dielectric properties.

### ASSOCIATED CONTENT

+ **Supporting Information**
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03229.

UV–vis diffuse reflectance spectrum, plots of $(ah\nu)^2$ versus energy ($h\nu$), and band gap of CaCu$_3$Fe$_2$Ta$_2$O$_{12}$.

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G.L. and L.L. designed and supervised the experiments. J.D., L.L., and Y.Y. prepared the sample. J.D. and F.H. performed dielectric properties, HRTEM, SAED, UV–vis diffuse reflectance spectrum, and electrical conductivity experiments. B.S. carried out magnetic property characterization. M.K., H.E., and M.H. performed SXRD and NPD experiments. Y.H. carried out the Mössbauer spectrum characterization. W.H. and W.J. proposed the fruitful suggestion on the manuscript. J.D. and F.H. wrote the manuscript. All authors discussed and contributed to the manuscript.

Notes
The authors declare no competing financial interest.

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