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supporting information at journals.iucr.org/bThe crystal structure of $\text{Rb}_2\text{Ti}_2\text{O}_5$ Rémi Federicci,^{a,*} Benoit Baptiste,^b Fabio Finocchi,^c Florin Popa,^d Luc Brohan,^d
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Recent results have demonstrated an exceptionally high permittivity in the range 200–330 K in crystalline titanium oxide $\text{Rb}_2\text{Ti}_2\text{O}_5$. In this article, the possibility of a structural transition giving rise to ferroelectricity is carefully inspected. In particular, X-ray diffraction, high-resolution transmission electron microscopy and Raman spectroscopy are performed. The crystal structure is shown to remain invariant and centrosymmetric at all temperatures between 90 K and 450 K. The stability of the $C2/m$ structure is confirmed by density functional theory calculations. These important findings allow the existence of a conventional ferroelectric phase transition to be ruled out as a possible mechanism for the colossal permittivity and polarization observed in this material.

1. Introduction

The ternary titanium oxides denoted by $M_2\text{Ti}_n\text{O}_{2n+1}$ with $M = \text{Li, Na, K, Rb, Cs, Fr}$, called the Andersson–Wadsley type alkali titanates (Tournoux *et al.*, 1986), with layered structure for $2 \leq n \leq 5$ and tunnel structure for $6 \leq n \leq 8$, are known for their interesting properties (Shripal *et al.*, 2005). In particular, some of them present ferroelectric phase transitions, with remarkably high Curie temperatures (Vikram *et al.*, 2010).

$M_2\text{Ti}_2\text{O}_5$ (MTO) compounds (Andersson–Wadsley compounds with $n = 2$) exhibit a fivefold coordination for titanium, which originally came as a surprise because Ti^{4+} mostly tends to adopt an energetically more stable sixfold coordination (Andersson & Wadsley, 1960). However, Ti^{4+} fivefold coordination was reported later in titanite and zirconolite minerals (Farges, 1997), in a natural titanosilicate mineral (Foster *et al.*, 1999), as well as in a few synthetic compounds (Lii, 1995; Roberts *et al.*, 1996). The MTO compounds offer a certain interest for chemistry because of their oxidation abilities (Wang & Chung, 2009; Wang *et al.*, 2011) but their electrical properties have not been investigated until recently (Federicci *et al.*, 2017).

Little information has been reported to date in the literature concerning the $\text{Rb}_2\text{Ti}_2\text{O}_5$ (RTO) compound. Early structural investigations were made on $\text{K}_2\text{Ti}_2\text{O}_5$ (KTO), where the space group is reported to be $C2/m$ and, more generally, on the MTO family (Andersson & Wadsley, 1960, 1961; Tournoux *et al.*, 1986). To our knowledge, only two reports exist so far on the synthesis and crystal structure of $\text{Rb}_2\text{Ti}_2\text{O}_5$, which was

stated to be consistent with the Cm space group (Schmitz-Dumont & Schulz, 1952; Schmitz-DuMont & Reckhard, 1959).

Recent work (Federicci *et al.*, 2017) on RTO has demonstrated superionic conduction properties stemming from the electrolytic nature of the material due to ionic migration. The ionic conductivity in the temperature range between 200 K and 330 K reaches $10^{-3} \text{ S cm}^{-1}$, whereas the electronic conduction is five orders of magnitude lower. These two properties were demonstrated to yield important polarization phenomena with colossal relative permittivity reaching 10^9 at low frequency (Federicci *et al.*, 2017). However, as these observations are also consistent with ferroelectric-like behavior, the question of a possible associated structural phase transition arises, as an alternative explanation.

In the present work, we report a systematic characterization of RTO crystal structure as a function of temperature. X-ray diffraction and Raman spectroscopy studies are presented. The experimental results are compared to theoretical calculations of the structural and vibrational properties, performed by density functional theory. The role of vacuum-annealing, which was previously found to be responsible for the 'activation' of the electric properties of the RTO material (Federicci *et al.*, 2017), is also studied and discussed.

2. Chemical synthesis

The synthesis of RTO was performed under air by melting TiO_2 (rutile) and RbNO_3 powders (with purities of 99.95%) in a platinum crucible at 1213 K for 3 h. The heating rate was 5 K min^{-1} . The crystals obtained after the slow cooling down process (5 K h^{-1} for 20 h, then 20 K h^{-1}) were kept under dry argon atmosphere in order to avoid hydration. The as-grown crystals exhibit a platelet-shape of typically 1 mm length and hundreds of μm width and thickness.

3. Characterization

3.1. Scanning electron microscopy

Immediately after the end of the chemical synthesis process, RTO crystals were isolated and scanning electron microscopy (SEM) images were acquired on SEM-FEG at low voltages (from 1 to 5 kV). Two SEM images which show the platelet shape of two different crystals are displayed in Fig. 1. The growth direction (larger dimension of the crystal) is found to correspond to the b axis. The crystals clearly show a lamellar structure and are shown to be easily cleavable along the ab planes. This aspect may be of interest either for obtaining a very smooth ab surface or a very thin sample.

3.2. Single-crystal X-ray diffraction

Single-crystal X-ray diffraction data on RTO were collected on a Bruker Kappa-APEXII four-circle diffractometer equipped with a CCD detector, with $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, graphite monochromator) at the IPCM X-ray diffraction platform (Université Pierre et Marie Curie, Paris). The measurements were conducted under a N_2 flux (Oxford

Cryostream 700) in order to protect the sample from humidity. They were carried out at various temperatures (400 K, 293 K and 150 K) in order to evaluate the stability of the structure. Data reduction, cell refinement, space group determination, scaling, and multiscan absorption correction were performed using *CrysAlis PRO* software (Rigaku Oxford Diffraction, 2015).

For all data, the structures were solved in the $C2/m$ space group by direct methods using *SHELXT* (Sheldrick, 2015) implemented in *Olex2* program (Dolomanov *et al.*, 2009). The refinements were then carried out with *SHELXL* (Sheldrick, 2015) by full-matrix least-squares minimization and difference Fourier methods. All atoms were refined with anisotropic displacement parameters.

The crystal structure remains unchanged from 150 to 400 K and the $C2/m$ space group was further confirmed by the fact that refinements conducted within noncentrosymmetric space groups did not improve the model nor the reliability factors

Figure 1
Scanning electron micrographs of two as-grown $\text{Rb}_2\text{Ti}_2\text{O}_5$ crystals from two different batches: (a) magnification $\times 369$ and (b) magnification $\times 4000$. The lamellar structure along the ab planes is clearly evidenced.

Table 1
Single-crystal X-ray diffraction data for $\text{Rb}_2\text{Ti}_2\text{O}_5$.

For all determinations: $0.5(\text{O}_{10}\text{Rb}_4\text{Ti}_4)$, $M_r = 346.74$, monoclinic with space group $C2/m$, $Z = 2$, $F(000) = 316$. Empirical absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm.

	400 K	293 K	150 K
CCDC number	1517161	1517160	1517159
Crystal data			
a, b, c (Å)	11.3419 (12), 3.8198 (5), 7.0103 (8)	11.3370 (13), 3.8244 (5), 6.9946 (8)	11.3457 (12), 3.8195 (5), 6.9699 (8)
β (°)	100.298 (11)	100.308 (12)	100.359 (11)
V (Å ³)	298.82 (6)	298.37 (6)	297.12 (6)
D_x (Mg m ⁻³)	3.854	3.860	3.876
μ (mm ⁻¹)	18.80	18.82	18.90
Crystal size (mm)	$0.3 \times 0.1 \times 0.05$	$0.3 \times 0.1 \times 0.05$	$0.2 \times 0.1 \times 0.05$
Data collection			
Diffractometer	Bruker Kappa-APEXII	Bruker Kappa-APEXII	Bruker Kappa-APEXII
Radiation source	Fine focus sealed tube (Mo)	Fine focus sealed tube (Mo)	Fine focus sealed tube (Mo)
$T_{\min}, T_{\max}$	0.277, 1.000	0.323, 1.000	0.400, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1859, 567, 511	1389, 351, 333	1205, 348, 320
R_{int}	0.023	0.021	0.041
θ values (°)	$\theta_{\max} = 32.5, \theta_{\min} = 3.0$	$\theta_{\max} = 26.4, \theta_{\min} = 3.0$	$\theta_{\max} = 26.4, \theta_{\min} = 3.0$
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.756	0.625	0.625
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.092, 1.08	0.028, 0.073, 1.17	0.050, 0.134, 1.11
No. of reflections	567	351	348
No. of parameters	30	29	29
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.82, -1.63	0.68, -1.45	1.52, -1.93

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$).

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

	Atom	x	y	z	$U(\text{eq})$
400 K	Rb1	988.8 (5)	5000	8486.6 (7)	26.7 (2)
	Ti1	3525.6 (6)	5000	5883.7 (11)	12.6 (2)
	O1	5000	5000	5000	24.5 (11)
	O2	3763 (4)	5000	8355 (5)	25.7 (8)
	O3	1780 (3)	5000	4786 (5)	17.4 (7)
293 K	Rb1	985.1 (5)	5000	8481.2 (8)	21.0 (3)
	Ti1	3524.9 (8)	5000	5884.9 (14)	10.8 (3)
	O1	5000	5000	5000	19.7 (13)
	O2	3762 (4)	5000	8367 (6)	20.7 (9)
	O3	1780 (3)	5000	4797 (5)	14.3 (8)
150 K	Rb1	981.2 (8)	5000	8472.5 (12)	14.9 (5)
	Ti1	3522.9 (14)	5000	5897 (2)	9.7 (5)
	O1	5000	5000	5000	15 (2)
	O2	3767 (6)	5000	8391 (9)	15.6 (15)
	O3	1772 (6)	5000	4776 (9)	14.9 (14)

whatever the temperature. Moreover, the atomic displacement parameters did not reveal any suspect elongated shape that would have been a sign of atomic positions incompatible with the $C2/m$ space group. The single-crystal data parameters and the atomic positions at 400 K, 293 K and 150 K are reported in Tables 1 and 2, respectively. (The reliability factors obtained from refinement of data collected at low temperature are less satisfactory due to the likely fragmentation of the crystal during the cooling.)

The unit cell of RTO is shown in Fig. 2 using *VESTA* software (Momma & Izumi, 2011). This two-dimensional

structure consists in alternate layers of Ti–O (namely $\text{Ti}_2\text{O}_5^{2-}$) and Rb (namely Rb^+) atoms stacked along the c axis. The Ti–O layers correspond to planes of pyramids pointing up or down and sharing either corners or edges. The Ti atoms are at the center of these slightly tilted square-based-pyramids and are therefore surrounded by five oxygen atoms.

The structure is consistent with the space group $C2/m$ and identical for all the measured temperatures. The volume as well as the cell parameter c are found to decrease with decreasing temperature, as expected. The pyramid apical

Figure 2
Structure of $\text{Rb}_2\text{Ti}_2\text{O}_5$ as obtained from the XRD measurements and visualized using *VESTA* software. The corresponding space group is $C2/m$. Please note the lamellar character of the structure, the alternate downward and upward pyramids and the fivefold coordination for Ti atoms.

angle O1—O2—O3 (within the bc plane) decreases linearly from 400 K to 150 K of about 0.3° . The distance between the apical oxygen and the titanium atom increases with decreasing temperature. This tends to indicate that the pyramid is more elongated at lower temperature. Of course this would deserve further confirmation by a more systematic study including more temperature points.

3.3. Powder X-ray diffraction

The X-ray powder diffraction (XRD) patterns were recorded at the IMPMC X-ray diffraction platform using an XPert Pro Panalytical diffractometer equipped with a Cu $K\alpha$ radiation source ($\lambda K\alpha_1 = 1.54056 \text{ \AA}$, $\lambda K\alpha_2 = 1.54439 \text{ \AA}$) with an XCelerator detector. The measurements were conducted under nitrogen atmosphere (under vacuum for 100 K acquisition) in an Anton Paar HTK 450 temperature-controlled chamber. Rietveld refinements (Rietveld, 1969) were performed with the *FullProf* suite of programs (Rodríguez-Carvajal, 1993) on X-ray powder diffraction patterns recorded in Bragg–Brentano geometry. The background was modeled using a 12-coefficient-polynome, and Thomson–Cox–Hasting

Table 3

Results of the Rietveld refinement on the X-ray powder patterns of $\text{Rb}_2\text{Ti}_2\text{O}_5$ at different temperatures.

	400 K	300 K	200 K	100 K
Space group	$C2/m$	$C2/m$	$C2/m$	$C2/m$
a (Å)	11.34378 (2)	11.34545 (2)	11.34381 (2)	11.34265 (3)
b (Å)	3.82905 (6)	3.82824 (5)	3.82756 (5)	3.82557 (6)
c (Å)	7.00371 (5)	6.99109 (5)	6.98718 (5)	6.96969 (6)
β ($^\circ$)	100.2413 (6)	100.2889 (5)	100.2939 (6)	100.3379 (7)
V (Å ³)	299.365 (8)	298.762 (7)	298.495 (7)	297.521 (9)
R_{Bragg} ($^\circ$)	13.4	9.86	12.1	13

Voigt functions (Finger *et al.*, 1994) were used as peak shape functions. Preferred orientation was taken into account in the refinements, as all (001) reflections were overestimated. Measurements in a capillary would have limited this effect but they were not possible because of the Bragg Brentano (reflection) geometry imposed by our cryostat. The diffractograms collected on RTO are displayed in Fig. 3 for different temperatures ranging between 100 K and 400 K. Table 3 gives the lattice parameters obtained from the Rietveld refinements performed on the X-ray powder patterns that are also shown in Fig. 3, with Cu $K\alpha$ spectroscopic wavelength.

An overall zero-shift parameter and lattice parameters were refined, together with profile parameters and atomic positions.

The atomic positions and lattice parameters extracted from the single-crystal and the powder measurements are found to be consistent and allow the $C2/m$ structure to be established, over the investigated range of temperature. The refinements reveal that the single-crystal structure is representative of the whole sample and further confirm the absence of structural transition from 100 K to 400 K. They also demonstrate that the structure is identical to the one previously reported for $\text{K}_2\text{Ti}_2\text{O}_5$ (Andersson & Wadsley, 1961).

3.4. High-resolution transmission electron microscopy

High-resolution transmission electron micrographs (HRTEM) were recorded at INSA (Lyon) for a RTO sample (using a HR-TEM JEM-2010F from JEOL Ltd, Tokyo, Japan). The TEM lamella were prepared using a Ga^{2+} focussed ion beam (NVision 40 from Carl Zeiss, Oberkochen, Germany). Fig. 4 allows us to assess the very good crystallinity of the crystal on a local scale.

The inset of Fig. 4 shows an enlargement of a particular region of the image. An overlay of the crystal structure as calculated from XRD data (as described above) is displayed on top of the micrograph, both in excellent agreement. This provides an additional confirmation that the $C2/m$ structure calculated from the XRD measurement is correct.

4. Raman spectroscopy

Raman spectroscopy measurements were performed on RTO crystals over the range of temperature 90–450 K under controlled atmosphere conditions. The set-up consisted of an argon laser source (Spectra-physics Argon 514.5 nm), a spec-

Figure 3
Rietveld refinements and $\text{Rb}_2\text{Ti}_2\text{O}_5$ powder X-ray diffraction patterns (Cu wavelength) at 300 K (top) and 100 K (bottom). The red circles are the experimental points, the black line is the calculated pattern, the green vertical ticks refer to Bragg reflections and the blue line is the difference between observed and calculated patterns. Similar diffractograms at 200 K and 400 K are displayed in the supporting information. The diffractograms are identical at all temperatures, ruling out strong evidence for a structural transition.

Figure 4

High-resolution transmission electron micrograph of an $\text{Rb}_2\text{Ti}_2\text{O}_5$ sample along the $[110]$ axis. A magnification of the image contained within the white rectangle is displayed in the inset with superposition of a simulated crystal structure obtained from X-ray diffraction data. The color codes for the atoms are the same as for Fig. 2.

trometer (T64000 HORIBA Jobin Yvon), a set of optical microscopy lens in order to focus the laser beam over a few micrometers and a cryostat (Linkham FTIR 600) used to control the helium atmosphere and the temperature. The power of the laser beam was set to 140 mW and the recording times to 30 s. Each Raman spectrum is an average from three distinct spectra acquired in a row.

Raman spectra recorded between 90 K and 450 K over the range $180\text{--}1300\text{ cm}^{-1}$ are plotted in Fig. 5. As-grown samples that had been kept under dry atmosphere were used. The measurements were performed in the following order: 300 K, then cooling down to 240 K, 200 K, 140 K, 90 K and then warming up to 450 K. The spectra remain qualitatively

Figure 5

Experimental Raman spectra obtained on an $\text{Rb}_2\text{Ti}_2\text{O}_5$ as-grown crystal as function of the temperature under helium atmosphere between 180 cm^{-1} and 1300 cm^{-1} . The first spectrum is taken at 300 K, then the following spectra are collected at 240 K, 200 K, 140 K and 90 K, then the last spectrum is taken at 450 K. No significant changes occur with temperature variation.

unchanged when temperature is varied between 300 K and 90 K, which attests to the stability of the structure over this range of temperatures. However some small features at around 300 cm^{-1} and 1000 cm^{-1} are seen to vary as function of temperature. (This may be related to some distortion in the structure due either to temperature or to small displacement of the laser beam with temperature but does not question the $C2/m$ structure.)

This Raman spectroscopy investigation represents therefore a second probe attesting to the overall stability of the centrosymmetric $C2/m$ crystal structure of RTO between 90 K and 300 K.

5. Density functional theory calculations

5.1. Crystal structure

The structural calculations were performed on the RTO unit cell, which consists of two formula units, through the *Quantum Espresso* package (Giannozzi *et al.*, 2009) that is based on the density functional theory (DFT). Both local density approximation (LDA) and generalized gradient approximation (GGA) functionals were used (Perdew *et al.*, 1996). We employed ultra-soft pseudopotentials, which include semi-core states for Rb and Ti. A Monkhorst–Pack $2 \times 6 \times 3$ grid and a cutoff energy of 50 Ryd for the expansion of the Kohn–Sham (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) orbitals in plane waves ($4\times$ as large for the charge density and potential) were enough to obtain the converged energies and the structural parameters.

The initial conditions of the structural optimization are the following: the space group was set to $C2/m$ and the atomic positions were those extracted from the X-ray diffraction measurements, which are given in Table 2. The lattice parameters, angles and atomic positions were then left free during the calculation. Their final values, within either the GGA or the LDA approximations, are collected in Table 4. A series of structural optimizations have been conducted at several volumes around the equilibrium volume. The Murnaghan equation of state (Murnaghan, 1944) was used to extract the four parameters: the equilibrium volume V_0 , the equilibrium internal energy E_0 , the bulk modulus B_0 and its pressure derivative B_0' , that are all given in Table 4.

The computed atomic positions are reported in Table 5. We see that the structural parameters that were computed within the GGA approximation are extremely close to their experimental counterparts that are collected in Table 1. The computed enthalpy of formation of RTO at zero pressure from the elementary stable phases $\text{Rb}_{(s)}$, $\text{Ti}_{(s)}$ and $\text{O}_{2(gas)}$ is -309.8 kJ^{-1} , within this approximation. These theoretical calculations thus confirm that the structure is thermodynamically stable and can be predicted with a high level of accuracy.

5.2. Band structure

The band structure pictured in Fig. 6 is calculated using the GGA functional for the corresponding optimized crystal

Table 4

Computed equilibrium lattice constants within the GGA and the LDA.

GGA: generalized gradient approximation; LDA: local density approximation. The equilibrium volume V_0 , bulk modulus B_0 and its pressure derivative B_0' have been obtained through a fit to the Murnaghan equation of state (see text).

	GGA	LDA
a (Å)	11.3318	11.1425
b (Å)	3.8322	3.7492
c (Å)	6.9863	6.7665
α (°)	90	90
β (°)	100.110	100.327
γ (°)	90	90
V_0 (Å ³)	298.688	278.105
E_0 (Ryd)	−980.1266 (6)	−980.4192 (1)
B_0 (GPa)	52.6 (4)	71.0 (2)
B_0'	8.8 (6)	4.6 (3)

structure. The path used along the Brillouin zone is chosen using the MCL structure (Setyawan & Curtarolo, 2010). A gap of at least 3.54 eV, which is likely to be underestimated as usual in the DFT-GGA, attests to the insulating nature of the RTO crystal.

5.3. Phonon modes

Phonon mode calculations are based on the density functional perturbation theory (Baroni *et al.*, 2001). These calculations were performed by using LDA or GGA functionals and carried out for the corresponding relaxed structures. The phonon frequencies at the center of the Brillouin zone were computed with ultrasoft pseudopotentials, whereas the Raman intensities were estimated by employing norm-conserving pseudopotentials on top of the phonon calculations, and are therefore less accurate than the frequencies themselves. The theoretical phonon spectra are convolved with Lorentzians and plotted in Fig. 7. The Raman intensities and the phonon

Figure 6

Band structure of $\text{Rb}_2\text{Ti}_2\text{O}_5$ calculated with GGA functional (see text). The high-symmetry points are chosen following the path of the MCL structure (Setyawan & Curtarolo, 2010). The highest occupied electronic level in the valence band is set at zero, while the dashed line marks the lowest electronic level in the conduction band.

Table 5

Fractional atomic coordinates ($\times 10^4$) after structural relaxation for the $\text{Rb}_2\text{Ti}_2\text{O}_5$ crystal, within the GGA.

Atom	x	y	z
Rb	1003	5000	8493
Ti	3524	5000	5912
O1	5000	5000	5000
O2	3754	5000	8469
O3	1769	5000	4811

frequencies are extracted from the DFT calculations whereas the full width at half-maximum is arbitrarily set to 1 in order to render them discernible.

With respect to the experimental data, the computed frequencies are higher with the LDA and lower with the GGA. This can be related to the fact that the LDA functional generally underestimates the lattice parameters and provides stiffer force constants, whereas the GGA does the reverse. When looking at the high-frequency part of the spectrum, the four phonon modes are bracketed by the theoretical phonon modes found with GGA and LDA functionals, which differ by not more than 56 cm^{-1} . These four phonon modes are denoted ν_1 , ν_2 , ν_3 and ν_4 , from small to high frequencies. The representations of these four phonon modes are sketched in Fig. 8. They all correspond to vibrational modes of the Ti—O bonds.

At low frequencies, ten theoretical modes were computed between 80 cm^{-1} and 330 cm^{-1} . They can be unambiguously related to the set of experimental modes in the same wavenumber range, even though their intensities do not match with the experimental ones. The representations of all the calculated phonon modes are displayed in the supplementary material. The good agreement between the calculated phonon spectrum for the simulated RTO system and the Raman spectrum obtained experimentally on a RTO crystal confirms that each mode can be assigned and analyzed in terms of a consistent set of atomic displacements and excludes the presence of singularities.

Figure 7

Experimental and simulated Raman spectra for $\text{Rb}_2\text{Ti}_2\text{O}_5$. The black squares represent the experimental Raman spectrum data points, between 10 cm^{-1} and 1200 cm^{-1} for a crystal of $\text{Rb}_2\text{Ti}_2\text{O}_5$ measured at 300 K. The blue and red curves are the theoretical Raman spectra simulated with DFT using respectively LDA and GGA functionals. The agreement is very good, as may be seen for the ν_1 , ν_2 , ν_3 and ν_4 phonon modes, taking into account the tendencies of LDA and GGA to respectively overestimate and underestimate the phonon frequencies. This confirms that the structure is consistent with the centrosymmetric $C2/m$ space group. The indicated ν_1 , ν_2 , ν_3 and ν_4 phonon modes are represented in Fig. 8.

The computed diagonal effective charges for Ti are $Z_{xx}^* = 4.71$, $Z_{yy}^* = 4.72$, $Z_{zz}^* = 3.08$, with much smaller off-diagonal elements Z_{xz}^* and Z_{zx}^* . In contrast to typical ferroelectric crystals such as BaTiO_3 (Rabe & Ghosez, 2007), the effective charges do not show a relevant anomalous contribution, which points toward the absence of an electrically-driven instability in RTO.

6. Role of vacuum annealing

As reported earlier (Federicci *et al.*, 2017), the remarkable electrical properties of RTO are strongly enhanced for

Figure 8

Representations of the vibrational phonon modes ν_1 , ν_2 , ν_3 and ν_4 calculated with density functional theory for $\text{Rb}_2\text{Ti}_2\text{O}_5$, using the generalized gradient approximation (GGA). The other phonon modes are shown in the supporting information.

Figure 9

Change of color observed for two different crystals (top and bottom) annealed alternatively under vacuum and oxygen at 400 K: (a) as-grown, (b) after vacuum annealing for two hours, (c) after oxygen annealing for two hours and (d) after vacuum annealing for two hours. A yellow color is observed after vacuum annealing which indicates the presence of oxygen vacancies. These vacancies seem to be destroyed by oxygen annealing, since a white color is recovered.

samples annealed under vacuum at 400 K for a couple of hours. As a matter of fact, these electrical properties can also be 'deactivated' when the material is annealed under 1 bar oxygen atmosphere at 400 K. This observation tends to indicate that the existence of these electrical properties is correlated with the presence of oxygen vacancies in the material. In addition, Fig. 9 shows that a reversible change of color operates when the material is alternatively annealed under vacuum and oxygen at 400 K. This is a strong indication in favor of the creation of oxygen vacancies since the material turns from white to yellow and yellow to white, similarly to what is observed in TiO_2 when oxygen vacancies are created (Sekiya *et al.*, 2000).

A subsequent XRD study has been conducted on RTO powder that was annealed *in situ* in the diffraction chamber under N_2 atmosphere. The corresponding diffractograms are displayed in Fig. 10 and do not show any change as function of the temperature excepted for the appearance of a diffraction peak around 24° below 250 K. This peak is attributed to a small contamination by water ice. Powder diffraction at room temperature was also performed on samples annealed for 24 h at 400 K under vacuum and again, the diffractogram was not modified.

In addition, Raman studies were conducted at 300 K on the same sample before and after activation. The results are presented in Fig. 11 for the part of the spectrum where four well-identified phonon modes are present. The green spectrum corresponds to the non-activated sample, the blue spectrum to the activated sample. The activation process clearly has the effect of shifting three of the phonon modes

Figure 10

Powder X-ray diffractograms for $\text{Rb}_2\text{Ti}_2\text{O}_5$ taken at different temperatures and displaced for clarity. From bottom to top: as-grown sample measured at 300 K, vacuum-annealed sample measured at 400 K, then at 300 K, 250 K, 150 K, 100 K, N_2 -annealed sample measured at 400 K. All annealing procedures were performed *in situ* and at 400 K. The annealing durations were 8 h. The peak at 24.17° ($3.68 \text{ \AA}$) comes from the formation of a very thin layer of H_2O ice on the surface of the sample. Heating the sample from 150 K up to 250 under vacuum allowed us to reversibly remove the ice and suppress the peak. This indicates that the sample structure is not altered by the presence of residual solid H_2O .

Figure 11

Raman spectra taken at 300 K for an as-grown sample (green line) and for an activated sample (blue line). (The curves are displaced for clarity.) Note the energy shift produced by the activation process for the ν_1 , ν_2 , ν_3 phonon modes whereas ν_4 remains unaffected. Additional peaks are also produced by the activation.

(ν_1 , ν_2 , ν_3 as represented in Fig. 8), whereas one (ν_4) remains unaffected. It also produces small additional peaks. This represents an indirect way of probing the microscopic effect of activation. (In particular oxygen vacancies should produce additional peaks as inversion symmetry should be lost.) This, therefore, deserves further investigation, more systematic measurement and DFT simulations taking into account the presence of oxygen vacancies or other defects.

Finally, it is known that X-ray diffraction does not easily discern the presence of oxygen vacancies in a crystal structure with heavy elements. However analysis of some diffuse scattering or of possible satellite reflections (that were not observed with our technique) obtained for instance by synchrotron radiation μ XRD as function of temperature might allow detection of a potential order/disorder transition of the oxygen vacancies or interstitial oxygens (Fratini *et al.*, 2010). This will be considered in future experiments. Neutron diffraction will be considered as well in order to study the presence of oxygen vacancies induced by the annealing processes.

7. Conclusion

The crystal structure of RTO has been characterized as a function of temperature using X-ray diffraction, electron microscopy and Raman spectroscopy. All methods are consistent with a $C2/m$ space group in the whole range of investigated temperature *i.e.* between 90 K and 450 K. The outcomes of the X-ray diffraction and Raman spectroscopy are compared to theoretical calculations performed with density functional theory and are in excellent agreement. In particular the computed phonon modes match very well the ones measured experimentally. The structure is also confirmed by transmission electron microscopy.

The special case of the activated material is also inspected by comparing XRD diffractograms of as-grown and annealed samples. While the centrosymmetric $C2/m$ structure is found to remain unchanged, further work would be necessary to investigate the possibility of variation of the diffuse scattering with temperature. The comparison between Raman spectra for as-grown and activated materials demonstrates an energy shift of some selective phonon modes that deserves more systematic investigation.

In any case, this work shows that the $C2/m$ structure of the material remains unchanged between 90 K and 450 K, thus excluding the existence of a structural transition between 200 K and 330 K. These findings rule out a conventional ferroelectric transition associated to a displacive structural transition as a mechanism responsible for the reported colossal polarizability of RTO. The role of the activation process is still to be investigated.

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