ABSTRACT

Several perovskite-structure oxide compounds, including CaTiO₃, SrTiO₃, BaTiO₃, KNbO₃, and KTaO₃ were irradiated by 800 keV Kr⁺ ions in order to investigate and compare their response to heavy-ion irradiation. The critical amorphization temperature $T_c$, above which amorphization could not be induced, was found to increase in the order SrTiO₃ → CaTiO₃ → BaTiO₃ → KNbO₃ → KTaO₃. No single physical parameter explains the observed sequence, although $T_c$ correlates well with the melting temperatures. The well-known temperature-driven phase transformations in these materials did not have a significant effect on the dose required for amorphization. Domain boundaries were observed in the pristine samples; however, after only a low dose, the boundaries became poorly defined and, with increasing dose, eventually disappeared. Dislocation loops were observed to aggregate at the domain boundaries.

Table I. Space groups and transition temperatures of the perovskite-structure oxides investigated in this study.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space Group</th>
<th>Transition Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO₃</td>
<td>Pcmn, Pm3m</td>
<td>1533</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>I4/mcm, Pm3m</td>
<td>108</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>Amm2, P4mm</td>
<td>273</td>
</tr>
<tr>
<td>KNbO₃</td>
<td>P4mm, Bmm2</td>
<td>393</td>
</tr>
<tr>
<td>KTaO₃</td>
<td>P4mm, Pm3m</td>
<td>690</td>
</tr>
</tbody>
</table>
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the combined charge of the A- and B-site cations must equal +6. Thus there exists a
large number of compounds with the perovskite structure. In this study we examine the
effects of irradiation on CaTiO₃, SrTiO₃, BaTiO₃, KNbO₃, and KTaO₃.

The ideal perovskite structure is cubic \(Pm3m\) (\(Z = 1\)). It can be viewed as a cubic
close-packed array of oxygen anions with one fourth of the oxygens regularly replaced
by an A-site cation (e.g., Ca, Sr, Ba, K; Fig. 1). The B-site cations fit into those
octahedral sites that are defined by oxygen atoms only. This arrangement can be
viewed as a simple-cubic array of BO₆ octahedra with the A site cations occupying the
interstices.

Many of the perovskite-structure oxides undergo one or more instantaneous
displacive phase transitions at temperatures that are achievable \textit{in-situ} in the
transmission electron microscope (TEM). The cubic phase is stable at high
temperatures but lowering the temperature causes the BO₆ octahedra to shift,
decreasing the symmetry. Some of the materials (e.g., KNbO₃) undergo cubic-to-
tetragonal-to-orthorhombic-to-rhombohedral phase transitions as the temperature is
lowered, while others (e.g., KTaO₃) maintain the cubic phase to low temperatures. The
temperatures at which these transitions occur are given in Table 1. Thus, the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Domain boundaries in tetragonal BaTiO₃ (A: before irradiation) and KNbO₃ (B:
after irradiation to \(\sim 0.25 \cdot D_e\)). The regions of mottled contrast are probably highly damaged
or amorphous zones.}
\end{figure}

perovskites provide a unique opportunity to study the competing effects of structure
(through the phase transitions) and chemistry (through variations on the A and B sites)
on radiation-induced amorphization.

**EXPERIMENTAL**

Crystals of CaTiO₃, BaTiO₃, KNbO₃, and KTaO₃ were grown by flux-type techniques
and SrTiO₃ was grown using the flame-fusion method. The resulting crystals were
colorless and translucent and ranged in diameter from 2 - 10 mm. The crystals were
sectioned in random orientations and prepared for TEM by hand thinning and ion milling
with 4 keV \(Ar^+\) ions. The samples were then irradiated by 800 keV Kr⁺ ions at the
HVEM-Tandem Facility at Argonne National Laboratory. The irradiation temperature
was controlled using a heating stage or a liquid helium cooling stage. Combined
ion/electron irradiations were also done in the HVEM Facility, but electron-only
irradiations were done using a JEOL 2010 TEM. Domain formation was monitored by
RESULTS AND DISCUSSION

In order to investigate the effects of moderate doses of irradiation on the development of the domain boundaries, samples of KNbO₃ and BaTiO₃ were heated to 730 and 420 K, respectively, to obtain the cubic phase, irradiated to a dose of ~0.25·D₀, and then cooled through the cubic-to-tetragonal phase transition temperature (Table 1). Domain boundaries appearing as straight lines developed almost immediately (Fig. 2) and spot-splitting was observed in selected-area electron-diffraction (SAD) pattern. Thus these lines are considered to be 90° domain boundaries across which there is a change in the lattice parameter.

Occasionally more curved boundaries were also observed, frequently highlighted by clusters of dislocation loops (Fig. 3). These are interpreted to be 180° boundaries on the basis of their curved shape. 180° domains should only be observable in dark-field images due to Freidel's law failure, but the aggregations of dislocation loops delineated the boundaries in conventional bright-field imaging. Heating the sample back into the cubic phase caused the dislocation loops to gradually assume a more random distribution, and, in fact, this effect could be repeatedly observed on cycling back and forth through the transition temperature. Domain walls may, therefore, be a low-energy sink for dislocation loops.

Contrast arising from bowl-type bending and strain contrast was also observed. This can potentially complicate the identification of the domain boundaries, however, tilting the sample readily confirmed the contrast that was due to bending. Domain boundaries were further confirmed by SAD patterns. Fig. 4 shows a specimen of SrTiO₃ irradiated to a dose of 1 x 10¹⁴ ions/cm² at room temperature and subsequently cooled
to \(-80\,\text{K}\). A mass of crossing lines is readily evident in the bright-field image. Some of these are straight 90° boundaries (a) which appear to intersect at \(-60°\) angles. The 180° domains are interpreted as curved lines that cut through the 90° domain boundaries and are marked by the letter (b). These 180° boundaries strongly resemble those observed in \(\text{PbTiO}_3\) by Chou and Wayman [2]. The lines marked by the letter (c) are bend contours; these moved or changed contrast when the sample was tilted.

The critical amorphization dose was obtained for all five materials at temperatures ranging from 20 to 800 K (Fig. 5). The critical amorphization temperature \(T_c\), above which amorphization was not induced, varied from 425 K (SrTiO\(_3\)) to 880 K (KTaO\(_3\)), a difference of over 450 K, despite the structural similarity of these materials. The critical amorphization temperature was higher for BaTiO\(_3\) than for the other two titanates. The \(T_c\) values, as well as several other physical parameters are given in Table 2. The effect of combined ion/electron irradiations was found to increase the dose required for amorphization, particularly for CaTiO\(_3\) and SrTiO\(_3\).

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The critical amorphization dose was determined by obtaining \(D_c\) at a narrow temperature interval across the cubic-to-tetragonal transition temperature in SrTiO\(_3\) (110 K) and BaTiO\(_3\) (390 K). The presence or absence of domain boundaries in the tetragonal or cubic phase, respectively, was

\[
\text{Table 2. Physical and experimental data for the perovskite-structure oxides. The electronic and nuclear stopping powers and the electronic-to-nuclear stopping power ratio (ENSP) were obtained from TRIM-96 [3] calculations.}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>(D_c)</th>
<th>(T_c)</th>
<th>(T_m)</th>
<th>(T_c/T_m)</th>
<th>(dE/dx_n)</th>
<th>(dE/dx_e)</th>
<th>(\rho)</th>
<th>ENSP</th>
<th>(t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO(_3)</td>
<td>0.90</td>
<td>440</td>
<td>2250</td>
<td>0.20</td>
<td>1375</td>
<td>1270</td>
<td>4.05</td>
<td>0.92</td>
<td>0.81</td>
</tr>
<tr>
<td>SrTiO(_3)</td>
<td>1.09</td>
<td>425</td>
<td>2350</td>
<td>0.18</td>
<td>1439</td>
<td>1378</td>
<td>5.11</td>
<td>0.96</td>
<td>0.86</td>
</tr>
<tr>
<td>BaTiO(_3)</td>
<td>0.46</td>
<td>550</td>
<td>1890</td>
<td>0.29</td>
<td>1421</td>
<td>1466</td>
<td>6.01</td>
<td>1.03</td>
<td>0.93</td>
</tr>
<tr>
<td>KNbO(_3)</td>
<td>0.35</td>
<td>770</td>
<td>1370</td>
<td>0.56</td>
<td>1327</td>
<td>1317</td>
<td>4.61</td>
<td>0.99</td>
<td>0.92</td>
</tr>
<tr>
<td>KTaO(_3)</td>
<td>0.64</td>
<td>880</td>
<td>1630</td>
<td>0.54</td>
<td>1486</td>
<td>1193</td>
<td>7.01</td>
<td>0.80</td>
<td>0.94</td>
</tr>
</tbody>
</table>

The effect of the phase transitions on the critical amorphization dose was determined by obtaining \(D_c\) at a narrow temperature interval across the cubic-to-tetragonal transition temperature in SrTiO\(_3\) (110 K) and BaTiO\(_3\) (390 K). The presence or absence of domain boundaries in the tetragonal or cubic phase, respectively, was
used to ensure that the material had achieved the desired phase for the irradiation. In contrast to previous proton-irradiation experiments in BaTiO₃ [4], the change in the critical amorphization dose was small (Fig. 5) and in fact was within experimental error in the case of SrTiO₃. In BaTiO₃ the critical amorphization dose decreased slightly across the transition temperature.

Previous workers have used a variety of physical parameters to predict the kinetics of amorphization in a large number of insulating ceramics [5,6]. Within the same structure types, melting points and bonding or thermodynamic considerations correlate moderately well with \( T_c \) (e.g., as in the olivine-structure oxides [7]), and theories to predict the kinetics of amorphization for insulators with widely varying structures have met with some limited success [8,9].

Within the perovskite structure type, the tolerance factor might be expected to correlate with \( T_c \). Perovskites with a tolerance factor close to unity could be more resistant to amorphization, while those at the limit of structural compatibility (\( t \sim 0.8 \)) might be more difficult to recrystallize during irradiation. Fig. 6 shows that this is, in fact, not what is observed. Apparently, structural considerations alone are insufficient to explain the observed differences in the temperature dependence of the critical amorphization dose within this group of compounds.

Bond length and ionicity values are also insufficient to predict the \( T_c \) values; in fact, \( T_c \) increases with the average bond ionicity, calculated using Pauling's rules [10] (Table 2; Fig. 6), contrary to the predictions of Naguib and Kelly [6] and with the results obtained previously, for example, in the compounds with the olivine structure [7]. The relationship between \( T_c \) and \( T_m \) does, however, give the expected inverse correlation (Fig. 6).

**CONCLUSIONS**

The critical amorphization dose was obtained as a function of temperature for a suite of five perovskite-structure oxides. The critical amorphization temperature was found to increase in the order SrTiO₃ → CaTiO₃ → BaTiO₃ →
KNbO₃ $\rightarrow$ KTaO₃. CaTiO₃ and SrTiO₃ are highly resistant to amorphization at elevated temperatures as compared with the other compounds. No single physical parameter was found to explain the observed differences, and the values obtained for $T_c$ are probably dependent on more complex combinations of structural and chemical factors.

The cubic-to-tetragonal phase transition was found to weakly affect the critical amorphization dose, particularly in BaTiO₃. The "direction" of the change was opposite to that observed in previous proton channeling investigations [4]. The development of domain boundaries was largely unaffected by low doses of irradiation. However, the domain boundaries were frequently marked by clusters of dislocation loops, suggesting that these locations serve as low-energy wells for defect clusters.

ACKNOWLEDGMENTS

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