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Ambient-temperature high-pressure-induced ferroelectric phase transition in CaMnTi$_2$O$_6$

J. Ruiz-Fuertes, T. Bernert, D. Zimmer, N. Schrodlt, M. Koch-Müller, B. Winkler, L. Bayarjargal, C. Popescu, S. MacLeod, and K. Glazyrin

$^1$MALTA-Consolider Team, Departament de Física Aplicada-ICMUV, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

$^2$Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

$^3$Institut für Geowissenschaften, Goethe-Universität, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

$^4$GFZ Potsdam, Sektion 4.3, Telegrafenberg, 14473 Potsdam, Germany

$^5$CELS-ALBA Synchrotron Light Facility, 08290 Cerdanyola del Vallés, Barcelona, Spain

$^6$Atomic Weapons Establishment, Aldermaston, Reading RG7 4PR, United Kingdom

$^7$Institute of Shock Physics, Imperial College London, London SW7 2AZ, United Kingdom

$^8$Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22603 Hamburg, Germany

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The ferroelectric to paraelectric phase transition of multiferroic CaMnTi$_2$O$_6$ has been investigated at high pressures and ambient temperature by second-harmonic generation (SHG), Raman spectroscopy, and powder and single-crystal x-ray diffraction. We have found that CaMnTi$_2$O$_6$ undergoes a pressure-induced structural phase transition (P$_{4}$mc $\rightarrow$ P$_{4}$2$\_$/nmc) at $\sim$7 GPa to the same paraelectric structure found at ambient pressure and $T_c$ = 630 K. The continuous linear decrease of the SHG intensity that disappears at 7 GPa and the existence of a Raman active mode at 244 cm$^{-1}$ that first softens up to 7 GPa and then hardens with pressure are used to discuss the nature of the phase transition of CaMnTi$_2$O$_6$, for which a $dT_c/dP$ = $-$48 K/GPa has been found. Neither a volume contraction nor a change in the normalized pressure on the Eulerian strain is observed across the phase transition with all the unit-cell volume data following a second-order Birch-Murnaghan equation of state with a bulk modulus of $B_0$ = 182.95(2) GPa.

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I. INTRODUCTION

Multiferroics have attracted a significant amount of attention as they potentially offer the prospect of doubling the capacity of information storage in combined MRAM-FRAM memories [1]. The largest coexisting ferroelectric and magnetic effects are found in type-I multiferroics, in which an ambient-temperature ferroelectric compound containing a magnetic ion shows an antiferromagnetic order at sufficiently low temperature. Unfortunately, while most type-I multiferroics have a large spontaneous polarization, they do not show bulk ferroelectricity due to their large leakage and coercive field [2]. Recently, Aimi et al. [3] have discovered that CaMnTi$_2$O$_6$ is a multiferroic with a moderate spontaneous coercive field at 7 GPa.

CaMnTi$_2$O$_6$ crystallizes in a tetragonal A-site-ordered-type double-perovskite structure [3] (Fig. 1), very similar to centrosymmetric CaFeTi$_2$O$_6$. In this structure, the Ca$^{2+}$ ions are tetrahedrally coordinated, Ti$^{4+}$ occupy tilted octahedra, one half of the Mn$^{2+}$ are tetrahedrally coordinated (Mn1), and the other half are in a pseudosquare planar configuration (Mn2). However, in contrast to CaFeTi$_2$O$_6$, the square-planar Mn$^{2+}$ and the octahedrally coordinated Ti$^{4+}$ are shifted along the c axis in CaMnTi$_2$O$_6$. This breaks the center of inversion, lowering the symmetry from space group P4$_2$/nmc observed in CaFeTi$_2$O$_6$ to P4$_2$mc and generates a spontaneous polarization. Tetrahedrally coordinated Mn$^{2+}$ and the Ca$^{2+}$ ions play almost no role in the ferroelectricity of CaMnTi$_2$O$_6$. Aimi et al. [3] have shown that with increasing temperature the off-centering of the square-planar coordinated Mn$^{2+}$ and of the Ti$^{4+}$ decreases. Concomitantly, the second-harmonic-generation (SHG) signal decreases monotonically with temperature up to the Curie temperature $T_c$ = 630 K, where it becomes zero due to the ferroelectric (space group P4$_2$mc) to paraelectric (space group P4$_2$/nmc) phase transition. In paraelectric CaMnTi$_2$O$_6$ the Ti$^{4+}$ ions move to the center of their octahedra but square-planar Mn$^{2+}$ keep their shift along c, with one half of the Mn$^{2+}$ ions shifting up and the other half shifting down [Fig. 1(c)]. Thus, overall, the total spontaneous polarization disappears, and a center of inversion emerges in space group P4$_2$/nmc.

In the present work we study the nature of the ferroelectric to paraelectric phase transition of CaMnTi$_2$O$_6$ by inducing it under high pressure. We perform SHG and Raman spectroscopic measurements to find the pressure-induced phase transition, understand the effect of pressure on the spontaneous polarization, and investigate the behavior of the Raman active modes. Finally, the high-pressure paraelectric structure of CaMnTi$_2$O$_6$ is solved by x-ray diffraction (XRD).

II. EXPERIMENTAL DETAILS

CaMnTi$_2$O$_6$ was synthesized using pure ilmenite-type MnTiO$_3$ and CaTiO$_3$ sealed inside a platinum capsule at 7 GPa and 1700 °C in a multianvil press for 30 min following the work by Aimi et al. [3]. The multianvil experiment was performed at GFZ Potsdam with a 18/11 assembly, which was calibrated at room temperature against the phase transitions in Bi.
Fig. 1. Projection of the A-site-ordered perovskite structure projected along the [010] direction for (a) the ferroelectric CaMnTi$_2$O$_6$ (space group $P4_2$mc), (b) CaFeTi$_2$O$_6$ (space group $P4_2/nmc$), and (c) paraelectric CaMnTi$_2$O$_6$ (space group $P4_2/nmc$).

III. RESULTS

A. Second-harmonic generation

The pressure dependence of the SHG signal $I_{2\omega}$ is shown in Fig. 2. With pressure, the SHG signal decreases linearly from an initial value of $\sim$1000 counts up to 7 GPa when, within our experimental accuracy, no signal can be detected anymore. We interpret this as the ferroelectric phase transition of CaMnTi$_2$O$_6$.

Hence, CaMnTi$_2$O$_6$ undergoes a ferroelectric to paraelectric phase transition either at ambient pressure [3] and $T_c = 630$ K or at ambient temperature and $P_c = 7$ GPa. This result associated with second-order phase transitions in ferroelectrics...
FIG. 2. Pressure dependence of the second-harmonic-generation signal showing a continuous decrease up to $\sim 7$ GPa. Different symbols correspond to different experiments. The solid circles are data from the single-crystal experiment, whereas the solid squares and triangles correspond to powder data. The vertical dashed line marks the phase boundary, and the red solid lines are guides for the eye.

[21] indicates that the Curie temperature of CaMnTi$_2$O$_6$ decreases with pressure at $dT_c/dP = -48$ K/GPa, similar to the value of $-52$ K/GPa observed for BaTiO$_3$ [21]. With the objective of investigating the behavior of the optical modes at the zone center and in order to solve the high-pressure structure of CaMnTi$_2$O$_6$, we present in the following sections the results of high-pressure Raman spectroscopy and XRD studies.

B. Raman spectroscopy

The A-site-ordered-type structure of CaMnTi$_2$O$_6$ with point group $4mm$ has 88 vibrational zone-center modes. Two of them, with irreducible representations $A_1 + E$, correspond to acoustic phonons, and the ten $A_2$ modes are silent. The remaining optic phonons ($17A_1 + 18B_1 + 10B_2 + 31E$) are Raman active, with the $A_1$ and $E$ modes being polar and therefore also IR active. Given the number of Raman active modes and the fact that 41 of them are polar and therefore will show longitudinal optical-transverse optical (LO-TO) splitting, one can expect a Raman spectrum with a continuous character, with a significant overlap of Raman bands and few distinct features. A selection of Raman spectra of CaMnTi$_2$O$_6$ at different pressures is shown in Fig. 3.

Although an unambiguous Raman assignment has not been possible because the size of the crystals ($< 50 \mu m$) has not allowed us to orient them, we can tentatively assign the most intense bands.

Although CaMnTi$_2$O$_6$ has almost six times more Raman active modes than polar ZnTiO$_3$ [22] in the LiNbO$_3$-type structure, the Raman spectra of these two compounds mutually resemble each other. This is reasonable if we consider that the polar crystal structures of both CaMnTi$_2$O$_6$ and ZnTiO$_3$ are related to the perovskite structure. In the case of CaMnTi$_2$O$_6$, the unit-cell edge is doubled in conjunction with a distortion of the TiO$_6$ octahedra to form the polar, tetragonal structure in $4mm$, while a distortion of the perovskite structure according to the LiNbO$_3$ structure leads to the polar, trigonal crystal class $3m$.

Similar to ZnTiO$_3$, CaMnTi$_2$O$_6$ also shows two intense bands located at around 244 cm$^{-1}$ ($\nu_2$) and 590 cm$^{-1}$ ($\nu_{11}$) and an isolated broad band at around 800 cm$^{-1}$ ($\nu_{12}$). In polar ZnTiO$_3$ [22,23] $\nu_2$ is an $A_1$ mode polarized along the $c$ direction and consists of an antiphase vibration of the Ti$^{4+}$ ion against the octahedral oxygen framework with the Zn$^{2+}$ ion at rest; $\nu_{11}$ is another $A_1$ mode that consists of a rocking mode of the oxygen octahedral framework with Ti$^{4+}$ and Zn$^{2+}$ at rest, and $\nu_{12}$ is the LO mode of $\nu_{11}$. As $\nu_2$ and $\nu_{11}$ are pure TiO$_6$ modes, it is reasonable to assume that they have a similar eigenvector in both compounds, and therefore, we tentatively assign them to $A_1$ modes in CaMnTi$_2$O$_6$ as well. This hypothesis is further supported under high pressure. While 11 of the 12 observed modes shift to higher energies with increasing pressure, the $\nu_2$ mode softens up to around 7 GPa.
(Fig. 3) when it overlaps with the mode at lower-frequency $\nu_1$ and starts hardening. Above 7.4 GPa other bands change their intensity or vanish, and additional bands appear. We interpret these changes in the Raman spectrum of CaMnTi$_2$O$_6$ at 7.4 GPa as the onset of the phase transition. This transition pressure is in good agreement with the transition pressure deduced from the disappearance of the SHG signal described above.

Different from CaMnTi$_2$O$_6$, in polar ZnTiO$_3$ [22] or MnTiO$_3$ [24] the $\nu_2$ [A$_1$ (2)] Raman mode vanishes in the first-order phase transition, while in CaMnTi$_2$O$_6$ it stays and hardens as an indication of a less abrupt phase transformation. In fact, the behavior observed in CaMnTi$_2$O$_6$ was previously reported in other pressure-induced second-order phase transitions [25] and indicates that even though the mode softening up to the phase transition is not driving the phase transition, it is sensitive to the motion of the ions involved in the transition process. This indicates that most likely the $\nu_2$ mode softens up to the phase transition, and once the Ti$^{4+}$ ion falls in the centrosymmetric site, the condition to introduce the center of inversion in the structure, the same mode starts hardening with pressure. Although this hypothesis will be reinforced in the next section, such behavior can be explained as follows.

Each Ti atom shares one oxygen atom with a Mn2. Under pressure the Mn2-O bond with respect to the $ab$ plane gets closer to 180$^\circ$, which should increase the frequency of the mode. However, the hardening is compensated below the phase transition by the softening of the mode produced by the fact that the Ti atoms are getting closer to the centrosymmetric position, and therefore, the vibration of the Ti atoms is facilitated. Once the Ti atoms occupy the center of inversion in the phase transition, their oscillation along c reduces, and the hardening due to the reduction of the Mn2-O angle with respect to the $ab$ plane takes over dominating the process.

Figure 4 shows the frequencies of the observed Raman active modes up to 12.9 GPa. As stated before, we observe that the frequencies of all but two modes in the low-pressure phase and all modes in the high-pressure phase increase with increasing pressure, while the frequency of the $\nu_2$ mode decreases until the onset of the phase transition. The pressure coefficients, $a_i = d \nu_i / dP$, obtained from linear fits, are shown in Table I together with their Grüneisen parameters $\gamma_i = B_0 \omega_i / \omega_i$.

C. X-ray diffraction

The pressure dependences of the unit-cell volume and of the a/c ratio, as well as the dependence of the normalized pressure $P$ on the Eulerian strain $f$ of CaMnTi$_2$O$_6$, are shown in Fig. 5 for PXRD and the SXRD experiments up to 5 and 14.3 GPa, respectively. We do not observe, within the resolution of our experiments, any indication of a phase transition up to the maximum pressure reached (14.3 GPa). The a/c ratio of the lattice parameters shows an increasing symmetrization of the metric with pressure. The dependence of the normalized pressure $P$ on the Eulerian strain $f$ often is a good indicator for a structural phase transition. Here, while there is significant scatter in our data, it seems that the best fit yields $dF/df = 0$, and therefore, all P-V data up to 14.3 GPa are well described with a single second-order Birch Murnaghan equation of state. This is in contrast to the results obtained from the SHG experiments and Raman spectroscopy discussed in previous sections that indicate the occurrence of a phase transition at ~7 GPa.

As we explained in the Introduction (Fig. 1), the structure of ferroelectric CaMnTi$_2$O$_6$ is described in the noncentrosymmetric space group P4$_2$mc; however, this structure is very similar to the structure of CaFeTi$_2$O$_6$ with the centrosymmetric space group P4$_2$/nmc. In the eight SXRD experiments performed at different pressures we did not find enough systematic extinctions to distinguish between tetragonal space groups P4$_2$, P4$_2$mc, and P4$_2$/nmc. Space group P4$_2$ is a translationengleiche subgroup of P4$_2$mc, which is simultaneously a translationengleiche subgroup of P4$_2$/nmc. In order to avoid any artificial symmetry constraints, we initially solved the structure of CaMnTi$_2$O$_6$ at different pressures in space group P4$_2$. We found that the structure in P4$_2$ remained identical to the structure solved by Aimi et al. [3] in space group P4$_2$mc up to 14.3 GPa. Then we used the program PLATON [26] to search for higher symmetry. We found that the symmetry of the structure was better described in P4$_2$mc up to 7 GPa as

![FIG. 4. Raman shifts of CaMnTi$_2$O$_6$ as a function of pressure measured during compression. The vertical dotted line marks the suggested phase-transition boundary. The solid and dotted blue straight lines are linear fits to the data. The red solid lines mark the linear fit to the two modes at low frequency, including the soft mode $\nu_2$. Modes are labeled according to Fig. 3.](image-url)
TABLE I. Phonon frequencies of CaMnTi$_2$O$_6$ in the low-pressure ferroelectric and high-pressure paraelectric phases. The pressure coefficients $a_i$ of the modes and their Grüneisen parameters $\gamma_i$ are calculated considering the bulk modulus $B_0 = 182.95(2)$ GPa obtained from single-crystal XRD for both phases. Modes are numbered with increasing frequency. In the paraelectric phase those modes that do not have a correspondence in the ferroelectric phase are marked with a prime.

<table>
<thead>
<tr>
<th>Mode (cm$^{-1}$)</th>
<th>Ferroelectric at 1 atm $\omega$ (cm$^{-1}$)</th>
<th>$a_i$ (cm$^{-1}$/GPa)</th>
<th>$\gamma_i$</th>
<th>Paraelectric at 7.4 GPa $\omega$ (cm$^{-1}$)</th>
<th>$a_i$ (cm$^{-1}$/GPa)</th>
<th>$\gamma_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>202</td>
<td>2.7</td>
<td>2.45</td>
<td>$v_2$</td>
<td>228</td>
<td>2.1</td>
</tr>
<tr>
<td>$v_2$</td>
<td>244</td>
<td>-3.5</td>
<td>-2.62</td>
<td>$v_3$</td>
<td>279</td>
<td>3.6</td>
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<tr>
<td>$v_3$</td>
<td>272</td>
<td>0.8</td>
<td>0.56</td>
<td>$v_4$</td>
<td>344</td>
<td>2.4</td>
</tr>
<tr>
<td>$v_4$</td>
<td>322</td>
<td>2.4</td>
<td>1.38</td>
<td>$v_5$</td>
<td>395</td>
<td>3.3</td>
</tr>
<tr>
<td>$v_5$</td>
<td>341</td>
<td>2.1</td>
<td>1.13</td>
<td>$v_6$</td>
<td>432</td>
<td>3.6</td>
</tr>
<tr>
<td>$v_6$</td>
<td>372</td>
<td>3.3</td>
<td>1.62</td>
<td>$v_7$</td>
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<td>3.9</td>
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<td>408</td>
<td>3.6</td>
<td>1.61</td>
<td>$v_8$</td>
<td>529</td>
<td>1.7</td>
</tr>
<tr>
<td>$v_8$</td>
<td>456</td>
<td>3.9</td>
<td>1.56</td>
<td>$v_9$</td>
<td>595</td>
<td>2.3</td>
</tr>
<tr>
<td>$v_9$</td>
<td>498</td>
<td>3.3</td>
<td>1.21</td>
<td>$v_{10}$</td>
<td>818</td>
<td>3.7</td>
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<tr>
<td>$v_{10}$</td>
<td>520</td>
<td>3.1</td>
<td>1.09</td>
<td>$v_{11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>578</td>
<td>2.3</td>
<td>0.73</td>
<td>$v_{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>791</td>
<td>3.7</td>
<td>0.86</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 5. (a) Pressure dependence of the unit-cell volume of CaMnTi$_2$O$_6$. The solid line denotes the fit to a second-order Birch-Murnaghan equation of state. (b) Pressure dependence of the $a/c$ ratio showing a monotonic increase. The solid line is a guide for the eye. (c) Relation between the Eulerian strain $f$ and the normalized pressure $F$. Data obtained from the powder diffraction experiment are represented by squares, and the single-crystal data are shown by circles.

FIG. 6. Pressure dependence of the anisotropic $U_{33}$ thermal displacement parameter of Mn$^{3+}$ in the Mn2 position for the ferroelectric (space group $P4_2/mmc$) up to 7 GPa and the paraelectric (space group $P4_2/mnc$) structures of CaMnTi$_2$O$_6$ considering no splitting. Solid lines are guides for the eye.

Aimi et al. [3] had shown at ambient temperature and pressure. However, from 9 to 14.3 GPa we found that the symmetry was higher and the structure was better described in space group $P4_2/mmc$, confirming the occurrence of a ferroelectric to paraelectric phase transition as deduced from the SHG experiments before. Using the transformation provided by PLATON, we refined the structures from 0.8 to 7 GPa in space group $P4_2/mmc$ and from 9 to 14.3 GPa in $P4_2/mnc$. We found that the paraelectric structure was identical to the structure of CaFeTi$_2$O$_6$, i.e., with no off-center shift along $c$ for Ti and Mn2. However, the $U_{33}$ term of the anisotropic thermal displacement matrix for Mn2 increased significantly across the phase transition. The pressure evolution of the Mn2 $U_{33}$ is shown in Fig. 6.

We found that up to 7 GPa $U_{33}$ takes a constant value of 0.02 Å$^2$, reasonably low considering that these are high-pressure data. However, from 9 GPa when the structure transforms to $P4_2/mmc$ and the Mn2 atoms are constrained by symmetry to stay in the center of the polyhedron [Fig. 1(b)], the value of their $U_{33}$ term abruptly increases to 0.12 Å$^2$ (Fig. 6). This behavior is not observed for the Mn1 or any of the other atoms and is indicative of a large positional disorder of Mn2 along $c$. At high temperature and ambient pressure, Aimi et al. [3] showed that the structure of paraelectric CaMnTi$_2$O$_6$ at 700 K, although described in space group $P4_2/mmc$, has 50% of the Mn2 shifted up along $c$ and the other 50% shifted down. When we refine the structure of CaMnTi$_2$O$_6$ with a split-atom position for Mn2 with an occupancy of 50%, we confirm that the pressure-induced ferroelectric transformation at ambient temperature is identical to the temperature-induced transformation at ambient pressure [27].

Although a temperature increase causes an expansion [3] of the lattice with $\sim 2.74 \times 10^{-5}$ K$^{-1}$ and pressure compresses the lattice, both increasing pressure and increasing temperature lead to a reduction of the Mn2 and Ti off-center shift along...
According to the point-charge model, the nominal charge of atom $i$ is the shift of atom $i$ along $c$. Therefore to a reduction of the spontaneous polarization $P_s$ ($\mu C/cm^2$), estimated

$$P_s = \sum q_i \delta_i V,$$

where $q_i$ is the charge of atom $i$ and $\delta_i$ is the shift of atom $i$ along $c$. The reduced spontaneous polarization $P_s$ and the pressure dependence of the spontaneous polarization $P_s$ estimated according to the point-charge model is shown in Fig. 7 for CaMnTi$_2$O$_6$ obtained from our SXRD experiments.

Our result shows that the phase transition of CaMnTi$_2$O$_6$ is entirely driven by the off-centering of the Ti$^{4+}$ ion. There are eight Ti$^{4+}$ ions and only two Mn$^{2+}$ ions on the Mn2 site. Thus, when the shift of the Ti$^{4+}$ ion gets close enough to the centrosymmetric position, i.e., a shift along $c$ of $\sim 0.1$ Å (Fig. 6), the phase transition occurs, forcing the Mn$^{2+}$ ion in the Mn2 site (still with a shift of $\sim 0.2$ Å) to quench its shift, resulting in a disordered Mn2 position, with the Mn2 keeping the distortion.

**IV. CONCLUSIONS**

With a combined pressure-dependent study of the second-harmonic-generation signal intensity, Raman spectroscopy, and single-crystal and powder x-ray diffraction, we have shown that CaMnTi$_2$O$_6$ undergoes a phase transition at $\sim 7$ GPa and ambient temperature to the same paraelectric structure observed above 630 K and ambient pressure. This has allowed us to determine that the Curie temperature decreases with pressure at $dT_c/dP = -48$ K/GPa. We have found with Raman spectroscopy a mode at zone center at 244 cm$^{-1}$ that softens with pressure. We have tentatively assigned this mode to an antiphase vibration of the Ti$^{4+}$ ion against its octahedral oxygen framework, indicating that the mode, despite not driving the phase transition, is coupled to the shift of Ti$^{4+}$.

With SXRD we have solved the structure of the high-pressure phase of CaMnTi$_2$O$_6$ and followed the evolution of both the Ti and Mn2 shifts with pressure. This has allowed us to observe that the phase transition is mostly dominated by the shift of the Ti atoms, with the Mn2 atom playing a minor role.

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[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.96.094101 to see the atomic coordinates of the refined structures at 0.8, 7, 9, and 14.3 GPa together with the data acquisition information and refinement results. The Le Bail refinements of two powder diffractograms are also shown.