Crystal structure and optical properties of the new 8O polytype of $\text{Ca}_2\text{Ta}_2\text{O}_7$

Stefan G. Ebbinghaus^{*,I}, Andreas Kalytta^I, Jürgen Kopf^{II}, Anke Weidenkaff^{III} and Armin Reller^I

^I Universität Augsburg, Lehrstuhl für Festkörperchemie, Universitätsstrasse 1, D-86159 Augsburg, Germany

^{II} Universität Hamburg, Institut für Anorganische und Angewandte Chemie, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

^{III} Eidgenössische Materialprüfungs- und Forschungsanstalt, Abteilung Festkörperchemie und Analytik, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

Dedicated to Professor Dr. Hans-Jörg Deiseroth on the occasion of his 60th birthday

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Abstract. Single crystals of the new 8O modification of $\text{Ca}_2\text{Ta}_2\text{O}_7$ were grown by optical floating zone melting and their structure was solved by X-ray diffraction. 8O $\text{Ca}_2\text{Ta}_2\text{O}_7$ crystallizes in space group $C222_1$ with $a = 7.3690(2)$ Å, $b = 12.7296(3)$ Å, $c = 48.263(1)$ Å. The structure is related to the weberite structure type and can be described as a stacking of 8 basic building units per unit cell. Each building unit consists of one Ta_3Ca and one Ca_3Ta layer with a cubic close packed arrangement. Optical spectroscopy in the UV-Vis and IR region reveals a high transparency in a wide energy range from 0.2–3.5 eV. Dielectric measurements yield a high ϵ' value of 60 at room temperature.

1. Introduction

Depending on preparation conditions and doping, $\text{Ca}_2\text{Ta}_2\text{O}_7$ shows a wide variety of different modifications. All polytypes of $\text{Ca}_2\text{Ta}_2\text{O}_7$ show a high structural similarity and are closely related to the structure of the mineral weberite ($\text{Na}_2\text{MgAlF}_7$). The basic building unit of all structures of $\text{Ca}_2\text{Ta}_2\text{O}_7$ is a 6 Å thick slab consisting of one Ca_3Ta and one Ta_3Ca layer (*vide infra*). These slabs are stacked along [001]. The various modifications of $\text{Ca}_2\text{Ta}_2\text{O}_7$ only differ in the crystal system and the number of slabs (N) within the unit cell. Therefore a shorthand notation can be used in which the polytypes are referred to by N and a capital letter denoting the crystal system. In this notation 7M corresponds to a monoclinic structure made up of 7 slabs, while 3T describes a trigonal modification with 3 slabs. Since the basic building unit for all

polytypes is the same, their cell parameters are very similar: All structures possess a (pseudo) hexagonal unit cell with $a_h \approx 7.3$ Å and $c_h \approx N \times 6$ Å. For the monoclinic structures and the new orthorhombic modification described in this paper, a C-centered super cell with $a = a_h$, $b = \sqrt{3}a_h$, $c = c_h$, has to be used. The known phases so far are 3T, 4M, 5M, 6M, 6T, and 7M. $\text{Na}_2\text{Ta}_2\text{O}_5\text{F}_2$ has a closely related structure and can be considered to be the 2M aristotype of the above-mentioned family of homologue structures [1].

Below 1450 °C pure polycrystalline $\text{Ca}_2\text{Ta}_2\text{O}_7$ adopts the trigonal 3T structure with $a = 7.355$ Å and $c = 18.09$ Å [2]. At higher temperatures it transforms to the 7M polytype. Single crystals of this monoclinic phase can be flux grown in sealed platinum tubes from a 50:50 wt% mixture of $\text{Ca}_2\text{Ta}_2\text{O}_7$ and $\text{Ca}_2\text{V}_2\text{O}_7$ by slow cooling from 1450 °C [3]. X-ray structure determination led to space group $C2$ with $a = 12.726$ Å, $b = 7.380$ Å, $c = 42.538$ Å and $\beta = 95.77^\circ$. The same growth experiment also yielded crystals of 6M $\text{Ca}_2\text{Ta}_2\text{O}_7$, a modification that is not accessible by solid state synthesis [4].

Doping of $\text{Ca}_2\text{Ta}_2\text{O}_7$ leads to the stabilization of additional polytypes: A substitution with 10 mole% Nb (e.g. $\text{Ca}_2\text{Ta}_{1.9}\text{Nb}_{0.1}\text{O}_7$) results in the formation of the 7M structure in polycrystalline samples at 1550 °C while a Nb content of 20 mole% leads to the stabilization of 5M $\text{Ca}_2\text{Ta}_{1.8}\text{Nb}_{0.2}\text{O}_7$ under the same preparation conditions. This modification crystallizes in space group $C2$ with the following cell parameters: $a = 12.753$ Å, $b = 7.349$ Å, $c = 30.244$ Å, $\beta = 94.26^\circ$ [3].

By crystal growth of $\text{Sm}_2\text{Ti}_2\text{O}_7$ -doped $\text{Ca}_2\text{Ta}_2\text{O}_7$ (using $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{V}_2\text{O}_7$ as flux in sealed platinum tubes at 1550 °C) the 6T and 5M polytypes were obtained [2]. Electron microprobe analysis showed the $\text{Sm}_2\text{Ti}_2\text{O}_7$ content in the 5M phase to be approximately 10 mole%, while for the 6T phase a content of about 5 mole% was found. 5M $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{Ta}_{1.8}\text{Ti}_{0.2}\text{O}_7$ possesses cell parameters very similar to 5M $\text{Ca}_2\text{Ta}_{1.8}\text{Nb}_{0.2}\text{O}_7$ ($a = 12.763$ Å, $b = 7.310$ Å, $c = 30.190$ Å, $\beta = 94.09^\circ$, space group $C2$). 6T

* Correspondence author
(e-mail: stefan.ebbinghaus@physik.uni-augsburg.de)

Fig. 1. Representation of the various modifications of $\text{Ca}_2\text{Ta}_2\text{O}_7$. Trigonal structures are viewed along the $[110]$ -direction, while monoclinic and orthorhombic structures are viewed along the $7.3 \text{ \AA}$ long axis. Circles represent the Ca ions, while the TaO_6 units are shown as polyhedra.

$\text{Ca}_{1.9}\text{Sm}_{0.1}\text{Ta}_{1.9}\text{Ti}_{0.1}\text{O}_7$ crystallizes in space group $P3_1$ with $a = 7.353 \text{ \AA}$ and $c = 36.264 \text{ \AA}$.

A mixture of single crystals of the 3T and 4M structure (both with the composition $\text{Ca}_{1.92}\text{Ta}_{1.92}\text{Nd}_{0.08}\text{Zr}_{0.08}\text{O}_7$) was obtained by flux growth of $\text{Ca}_2\text{Ta}_2\text{O}_7$, doped with $\text{Nd}_2\text{Zr}_2\text{O}_7$ [5]. The 4M crystals possess a unit cell with $a = 12.761 \text{ \AA}$, $b = 7.358 \text{ \AA}$, $c = 24.565 \text{ \AA}$, $\beta = 100.17^\circ$ (space group $C2$), while the 3T compound crystallizes in $P3_1$ with $a = 7.356 \text{ \AA}$ and $c = 18.116 \text{ \AA}$.

Figure 1 shows a comparison of the various structure types of (doped) $\text{Ca}_2\text{Ta}_2\text{O}_7$. In this article we describe the crystal growth, structure determination and optical properties of a new 8O polytype of pure $\text{Ca}_2\text{Ta}_2\text{O}_7$.

2. Experimental

2.1. Synthesis

Polycrystalline $\text{Ca}_2\text{Ta}_2\text{O}_7$ was prepared by classical solid state synthesis starting from CaCO_3 and Ta_2O_5 . The thoroughly ground mixture of these starting materials was

heated in an alumina crucible for 24 hours at 1400°C in air. X-ray powder diffraction confirmed that the reaction product was single-phase 3T $\text{Ca}_2\text{Ta}_2\text{O}_7$. The powder was pressed into two bars of $70 \times 4 \times 4 \text{ mm}^3$ and $15 \times 2 \times 2 \text{ mm}^3$, respectively, which served as feed and seed rod for the crystal growth experiment. The rods were sintered for 12 h at 1400°C to increase their mechanical stability and density. Crystal growth was carried out in a GERO SPO optical floating zone furnace. This furnace is equipped with two 1000 W halogen lamps, the radiation of which is focussed by two ellipsoidal gold-coated mirrors. Growth speed was adjusted to 5 mm/h . During the experiment the seed rod was rotated at a speed of 30 rpm, while the feed rod was kept still. The growth resulted in a colorless crystal boule of approximately 2 cm length and 5 mm diameter. From a thin slice of the boule several small cubes were cut for the X-ray structure analysis, while a second slice was used for the spectroscopic measurements.

2.2. Structure analysis

X-ray intensity data were collected at room temperature on a BRUKER SMART APEX CCD diffractometer using MoK_α -radiation ($\lambda = 0.71073 \text{ \AA}$). Raw data were processed with the BRUKER program SAINT. The crystal structure was determined by direct methods using SHELXS-97 [6] and subsequent difference Fourier calculations. For the full-matrix least-squares structure refinement on F^2 the program SHELXL-97 was used [7]. The intensity data were originally indexed with a hexagonal unit cell with $a = 7.36 \text{ \AA}$, $c = 48.26 \text{ \AA}$. All attempts to find a structure solution in the trigonal or hexagonal crystal system failed and the internal R value was exceptionally high ($R_i = 0.318$). We therefore transformed the unit cell to the orthorhombic system. This resulted in a strong decrease of R_i to a value of 0.156 for the uncorrected data. An inspection of the systematic absence conditions led to the only suggested space group $C22_1$. Structure solution with SHELXS-97 [6] using direct methods immediately yielded the positions of the great majority of Ta and Ca and most of the oxygen ions. Remaining atomic positions were found by difference Fourier calculation. The absorption correction turned out to be a very critical point of the structure analysis. Due to the high absorption coefficient of the title compound ($\mu \approx 40 \text{ mm}^{-1}$) the internal R value of the uncorrected data set was quite high ($R_i = 0.156$) and the displacement parameters of the Ta ions were found to be unreliably small. Various approaches for the absorption correction were tested. These included i) numerical correction based on the shape of the face-indexed crystal ii) HABITUS optimization based on R_i [8] iii) several runs with the BRUKER absorption program SADABS using different parameter settings. Unexpectedly, the trials i) and ii) did not significantly improve the R_i value. The SADABS runs led to a decrease of R_i to a value of approximately 0.07–0.08 (depending on the options chosen) but yielded displacement parameters of zero $\text{\AA}^2$ for the Ta ions. The best results were achieved with the MULABS option implemented in the program suite PLATON [9]. Although the

Table 1. Crystallographic data and details of the structure refinement of Ca₂Ta₂O₇.

Empirical formula	Ca ₂ Ta ₂ O ₇
Formula weight	554.06 g/mol
Temperature	293 K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, C222 ₁ (No. 20)
Unit cell dimensions	$a = 7.3690(2)$ Å $\alpha = 90^\circ$ $b = 12.7296(3)$ Å $\beta = 90^\circ$ $c = 48.263(1)$ Å $\gamma = 90^\circ$
Volume	4527.3(2) Å ³
Z, Calculated density	32, 6.50 g · cm ⁻³
Absorption coefficient	40.44 mm ⁻¹
$F(000)$	7744
Crystal shape	Cube
Crystal size	0.17 × 0.13 × 0.11 mm ³
Theta range for data collection	0.84 to 44.70°
Index ranges	$-14 \leq h \leq 14$, $-25 \leq k \leq 25$, $-95 \leq l \leq 95$
Total reflections	153826
Unique reflections, R_{int}	17865, 0.1009
Unique reflections with $F_o > 4\sigma$	14603
Completeness to $2\theta = 42.45^\circ$	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17865/0/398
Goodness-of-fit on F^2	1.241
Flack parameter	0.016(10)
Final R indices ($F_o > 4\sigma$)	$R_1 = 0.0413^a$, $wR_2 = 0.0795^b$
R indices (all data)	$R_1 = 0.0507^a$, $wR_2 = 0.0808^b$
Weight parameters a , b^c	0.0121, 0.0000
Extinction coefficient	0.000061(2)
Largest diff. peak and hole	4.96 and -5.05 e · Å ⁻³

Note:

a: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

b: $wR_2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2))^2]^{1/2}$

c: $w = 1/[(\sigma(F_o^2))^2 + (aP)^2 + bP]$ with $P = (\max(F_o^2) + 2F_c^2)/3$

obtained value of $R_i = 0.10$ is not completely satisfying, we believe it can be accepted, taking into account that almost 154 000 reflections have been merged.

The structural model was tested for a possible higher symmetry using PLATON [9]. No additional symmetry elements were detected. Since many of the known structures of Ca₂Ta₂O₇ crystallize in monoclinic space groups, we additionally tried to reduce the symmetry. Attempts to refine the structure in the non-isomorphic subgroups $C2$ and $P2_1$ did not yield satisfying results. We therefore conclude that $C222_1$ actually is the correct space group.

The final structure refinement converged smoothly to the results given in Table 1. Although the scattering power of oxygen is quite small compared to the contribution of the cations, it was possible to refine the displacement parameters of the oxide ions anisotropically. Only for one oxygen (O27) we observed a strongly oblate displacement tensor with one principal axis being unreliably small (≈ 0.002 Å²). For this reason we decided to refine this atom isotropically.

2.3. Optical measurements

A thin slice was cut from the crystal boule ground to a thickness of 0.2 mm. This disk was polished at both sides. Measurements in the UV-Vis region were carried out using a VARIAN CARY 50 spectrometer. For the IR regime a BRUKER EQUINOX 55 spectrometer was used.

3. Results and discussion

Figure 2 shows the atoms within one unit cell of 8O Ca₂Ta₂O₇. Displacement ellipsoids are given with a 90% probability. Atomic positions and displacement parameters are listed in Tables 2 and 3, respectively.

The 8O structure is closely related to the other polymorphs of Ca₂Ta₂O₇. As can be seen in Fig. 2 as well as in the polyhedral representation in Fig. 1, the 8O structure consists of the same 6 Å thick basic building slabs as the other known modifications. One of these slabs is shown in more detail in Fig. 3. It can be described as a double layer

Fig. 2. Crystal structure of 8O Ca₂Ta₂O₇ viewed approximately along the [100]-direction. Displacement ellipsoids are drawn at the 90% probability level. Grey, blue and red ellipsoids correspond to Ta, Ca and O ions, respectively.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (in Å²). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Ta11	0.26100(6)	0	0	0.01361(6)
Ta12	0.50776(4)	0.74902(2)	0.00159(1)	0.01306(4)
Ca1	0.2606(4)	0.50000(0)	0.00000(0)	0.0245(4)
Ta2	0.24125(4)	0.65440(2)	0.06271(1)	0.01362(4)
Ca21	0.7551(3)	0.6769(1)	0.06366(4)	0.0224(3)
Ca22	0.0102(2)	0.4206(1)	0.06263(4)	0.0195(3)
Ca23	0.5222(2)	0.4215(1)	0.06076(4)	0.0212(3)
Ta31	0.25417(5)	0.33590(2)	0.12450(1)	0.01346(5)
Ta32	0.50425(5)	0.58398(3)	0.12619(1)	0.01311(5)
Ta33	0.75271(5)	0.33433(2)	0.12357(1)	0.01332(5)
Ca3	0.4991(3)	0.0827(2)	0.12569(4)	0.0257(4)
Ta4	0.27356(4)	0.00083(2)	0.18881(1)	0.01380(5)
Ca41	0.9956(3)	0.2464(1)	0.18599(4)	0.0240(4)
Ca42	0.2477(3)	0.4984(1)	0.18765(3)	0.0204(3)
Ca43	0.4956(3)	0.2569(2)	0.18563(5)	0.0306(5)
Ta51	0.50000(0)	0.41122(4)	0.25000(0)	0.01359(8)
Ta52	0.75044(5)	0.16033(2)	0.24719(1)	0.01377(5)
Ca5	0.00000(0)	0.4094(2)	0.25	0.0285(6)
O1	0.5570(7)	0.3985(4)	0.0059(1)	0.0181(10)
O2	0.9637(7)	0.4020(4)	0.0062(1)	0.0157(10)
O3	0.2611(8)	0.2779(4)	0.0122(1)	0.0206(9)
O4	0.5690(8)	0.2282(5)	0.0384(1)	0.0203(10)
O5	0.9561(7)	0.2271(5)	0.0407(1)	0.0175(10)
O6	0.7624(8)	0.0233(4)	0.0442(1)	0.0171(8)
O7	0.2581(8)	0.0176(4)	0.0408(1)	0.0183(9)
O8	0.9434(8)	0.1057(4)	0.0864(1)	0.0181(10)
O9	0.5351(7)	0.1002(4)	0.0819(1)	0.0176(10)
O10	0.7453(8)	0.2979(4)	0.0840(1)	0.0164(8)
O11	0.2826(7)	0.3423(4)	0.0841(1)	0.0174(9)
O12	0.8397(8)	0.1993(4)	0.1374(1)	0.0181(9)
O13	0.6735(8)	0.4759(4)	0.1126(1)	0.0187(10)
O14	0.5046(9)	0.2840(4)	0.1299(1)	0.0214(10)
O15	0.2023(8)	0.1859(4)	0.1198(1)	0.0204(10)
O16	0.2992(7)	0.4881(4)	0.1300(1)	0.0158(9)
O17	0.9999(8)	0.3885(4)	0.1183(1)	0.0171(9)
O18	0.4607(7)	0.0794(5)	0.1702(1)	0.0179(9)
O19	0.0624(7)	0.0651(4)	0.1653(1)	0.0176(10)
O20	0.2337(8)	0.3288(4)	0.1655(1)	0.0180(9)
O21	0.7530(9)	0.3792(4)	0.1627(1)	0.0187(8)
O22	0.2250(8)	0.1261(4)	0.2114(1)	0.0201(10)
O23	0.7435(8)	0.1784(4)	0.2074(1)	0.0180(8)
O24	0.5670(7)	0.4216(5)	0.2101(1)	0.0171(9)
O25	0.9628(7)	0.4212(5)	0.2059(1)	0.0187(10)
O26	0.8031(7)	0.0109(4)	0.2399(1)	0.0169(9)
O27	0	0.6162(6)	0.25	0.0229(15) ^a
O28	0	0.2175(5)	0.25	0.0160(12)
O29	0.3224(8)	0.3007(4)	0.2410(1)	0.0198(10)

a: U_{iso}

of TaO₆ octahedra. Within the lower layer, the octahedra are tilted and share common corners. Neglecting the tilting, it can be said that the crystallographic c axis lies parallel to one four-fold axis of the octahedra. This connect-

ing scheme reminds of the arrangement found in the large family of (cubic) perovskites. In the upper layer the TaO₆ octahedra are oriented in a way that one of their three-fold axes lies parallel to c . This orientation is typical for the family of hexagonal perovskites. These considerations reveal a number of similarities between the weberite and the perovskite structures although they are not directly related.

Focusing on the metal ions, the basic 6 Å unit can be described as consisting of one Ca₃Ta layer and one Ta₃Ca layer. The arrangement of the TaO₆ octahedra within these two layers is shown in Fig. 4. For the Ta₃Ca layers, six corner-sharing octahedra form a hexagonal ring, the center of which is occupied by the larger Ca ion. The Ca₃Ta layers show a complementary arrangement. In these layers hexagonal rings of Ca ions are found and the Ta ions are located in the centers of these rings. As a consequence, the TaO₆ octahedra in these layers are not connected to each other.

The oxygen coordination of the Ca ions in the Ca₃Ta and Ta₃Ca layers is shown in Fig. 5. Within the Ta₃Ca layers the Ca ions possess a hexagonal bipyramidal oxygen coordination. These bipyramids are not connected to each other and slightly tilted with respect to the c axis. The Ca coordination geometry within the Ca₃Ta layers is less symmetric. It can either be described as highly distorted cubes or as distorted hexagonal bipyramids. These cubes/bipyramids share common edges.

Bond lengths for the Ta and Ca ions are listed in Table 4. Since the number of individual bonds is quite large we decided to only give the maximum and minimum values and the average distances. The Ta–O distances lie in the interval from 1.898 Å to 2.119 Å. Average bond lengths for the TaO₆ octahedra range from 1.964 Å to 1.999 Å. These values are quite similar to the ones observed for other modifications of Ca₂Ta₂O₇. For the 4M, 5M, 6T and 7M polytypes average Ta–O distances between 1.95 Å and 2.01 Å were found [2, 3, 5]. Additionally, the shortest and longest Ta–O distances for all these structures are in the range between 1.89 Å and 2.17 Å. Looking at table 4 it is striking that while most of the TaO₆ octahedra are only slightly distorted (i.e. the individual bond distances show little deviations from their average values), the coordination geometry around Ta2 and Ta4 is highly distorted. The reason is that these two tantalum ions are shifted away from the centers of the corresponding octahedra towards two of the oxygen ions. As a result, two Ta–O bonds become extraordinarily short, while the two opposite bonds are elongated. Both Ta ions belong to Ca₃Ta layers, i.e. to those layers in which the TaO₆ octahedra are not directly connected.

Similar results were found for other Ca₂Ta₂O₇ modifications. In all cases, the shortest and the longest Ta–O distances were found for tantalum ions within the Ca₃Ta layers and were caused by a shift of the Ta ions away from the centers of the octahedra. This displacement reminds of the situation found in BaTiO₃, where the Ti ions are shifted towards one of the oxygen atoms. Consequently, it has been speculated that the observed distortion of the TaO₆-octahedra might be the origin of the observed high dielectric constants of about 25 found for other modifications of Ca₂Ta₂O₇ [3; 10]. It would be interesting to see if by a suitable substitution the structural distortion of

Table 3. Anisotropic displacement parameters (in Å²) for Ca₂Ta₂O₇. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta11	0.0139(1)	0.0133(1)	0.0136(2)	−0.0001(1)	0	0
Ta12	0.0133(1)	0.0128(1)	0.0131(1)	0.0001(1)	−0.0001(1)	0.0002(1)
Ca1	0.027(10)	0.0355(11)	0.0111(8)	−0.0025(7)	0	0
Ta2	0.0145(1)	0.0133(1)	0.0131(1)	0.0003(1)	−0.0004(1)	0.0001(1)
Ca21	0.0256(7)	0.0158(5)	0.0259(7)	−0.0062(5)	−0.0067(7)	0.0060(6)
Ca22	0.0165(5)	0.0183(5)	0.0238(7)	−0.0003(6)	−0.0012(6)	0.0005(5)
Ca23	0.0153(6)	0.0250(6)	0.0233(7)	0.0076(6)	0.0021(6)	−0.0007(5)
Ta31	0.0140(1)	0.0129(1)	0.0134(1)	0.0002(1)	0.0002(1)	−0.0001(1)
Ta32	0.0136(1)	0.0120(1)	0.0138(1)	0.0001(1)	−0.0009(1)	0.0003(1)
Ta33	0.0133(1)	0.0129(1)	0.0138(1)	−0.0006(1)	0.0003(1)	0.0007(1)
Ca3	0.0376(10)	0.0280(8)	0.0115(6)	0.0016(6)	0.0021(7)	0.0114(9)
Ta4	0.0144(1)	0.0136(1)	0.0134(1)	−0.0005(1)	−0.0004(1)	0.0002(1)
Ca41	0.0229(8)	0.0194(7)	0.0298(9)	−0.0049(6)	0.0088(7)	−0.0042(8)
Ca42	0.0229(6)	0.0169(5)	0.0215(6)	0.0002(5)	0.0001(6)	0.0009(9)
Ca43	0.0330(10)	0.0213(8)	0.0377(11)	−0.0089(7)	−0.0205(9)	0.0102(9)
Ta51	0.0149(2)	0.0121(2)	0.0138(2)	0	0.0002(1)	0
Ta52	0.0142(1)	0.0132(1)	0.0139(1)	0.0002(1)	0.0003(1)	0.0004(1)
Ca5	0.0404(15)	0.0277(13)	0.018(13)	0	−0.0033(11)	0
O1	0.019(2)	0.010(2)	0.025(3)	0.001(2)	0.002(2)	−0.002(2)
O2	0.013(2)	0.018(2)	0.016(2)	−0.005(2)	−0.000(2)	0.004(2)
O3	0.018(2)	0.022(2)	0.022(2)	−0.002(2)	−0.003(2)	0.000(2)
O4	0.021(2)	0.023(3)	0.017(2)	0.001(2)	−0.003(2)	0.003(2)
O5	0.014(2)	0.022(2)	0.016(2)	0.004(2)	0.003(2)	−0.002(2)
O6	0.018(2)	0.014(2)	0.019(2)	−0.002(1)	0.001(2)	0.001(2)
O7	0.022(2)	0.018(2)	0.015(2)	−0.002(1)	−0.001(2)	0.001(2)
O8	0.020(2)	0.018(2)	0.017(2)	0.002(2)	−0.001(2)	0.005(2)
O9	0.018(2)	0.020(2)	0.016(2)	−0.003(2)	0.000(2)	0.001(2)
O10	0.019(2)	0.014(2)	0.016(2)	−0.003(1)	−0.001(2)	−0.002(2)
O11	0.021(2)	0.017(2)	0.014(2)	0.001(2)	0.001(2)	−0.000(2)
O12	0.024(2)	0.013(2)	0.018(2)	−0.001(2)	−0.001(2)	0.006(2)
O13	0.025(2)	0.012(2)	0.019(2)	−0.000(2)	0.008(2)	0.006(2)
O14	0.023(3)	0.014(2)	0.027(3)	0.002(2)	0.001(2)	−0.003(2)
O15	0.023(3)	0.020(2)	0.018(2)	0.004(2)	−0.004(2)	−0.002(2)
O16	0.012(2)	0.008(2)	0.028(3)	−0.000(2)	0.000(2)	−0.002(1)
O17	0.008(2)	0.024(2)	0.019(2)	0.003(2)	−0.001(2)	−0.002(2)
O18	0.019(2)	0.022(2)	0.013(2)	−0.002(2)	0.002(2)	−0.003(2)
O19	0.017(2)	0.018(2)	0.017(2)	−0.002(2)	−0.001(2)	0.003(2)
O20	0.023(2)	0.018(2)	0.013(2)	0.003(1)	0.000(2)	−0.003(2)
O21	0.022(2)	0.019(2)	0.015(2)	−0.006(1)	0.003(2)	0.001(2)
O22	0.024(3)	0.017(2)	0.018(2)	−0.004(2)	−0.007(2)	0.004(2)
O23	0.017(2)	0.017(2)	0.020(2)	0.003(2)	0.000(2)	0.001(2)
O24	0.016(2)	0.019(2)	0.016(2)	−0.002(2)	0.004(2)	−0.006(2)
O25	0.018(2)	0.020(2)	0.018(2)	0.002(2)	−0.000(2)	0.002(2)
O26	0.021(2)	0.018(2)	0.012(2)	0.001(2)	0.001(2)	0.001(2)
O27 ^a	0.023(2)	0.023(2)	0.023(2)	0	0	0
O28	0.018(3)	0.006(2)	0.024(3)	0	−0.002(3)	0
O29	0.023(2)	0.014(2)	0.022(2)	0.002(2)	−0.002(2)	−0.003(2)

a: U_{iso}

8O Ca₂Ta₂O₇ can be fine-tuned and how these changes affect the dielectric properties.

The individual Ca—O distances found for 8O Ca₂Ta₂O₇ stretch over a wide range from 2.144 Å to 3.111 Å. Aver-

age values for the CaO₈ units are in the interval 2.524–2.604 Å. Again, these values are comparable to the ones found for the other modifications. The shortest Ca—O distance of 2.08 Å was found for the 4M structure [5], while

Fig. 3. Basic building block of the weberite-related structures of $\text{Ca}_2\text{Ta}_2\text{O}_7$.

the longest distance was reported for the 7M modification (3.06 Å) [3].

UV-Vis and infrared measurements of 80 $\text{Ca}_2\text{Ta}_2\text{O}_7$ are shown in Figs. 6 and 7. Since the two regions of the electromagnetic spectrum are usually recorded as a function of wavenumber and wavelength, respectively, we have added a uniform energy scale (in eV) as a second x -axis on top of the two plots. Looking at the figures, it is striking that $\text{Ca}_2\text{Ta}_2\text{O}_7$ shows a high transparency in a wide frequency range both in the infrared and visible region. In the IR regime a transmission of about 90% is observed for wavenumbers above 1750 cm^{-1} . We believe that the real trans-

Fig. 4. Ta-oxygen coordination within the Ca_3Ta and Ta_3Ca layers of the basic building unit shown in Fig. 3. Large circles represent the Ca ions.

Ca_3Ta layer

Ta_3Ca layer

Fig. 5. Ca-oxygen coordination within the Ca_3Ta and Ta_3Ca layers of the basic building unit shown in Fig. 3. Grey circles represent the Ta ions.

Table 4. Selected $M\text{--O}$ bond lengths in Å.

Atom	range	average
Ta11	1.969–2.003	1.985
Ta12	1.945–2.003	1.970
Ca1	2.155–2.887	2.533
Ta2	1.898–2.119	1.994
Ca21	2.309–2.796	2.571
Ca22	2.440–2.753	2.592
Ca23	2.323–2.826	2.571
Ta31	1.961–2.012	1.980
Ta32	1.950–1.990	1.969
Ta33	1.952–1.971	1.964
Ca3	2.144–2.970	2.534
Ta4	1.912–2.097	1.999
Ca41	2.271–3.111	2.582
Ca42	2.411–2.811	2.588
Ca43	2.331–3.012	2.604
Ta51	1.971–1.990	1.983
Ta52	1.934–2.053	1.972
Ca5	2.149–2.784	2.524

Note: Estimated standard deviations: 0.005 Å for Ta–O and 0.006 Å for Ca–O

Fig. 6. UV-Vis spectrum of 8O $\text{Ca}_2\text{Ta}_2\text{O}_7$.

parency of the sample is even higher and that the small loss is caused by scattering or reflection of the radiation at the sample surface due to the surface roughness or a slight tilt of the sample with respect to the incident beam. For wave numbers below 1500 cm^{-1} a number of broad overlapping absorption bands are found corresponding to the various M–O–M stretching and bending modes which can occur in the framework of $\text{Ca}_2\text{Ta}_2\text{O}_7$. Since the crystal structure is rather complex and the different peaks can not be separated, no attempts were made to assign the observed bands to individual vibrational modes.

In the near ultraviolet and the visible part of the spectrum a high transparency of the sample was found with no significant absorption bands. At least for the visible region this result was already expected since the sample is completely colorless. At wavelengths below 400 nm the absorption of 8O $\text{Ca}_2\text{Ta}_2\text{O}_7$ increases drastically and reaches a maximum at approximately 245 nm. With the given thickness of the sample the transmission drops to zero. Attempts to reduce the thickness by further grinding and polishing failed because the disc became very fragile and tended to crack.

The observed strong absorption below 400 nm is most likely caused by charge transfer from the occupied oxygen 2p orbitals to vacant Ta 5d states. We are currently trying to assign the absorption spectrum to transitions between individual electronic states using LDA band structure cal-

culations. Unfortunately, these calculations are highly time consuming due to the very large number of atoms within the unit cell.

Ternary (and higher) tantalum oxides often possess interesting dielectric properties making these compounds valuable candidates for technical applications, e.g. in capacitors or frequency filters. Polycrystalline 3T $\text{Ca}_2\text{Ta}_2\text{O}_7$, for example, shows a dielectric constant of about 25 at 1 MHz [10]. For applications in electronic devices dielectric materials must fulfill two more requirements: The quality factor $Q = \epsilon'/\epsilon''$ should be as high as possible and ϵ' should be temperature and frequency independent. Doping of $\text{Ca}_2\text{Ta}_2\text{O}_7$ with Nb seems to be a promising strategy to tailor-made such a material because by a proper choice of the niobium content the temperature coefficient of ϵ' can be tuned to almost zero.

The dielectric properties of $\text{Nd}_2\text{Zr}_2\text{O}_7$ doped 3T $\text{Ca}_2\text{Ta}_2\text{O}_7$ and of Nb doped 5M and 7M $\text{Ca}_2\text{Ta}_2\text{O}_7$ are quite similar [3]: ϵ' is almost frequency-independent in the range 10^4 – 10^9 Hz with values of about 20. Only for frequencies above 5 GHz an increase of ϵ' is observed. The quality factor is in the order of 200, a value that is quite high but not satisfying for technical applications.

The observed distortion of some of the TaO_6 octahedra led us to investigate the dielectric properties of 8O $\text{Ca}_2\text{Ta}_2\text{O}_7$. To our surprise the dielectric response of this modification is quite different from the ones described above. 8O $\text{Ca}_2\text{Ta}_2\text{O}_7$ shows a dielectric behavior typical for a ferroelectric relaxor. ϵ' is much higher than for the other modifications and reaches values of about 60 at room temperature. Upon cooling ϵ' increases to a value of almost 90 at 50 K. This large dielectric constant makes the new modification of calcium tantalate an interesting material for electronic devices. Further investigations of the electric properties are currently in progress and results will be published elsewhere.

4. Conclusions

The simple oxide $\text{Ca}_2\text{Ta}_2\text{O}_7$ shows a number of different modifications. The undoped polycrystalline material transforms from the 3T to the 7M structure at a temperature of about 1450°C . Flux growth yields single crystals of the 7M and 6M polytype. By optical floating zone melting we managed to prepare single crystals of the new 8O modification of $\text{Ca}_2\text{Ta}_2\text{O}_7$. Single crystal X-ray structure determination shows that the 8O modification is very closely related to the other known polytypes and has an orthorhombic weberite-related structure. The unit cell consists of 8 layers of the basic building unit of all modifications. This unit is built of one Ca_3Ta and one Ta_3Ca layer. Both layers contain (distorted) TaO_6 octahedra and CaO_8 hexagonal bipyramids. Within the Ca_3Ta and Ta_3Ca layers these polyhedra possess a different connecting scheme. Some of the TaO_6 octahedra show a strong distortion caused by a shift of the tantalum ion towards one of the octahedral edges. This structural peculiarity might be the origin of the high dielectric constant of $\epsilon' = 60$ – 90 observed for 8O $\text{Ca}_2\text{Ta}_2\text{O}_7$. The potential to alter the dielectric properties by appropriate doping might lead to a fu-

Fig. 7. Infrared spectrum of 8O $\text{Ca}_2\text{Ta}_2\text{O}_7$.

ture technical application of the ternary oxide calcium tantalate in electronic devices.

The high transparency over a wide spectral range from 0.2 eV to 3.5 eV makes $8O\text{Ca}_2\text{Ta}_2\text{O}_7$ an interesting material for optical applications. For example, we are currently investigating the possibility to use $\text{Ca}_2\text{Ta}_2\text{O}_7$ as host lattice for luminescence dopants.

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