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Albrecht, Elisabeth K.; Graubner, Tim; Ivlev, Sergei I.; Rautama, Eeva-Leena; Karppinen, Maarit; Kraus, Florian; Karttunen, Antti J. Low-Temperature Single-Crystal Structure and Phonon Properties of A-Site Ordered Double Perovskite CaMnTi₂O₆

Published in: ChemistrySelect

DOI: 10.1002/slct.202402132

Published: 04/10/2024

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version:

Albrecht, E. K., Graubner, T., Ivlev, S. I., Rautama, E.-L., Karppinen, M., Kraus, F., & Karttunen, A. J. (2024). Low-Temperature Single-Crystal Structure and Phonon Properties of A-Site Ordered Double Perovskite CaMnTi₂O₆. *ChemistrySelect*, 9(37), Article e202402132. https://doi.org/10.1002/slct.202402132

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Low-Temperature Single-Crystal Structure and Phonon Properties of A-Site Ordered Double Perovskite CaMnTi₂O₆

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We have used high-pressure methods to synthesize $CaMnTi_2O_6$ single crystals with edge lengths of up to 70 μ m. Compared to previously reported synthetic pathways, we were able to use gold capsules and smaller pressures of 4 GPa. X-ray diffraction analysis of the single crystals at low temperatures between 100 and 230 K confirmed that no phase transitions occur in this temperature range. We found square planar-coordinated Mn

Introduction

CaMnTi₂O₆ is a promising material due to its various multifunctional properties such as ferro- and pyroelectricity. It could be utilized for example as a potential ferroelectric-photovoltaic material^[1] or to power small electronics, for example sensors in pyroelectric energy harvesting applications. CaMnTi₂O₆ is a double perovskite with columnar ordering of the A-site cations (Figure 1).^[2] Together with Glazer tilt system $a^+a^+c^-$, this cation ordering leads to space group P42mc at the room temperature. $^{\scriptscriptstyle [3,4]}$ Above 630 K, CaMnTi_2O_6 transforms to centrosymmetric space group P4₂/nmc and becomes paraelectric.^[2] What is noteworthy about CaMnTi₂O₆ as a new multifunctional material is the elements it consists of. Compared to other, highperforming, ferroelectrics such as lead zirconate titanate (PZT), it does not contain any poisonous or heavy elements like lead or bismuth. Additionally, all its elements are abundant and the precursors for CaMnTi₂O₆ are relatively cheap and easily available.

So far, $CaMnTi_2O_6$ has mainly been studied experimentally at room temperature, high temperature, and high pressure.^[1,2,6–8] Little is known about its low-temperature behavior, about possible structural changes and about how the low temperature might influence its properties. Phase transitions at low temperatures could reveal new ferroelectric

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- Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202402132
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ions to shift further out of the plane with lower temperatures which could lead to a higher polarization. The measured Raman spectrum of CaMnTi₂O₆ has been compared with quantum chemically calculated Raman spectrum to assign the vibrational modes. Calculated single-crystal Raman spectrum has also been also analyzed from the point of view of direction dependency of the Raman intensities.



Figure 1. Crystal structure of CaMnTi₂O₆ in columnar A-site ordering.^[2] Ca atoms in grey, Mn atoms with tetrahedral and square-planar coordination polyhedra in purple, Ti atoms with octahedral coordination polyhedra in blue, and O atoms in red. Image created using VESTA.^[5]

crystal structures with dielectric properties and spontaneous polarization different from the room-temperature crystal structure.

Some previous computational studies have been done on CaMnTi₂O₆. Gou *et al.* studied the origin of ferroelectricity in CaMnTi₂O₆ by using Density Functional Theory (DFT).^[1] Herrero-Martín *et al.* did a computational study on the A'-site Mn atom to find its spin configurations.^[6] Maier *et al.* investigated in what way Mn substitutes Ca in CaTiO₃.^[9]

Here we synthetize $CaMnTi_2O_6$ single crystals, using a novel synthetic pathway in comparison to previously reported ones. The single crystals are studied with X-ray diffraction to understand the low-temperature behavior of ferroelectric CaMnTi₂O₆. Single crystals also facilitate the study of directional depend-



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ency of dielectric and spectroscopic properties due to anisotropy. We investigate the Raman spectrum of CaMnTi₂O₆ single crystals both experimentally and with quantum chemical methods.

Results and Discussion

Nearly phase-pure CaMnTi₂O₆ was obtained, with less than 2% of polycrystalline impurity phases. The synthetized CaMnTi₂O₆ single crystals do not undergo any phase transition down to 100 K. The Raman spectrum showed a strong directionallity of the sample.

Synthesis

Confirmed by scanning electron microscopy (Figure 2) and single crystal X-ray diffraction, it is possible to obtain $CaMnTi_2O_6$ single crystals already at 4 GPa pressure and 1250 °C, using gold capsules. Aimi *et al.*^[2] used gold capsules in their work to obtain bulk samples while they used platinum capsules to obtain single crystals. While the synthesis temperature is not exactly specified, the different capsule materials likely denote different





Figure 2. Scanning electron microscope images of CaMnTi $_2O_6$ single crystals. Dimensions of the crystals are given in micrometers.

synthesis temperatures as platinum has a higher melting temperature than gold. So, contrary to Aimi et al., who obtained bulk samples using gold capsules, (likely at about 1200°C,) and single crystalline samples using platinum capsules (likely at about 1700°C), the platinum capsules and thus the high temperatures are not necessary to obtain single crystals. The capsule material itself does not have an influence either as platinum and gold capsules lead to the same results in our experiments. The amount of consecutive pressings or, more likely, the overall time at high pressure determines the fraction of single crystals in the sample. Further research is necessary to determine the lowest possible pressure and temperature to obtain CaMnTi₂O₆ single crystals. Typical sizes of the crystals are shown in Figure 2 with a medium-sized crystal having an edge length of about 32 µm. Larger crystals can have edge lengths over 70 µm. And smaller crystals are in the range of 20–30 µm edge lengths.

The powder X-ray diffraction pattern in Figure 3 shows the recorded (black) and Rietveld refined (red) diffraction pattern of the CaMnTi₂O₆ single crystals. Small amounts of impurities of TiO₂ at 29.4° 2 θ , MnTiO₃ at 32.1° 2 θ , and CaCO₃ at 27.4° 2 θ can be observed (the amount of each impurity is less than 1%). These impurities can be attributed to additional polycrystalline phases in the sample. The relatively large χ^2 of 11.8 (R_p : 6.09; R_{wp} : 9.59; R_{exp} : 2.79) could be explained by some intensity mismatches originating from another, undetected impurity phase but are much more likely an effect of the high-pressure synthesis and the resulting internal strain. Another reason could be that some of the Mn ions occupy some B-sites normally occupied by Ti atoms. The Rietveld refinement suggests nearly phase.

Low-Temperature Crystal Structures

We did not observe any phase transitions for tetragonal CaMnTi₂O₆ (space group $P4_2mc$, Pearson symbol tP40) between room temperature and 100 K. Only small changes in the lattice parameters and atomic positions were observed. Table 1 lists the lattice parameters for the studied temperature range, 100 to 230 K, and room temperature.^[2] Tables S8 to S21 in the Supporting Information contain the atomic positions of the refined low-temperature crystal structures.

As it can be expected, the unit cell volume of $CaMnTi_2O_6$ becomes smaller as temperature decreases. The square planar Mn(II) cations that play a key role in the ferroelectricity of CaMnTi₂O₆ show an increasing shift out of the square plane when temperature decreases. At 230 K, the *z*-coordinate of the square planar coordinated Mn cation is 0.7882(2) whereas at 100 K the *z*-coordinate changes to 0.78988(17). The Mn(II) is pushed out of the coordination plane further due to the shrinkage of lattice parameters and therefore a smaller coordination plane. The larger displacement could lead to a larger polarization. Further low-temperature dielectric measurements would be necessary to confirm this. The position of the Ti(IV) cations, which also affect the polarization of CaMnTi₂O₆, Research Article



Figure 3. Powder XRD pattern of CaMnTi₂O₆ single crystals. Measured pattern in black, refined pattern as a red dotted line, difference curve in blue, and Bragg positions in green. R_p: 6.09; R_{wp}: 9.59; R_{exp}: 2.79; Chi²: 11.8.

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Table 1. Lattice parameters of the refined single crystal structures of CaMnTi₂O₆ at the studied temperature range (100 to 230 K). The room temperature lattice parameters determined with powder XRD and the room-temperature lattice parameters determined by Aimi et al.^[2] are listed for comparison.

<i>Т</i> [K]	a [Å]	<i>c</i> [Å]	<i>V</i> [ų]
100	7.5220(2)	7.5976(4)	429.88(3)
110	7.5223(2)	7.5968(3)	429.86(3)
120	7.5229(2)	7.5967(3)	429.93(3)
130	7.5234(2)	7.5968(3)	429.99(3)
140	7.52350(10)	7.5966(3)	429.99(2)
150	7.52420(10)	7.5968(2)	430.082(16)
160	7.52440(10)	7.5971(2)	430.122(16)
170	7.52470(10)	7.5978(3)	430.20(2)
180	7.5245(2)	7.5984(3)	430.21(3)
190	7.5248(3)	7.5983(4)	430.24(4)
200	7.52680(10)	7.5974(2)	430.413(16)
210	7.52750(10)	7.5974(2)	430.493(16)
220	7.52850(10)	7.5976(2)	430.619(16)
230	7.52920(10)	7.5978(2)	430.711(16)
293 (PXRD)	7.54291(3)	7.60323(4)	432.590(3)
293 ^[2]	7.5376(7)	7.6002(12)	431.81(9)

does not change significantly with the temperature. The zcoordinates of the Mn ions for all studied temperatures are in the Supporting Information (Table S1).

To get a better view into the change of polarization with temperature, Figure 4 shows the distance between the positive and the negative center of charge in the unit cell. Since the polar axis in CaMnTi₂O₆ is the *c*-axis, the *x*- and *y*-coordinates for positive and negative center of charge are the same. The zcoordinate, however, differs and leads to the distance shown in Figure 4. The distance has been determined by using Eq. (1) to calculate the position $d_{p/n}$ of the positive and negative center of charge, respectively and then subtracting the absolute values from each other. In Eq. (1), we use the atomic positions of the cations and anions, weighted by the charge of the respective ion:

$$d_{p/n} = c \times \frac{1}{\nu_{total}} \sum_{1}^{N_{p/n}} z \nu_z \tag{1}$$

Here, c is the lattice parameter in the polar direction, $N_{p/n}$ is the number of positively/negatively charged ions in the unit cell, z is their coordinate in the polar direction, v_z the (ideal) charge of the respective ion, and $v_{\textit{total}}$ the total charge of the positive/negative ions. The displacement of the Mn(II) cations overcompensates the shrinking of the unit cell with lower temperatures and therefore the absolute distance between the positive and negative center of charge increases.

Raman and IR Spectroscopy

The Raman spectrum measured for the CaMnTi₂O₆ single crystals (Figure 5, black spectrum) is similar to the one reported by Ruiz-Fuertes et al. in 2017.^[8] The red spectrum in Figure 5 is calculated using Density Functional Theory (DFT). Intensity differences aside, the band positions mostly correlate to those of the measured spectrum. Full interpretation of the vibrational

Research Article doi.org/10.1002/slct.202402132



Figure 4. The absolute distance between the positive and the negative center of charge in the unit cell of $CaMnTi_2O_6$. The distance has been calculated for the single crystal structures at temperatures of 230 to 100 K. A standard deviation of 2 K in the temperature has been assumed. The standard deviations obtained by error propagation of the standard deviations of the atomic positions are presented as error bars for the distances between the positive and negative centers of charge.



Figure 5. Measured (black) and calculated (red) Raman spectra of CaMnTi₂O₆ (DFT-PBE0 method). Measurements were carried out on single crystals at room temperature. The peak numbering corresponds to the numbers in Tables S2 and S3 in the Supporting Information.

modes is available in Tables S2 and S3 in the Supporting Information.

Most prominent bands are labeled with numbers. For a more detailed explanation of the Raman-active modes, see Ruiz-Fuertes *et al.*^[8] Here we will discuss the calculated vibrations that correspond to the labeled bands. Table S2 in the Supplementary Information lists all bands with their labels and the corresponding interpretation of the vibrational modes. Most of these vibrational modes cause some kind of polarization in the unit cell. The calculated band with largest intensity, labeled 15, at about 620 cm⁻¹ corresponds to a strongly polarizing vibration where those O anions that form O-Ti-O chains along the *c*-axis shift against the Ti(IV) cation sublattice (Figure 6).

The intensity of certain Raman modes has a strong direction dependence. While the calculated spectrum is an isotropic average over all crystallographic directions as in a polycrystalline sample, the measured single crystal spectrum may show anisotropy and direction-dependence of the intensities. Figure 7 shows the calculated single-crystal Raman spectrum, separated into its direction-dependent components. Several low-intensity bands in the measured spectrum in Figure 5 (black) can be



Figure 6. Vibrational mode corresponding to the most intense band in the calculated Raman spectrum of CaMnTi₂O₆ (band 15), indicated with dark green arrows. Ca cations in grey, Mn cations in purple, Ti cations and octahedra in blue and O anions in red. Image created using VESTA.^[5]



Figure 7. Calculated single-crystal Raman spectrum of CaMnTi₂O₆ separated in different directional components. Since *x* and *y* direction are equivalent in the tetragonal crystal system, some components are superimposed and might not be visible. For *xx* and *yy*, only the pink (*yy*) spectrum is visible and for *xz* and *yz*, only the gray (*yz*) spectrum is visible.

attributed to modes with large *zz* component in Figure 7. The most prominent band 15 in the calculated spectrum has nearly no intensity in the measured spectrum. The green spectrum in Figure 7 shows how this mode has a large *zz* component. The same argument applies for peaks 7 and 9 which have a much higher intensity in the calculated spectrum than in the measured one. Both correspond to a mode with large *zz* component. Apparently, the intensities of the modes with large *zz* component are somewhat damped in our experimental Raman spectrum.

The calculated infrared (IR) spectrum of CaMnTi₂O₆ is shown in Figure 8. The data was acquired alongside the data for the Raman spectrum. It can be used as a prediction for future IR measurements. Some bands, for example band 15 at about 620 cm^{-1} in Figure 5 also appear in the IR spectrum in Figure 8, as well as peak 14 at about 595 cm⁻¹ right next to it, even though Raman and IR intensities are based on different selection rules. It appears that modes which contain a *z* component seem to be prominent. For example, also bands 7 and 9 at about 320 cm⁻¹ and 370 cm⁻¹ are very intense in the IR spectrum, even though in the IR spectrum there is a double band where there is a single band (band number 7) in the

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Elastic and Piezoelectric Properties

The synthetized CaMnTi₂O₆ single crystals could not be used for further characterization of physical properties, but we used DFT-PBE0 to study the elastic and piezoelectric properties of the material. The predicted Reuss bulk modulus of CaMnTi₂O₆ is 178 GPa. This is comparable to the experimentally determined bulk modulus of CaTiO₃, 170.96 \pm 1.4 GPa.^[10] The calculated C₁₁ and C₃₃ elastic constants are 356 and 244 GPa, respectively. The predicted piezoelectric strain constant d_{33} of CaMnTi₂O₆ is 18.9 pCN⁻¹, which is larger compared to non-ferroelectric ZnO (12.4 pCN⁻¹), but almost an order of magnitude smaller than in ferroelectric BaTiO₃ (149 pCN⁻¹).^[11] The calculated d_{15} coefficient of CaMnTi₂O₆ is 10.7 pCN⁻¹, while in hexagonal ZnO the same coefficient has a negative sign (-8.3 pCN⁻¹) and in tetragonal BaTiO₃ the coefficient has a clearly larger positive value (242 pC N⁻¹).^[11]

Conclusions

CaMnTi₂O₆ single crystals with a size up to 70 μ m edge length can be synthetized at 4 GPa pressure and with both gold or platinum capsules. The time the sample is held at high pressure determines the yield of the single crystals. While a holding time of 30 min at high pressure (4 GPa) and high temperature (1250 °C) only results in a low amount of single crystals, a purely single crystalline result can be achieved by two consecutive pressings at 4 GPa, without holding time, before a pressing at high pressure and temperature for 30 min. X-Ray diffraction shows no phase transitions in the low-temperature regime of CaMnTi₂O₆ down to 100 K. At lower temperatures, the square planar-coordinated Mn ions shift even more out of plane compared to the room temperature structure, which could lead to a higher polarization. Single-crystal Raman spectrum of CaMnTi₂O₆ shows strong direction-dependence of intensities, which can be investigated in detail by comparisons to DFT calculations. Understanding the 0 K phonon properties of single-crystal CaMnTi₂O₆ facilitates further computational studies on the finite-temperature phonon properties and potential pyroelectricity of CaMnTi₂O₆.^[12]

Experimental

High pressure and high temperature was used to synthesize CaMnTi₂O₆ single crystals. The low-temperature structure of the crystals was analyzed, and a Raman spectroscopic study was carried

High-Pressure Synthesis

Stoichiometric amounts of CaTiO₃ (Alfa Aesar, 99% purity), TiO₂ (Alfa Aesar, 99.5% purity), and MnO (Sigma Aldrich, 99% purity) were ground under ethanol with mortar and pestle and, after evaporating the ethanol, encapsulated in gold capsules. Single crystals of CaMnTi₂O₆ were synthesized under 4 GPa pressure in a cubic anvil geometry (for HP synthesis details see Ref. [13]). During the synthesis, temperature up to about 1250°C was applied in order to prevent the gold capsules from melting (approximate melting temperature of gold at the applied pressure). The anvils were in a cubic geometry. The sample was heated through resistive heating via a carbon resistor around the sample but electrically insulated from it. When samples were kept at high temperature and pressure for 30 minutes, small amounts of single crystals were formed. When the samples were pressed and decompressed again immediately for two times, followed by one pressing, heating and keeping for 30 minutes, the whole sample turned into single crystals.

Single-Crystal X-Ray Diffraction

Single crystals of CaMnTi₂O₆ were selected under oil (Immersion oil type NVH, Cargille Laboraties) and mounted with a MiTeGen loop. The dimensions of the selected single crystal are given in Tables S4 and S6 in the Supporting Information. Intensity data of a suitable crystal were recorded with a D8 Quest diffractometer (Bruker) at different temperatures from 230 to 100 K in increments of 10 K. The diffractometer was operated with monochromatized MoK_a radiation (0.71073 Å, multi layered optics) and equipped with a PHOTON III C14 detector. Evaluation, integration, and reduction of the diffraction data was carried out with the APEX5 software suite.^[14] The diffraction data were corrected for absorption utilizing the multi-scan and numerical method of SADABS within the APEX5 software suite. The structures were solved with dualspace methods (SHELXT) and refined against F² (SHELXL).^[15,16] All atoms were refined with anisotropic displacement parameters. The crystal structure data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service (www.ccdc.cam.ac.uk/structures) as deposition numbers 2334528, 2334529, 2334530, 2334531, 2334532, 2334533, 2334534, 2334535, 2334536, 2334537, 2334538, 2334539, 2334540, and 2334541.

Characterization

Phase purity was confirmed and lattice parameters for CaMnTi₂O₆ determined by powder XRD using a PANalytical X'Pert Powder Xray diffractometer (alpha-1) with a Cu $K\alpha_1$ X-ray source. The sample was taken out of the gold capsule and the single crystals detached from each other by grinding them in a mortar. Due to the small size

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of the individual crystallites, the sample was treated as a powder sample in powder XRD measurements. The software FullProf Suite was used to carry out Rietveld refinements. Scanning Electron Microscope imaging was carried out with a Hitachi TM-4000 Plus. Raman spectra were obtained using a Renishaw inVia[™] Confocal Raman Microscope with 50 accumulations at a wavelength of 532 nm.

Computational Details

All quantum chemical calculations on CaMnTi₂O₆ (P4₂mc) were carried out with the CRYSTAL23^[17] program package. Hybrid PBE0 density functional method (DFT-PBE0, 25% exact exchange)^[18,19] was used in combination with all-electron, Gaussian-type basis sets derived from Karlsruhe def2 basis sets.^[20] Triple- ζ -valence + polarization level basis sets were used for Mn, Ti, and O atoms,^[21,22] while a split-valence + polarization level basis set was used for Ca atoms.^[4] The crystal structure optimized at the used level of theory was taken from the previous study on CaMnTi₂O₆.^[4] 4×4×4 Monkhorst-Pack type k-mesh was used for sampling the reciprocal space. Default DFT integration grids of CRYSTAL23 were applied in all calculations. The calculations were carried out with Coulomb and exchange integral tolerance factors (TOLINTEG) set to tight values of 8, 8, 8, 8, and 16. The harmonic vibrational frequencies, IR intensities, and Raman intensities were obtained by using the computational schemes implemented in CRYSTAL.[23-26] In the vibrational spectrum calculations, tight SCF convergence criterion (TOLDEE keyword) of 10^{-10} a.u. was applied. The Γ -point harmonic frequency calculation at 0 K did not yield any imaginary frequencies for the ferroelectric CaMnTi₂O₆. The final IR spectrum was obtained by using Lorentzian peak profile with FWHM of 8 cm⁻¹. The Raman intensities were calculated for conditions corresponding to the experimental setup (T=298 K, λ =532 nm). The polycrystalline Raman spectrum was obtained by using a pseudo-Voigt peak profile (50:50 Lorentzian:Gaussian) and an FWHM of 8 cm⁻¹ (total isotropic intensity in arbitrary units). The peak assignments were carried out by visual inspection of the normal modes with the Jmol program package.^[27] The elastic and piezoelectric tensor were calculated with the ELAPIEZO algorithm implemented in CRYSTAL.[28,29]

Supporting Information

The Supporting Information contains further crystallographic details and interpretation of the Raman modes.

Acknowledgements

E.K.A. and A.J.K. acknowledge funding from the Academy of Finland (grant no. 317273) and the Finnish Cultural Foundation. We thank Topias Jussila (Aalto University) for help with Raman measurements, CSC – The Finnish IT Center for Science for computational resources, and RawMatTERS Finland Infrastructure (RAMI) at Aalto University.

Conflict of Interests

The authors have no conflict of interest to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: crystal structure · density functional calculations · double perovskites · high-pressure chemistry · raman spectroscopy

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Manuscript received: June 26, 2024