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A SINGLE-CRYSTAL INFRARED SPECTROSCOPIC AND X-RAY-DIFFRACTION STUDY OF UNTWINNED SAN BENITO PEROVSKITE CONTAINING OH GROUPS

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ABSTRACT

An untwinned crystal of perovskite ($CaTiO_3$) from the Benitoite Gem mine, San Benito County, California, was investigated by polarized infrared spectroscopy and by single-crystal X-ray methods. The crystal structure [*a* 5.380(1), *b* 5.440(1), *c* 7.639(1) Å, *V* 223.56(7) Å^3, Z = 4, space group *Pbnm*] was refined to a final *R* of 2.7%. Atomic coordinates and anisotropic displacement parameters are in good agreement with previously published refinements of synthetic crystals of $CaTiO_3$ perovskite grown at high temperature. Infrared spectra show two OH absorption bands centered at 3394 and 3326 cm^{-1}. These bands are weakly pleochroic in the (001) section, but show a more distinct anisotropic behavior in the (110) section, with a stronger component of absorption perpendicular to [001]. This finding suggests an alignment of the OH vectors preferentially parallel to the [110] direction (*a* of the pseudocubic cell). The proposed mechanism of hydrogen incorporation, with O2 (= OH) atoms acting as donor oxygen atoms in hydrogen bonding, is explained by cation substitutions coupled with cation vacancies. Even though the approximate H_2O content derived from the intensity of the absorption bands is rather low (*ca.* 70 ppm), similar concentrations are considered to occur in natural (Mg,Fe)SiO_3 perovskite in the Earth's lower mantle.

Keywords: perovskite, trace hydroxyl, IR-spectroscopy, crystal structure, San Benito, California.

SOMMAIRE

Nous avons étudié un cristal unique de pérovskite ($CaTiO_3$) non maclée provenant de la mine Benitoite Gem, du comté de San Benito, en Californie, par spectroscopie infra-rouge polarisée et par diffraction X. Nous en avons affiné la structure cristalline [*a* 5.380(1), *b* 5.440(1), *c* 7.639(1) Å, *V* 223.56(7) Å^3, Z = 4, groupe spatial *Pbnm*] jusqu'à un résidu *R* de 2.7%. Les coordonnées des atomes et les paramètres de déplacement anisotrope concordent bien avec les résultats publiés antérieurement à propos de cristaux de pérovskite $CaTiO_3$ synthétisés à température élevée. Les spectres infra-rouges révèlent deux bandes d'absorption OH centrées à 3394 et 3326 cm^{-1}. Ces bandes sont faiblement pléochroïques dans le plan (001), mais elles sont plus distinctement anisotropes dans le plan (110), avec une composante d'absorption plus forte dans une direction perpendiculaire à [001]. Nos observations font penser qu'il y a alignement préférentiel des vecteurs OH dans une direction parallèle à [110] (*a* de la maille pseudocubique). Nous préconisons un mécanisme d'incorporation de l'hydrogène dans lequel les atomes O2 (= OH) jouent le rôle de donneurs dans les liaisons hydrogène, et qui serait lié aux substitutions impliquant les cations et la présence de lacunes. Quoique la teneur en H_2O dérivée de l'intensité des bandes d'absorption semble très faible, environ 70 ppm, des quantités comparables seraient présentes dans la pérovskite (Mg,Fe)SiO_3 naturelle du manteau inférieur.

(Traduit par la Rédaction)

Mots-clés: pérovskite, traces d'hydroxyle, spectroscopie infra-rouge, structure cristalline, San Benito, Californie.

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INTRODUCTION

The perovskite structure is commonly adopted by a great variety of compounds with the general formula ABX_3. Perovskite phases and structures have been the subject of extensive experimental studies and are of great theoretical and practical significance. For example, synthetically produced perovskites such as ferroelectrics and high-temperature superconductors are of enormous technological interest. Significant interest also exists in perovskite ceramics as a potential agent for the storage of nuclear waste (Banfield & Veblen 1992). Phase transitions in perovskite compounds, melting behavior, diffusion experiments, and conductivity calculations (Gautason & Muehlenbachs 1993, Gillet *et al.* 1993, Zerr & Boehler 1993) are important in geology because high-pressure $(Mg,Fe)SiO_3$ perovskite is most likely the dominant phase in the Earth's lower mantle (Liu 1976). Despite being a rare mineral, $CaTiO_3$ perovskite forms under a wide variety of geological environments and shows a wide range of compositions (Hu *et al.* 1992).

The interpretation and understanding of the physical properties of numerous nominally anhydrous mineral phases hinge upon trace amounts of hydrogen to an extent that is far out of proportion to its low concentration. These properties include melting processes, rheology, mechanical strength, and electrical conductivity. $(Mg,Fe)SiO_3$ perovskite may indeed be an important storage site for hydrogen, and this H-bearing phase may strongly influence the properties of the Earth's lower mantle. From synchrotron infrared (IR) measurements on $MgSiO_3$ perovskite crystals, grown directly from an H_2O-rich melt, Meade *et al.* (1994) observed two moderately pleochroic absorption bands at 3483 and 3423 cm^{-1}, which were attributed to OH groups. Hydrogen in annealed synthetic perovskite ceramics was reported by Baikov & Shalkova (1992).

No data exist on the hydrogen content of naturally occurring perovskite minerals. In this paper, we present polarized IR data from a natural single crystal of $CaTiO_3$ perovskite that contains significant amounts of hydrogen, and propose a model for the mode of hydrogen incorporation in the crystal structure. Since no modern structural parameters from naturally formed perovskite were available, it was also decided to refine the crystal structure. The fact that single crystals of adequate quality for an X-ray-diffraction study as well as for an IR microspectroscopic study are extremely rare makes the examination of natural $CaTiO_3$ perovskite a difficult task.

Although a large number of natural, yet twinned, crystals was investigated, the crystal structure was first refined on synthetic material by Kay & Bailey (1957), who confirmed the orthorhombic cell and space group *Pcmn*. Accurate single-crystal X-ray structure refinements of synthetic perovskite grown at high temperature were presented by Sasaki *et al.* (1987), and with special emphasis on the electron densities, by Buttner & Maslen (1992). A structure refinement using neutron-diffraction data from a synthetic powder was published by Koopmans *et al.* (1983). Hu *et al.* (1992) investigated the microstructure of natural perovskite from different localities by energy-dispersion X-ray analysis (EDX) and transmission electron microscopy (TEM). Their results indicate that perovskite from San Benito, California is the least twinned among all natural samples. A similar TEM study of domain structures was performed by Wang & Liebermann (1993). Twinning and formation of faults in natural perovskite were attributed to phase transitions at high temperatures (Guyot *et al.* 1993, Liu & Liebermann 1993). Different rates of cooling and maximum temperatures of formation also can be correlated with different twin laws (Keller & Buseck 1994).

SAMPLE DESCRIPTION AND EXPERIMENTAL

The single crystal used for this work comes from the famous Benitoite Gem mine, Diablo Range, San Benito County, California. At this locality, perovskite occurs as a product of metasomatism in small calc-silicate veins scattered within a block of metamorphosed serpentine (Wise & Gill 1977). A hand specimen from this locality was found to contain several transparent, yellow-brown crystals up to 1.5 mm in size, associated with magnetite on a matrix of chlorite. Larger crystals are ball-shaped and consist of polycrystalline aggregates or multiple twins. A small, flat, gem-quality crystal of dimensions 1.2 × 0.7 × 0.3 mm proved to be almost a single crystal (Fig. 1). Under the microscope, it seems homogeneous, except for a few extremely thin lamellae near the rim of the (001) face, and there is no sign of impurities and included phases. Results of a chemical analysis of San Benito perovskite are given in Hu *et al.* (1992), who found it to have the most nearly ideal composition of those natural samples of perovskite investigated. The only minor constituents present are 0.11 wt.% Na_2O, 0.36% Ce_2O_3, 0.17% La_2O_3, 0.24% Nb_2O_5, and 0.24% FeO.

A preliminary examination by the X-ray precession method confirmed that the perovskite is a single crystal with a negligible amount of (110) twinning. A photograph of the $(001)^*$ plane yielded the measured unit-cell parameters *a* 5.38, *b* 5.44 Å. The maximum dimension of the crystal (1.2 mm) was found to be parallel to [110] (Fig. 1). The crystal was attached by its natural (001) face to a self-constructed crystal grinder and ground and polished on the opposite side to a final thickness of 0.200(2) mm. The natural (001) surface did not need any further polishing procedures. After the first series of IR measurements were performed on (001), the crystal slab was embedded in epoxy resin, and a plate cut parallel to (110) was prepared using a low-speed diamond saw. After additional grinding and polishing, the plane-parallel

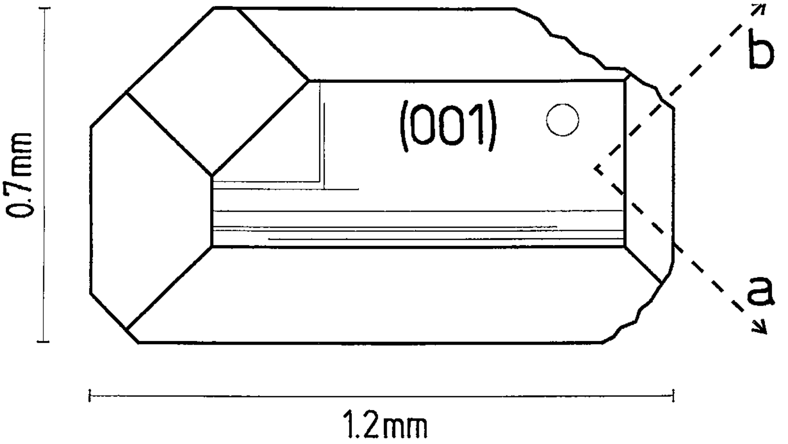

FIG. 1. Schematic drawing of the perovskite single-crystal from the Benitoite Gem mine, California, used for this study. The crystal's thickness was about 0.3 mm. The thin lines mark optically visible thin lamellae of (110) twins. The circle denotes the approximate field of measurement for the acquisition of IR spectra.

(110) slab had a thickness of 0.455(2) mm. The maximum angular deviations of the polished slabs from the ideal orientations are estimated to be ±2°.

Single-crystal spectra were recorded with a FTIR spectrometer 1760X, which was equipped with a FTIR microscope having 0.60 numerical aperture mirror lenses (cassegrains), a liquid-nitrogen-cooled MCT detector, and a gold-wire grid polarizer with an extinction ratio better than 1:100 in the 4000 – 3000 cm^{-1} region. Background and sample spectra were obtained from 64 scans each in air and in the sample crystal, with 4 cm^{-1} resolution. The spots measured were chosen according to the dimensions of the completely clear parts of the crystal, and these varied from 50 × 50 to 100 × 100 μm. Data handling and calculations were carried out with the program IRDM. Unpolarized and polarized spectra were recorded in the (001) and (110) planes. An unpolarized spectrum from a (001) section is given in Figure 2. Absorption figures from both sections were obtained after rotation of the polarizer over a range of 360° in steps of 10°. Figure 3 shows the linear absorption coefficients (α) in cm^{-1} defined by $\alpha = A/t$, where A is the linear absorbance (log $[I_0/I]$), and t is the thickness of the crystal plates measured in cm (Beran *et al.* 1993, Libowitzky & Beran 1995).

For the collection of a set of single-crystal X-ray data, many small crystals and fragments of perovskite were prepared from the San Benito hand specimen and were then tested for quality by the X-ray precession method or directly on a four-circle diffractometer. However, none of them was suited for collection of intensity data. Finally, some small chips were separated from the untwinned crystal used for the IR study. One of them, a piece with dimensions of approximately 0.25 × 0.25 × 0.20 mm, was mounted on a needle of silica glass, and an investigation on the four-circle diffractometer was done. The crystal showed sharp reflections and allowed an unambiguous determination of the correct cell constants. Only in

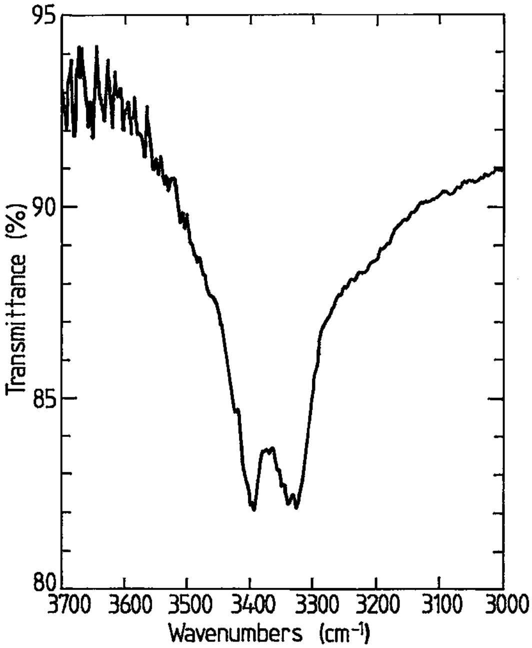

FIG. 2. Unpolarized IR spectrum in the OH-stretching region of the perovskite crystal from San Benito. The transmittance measurements of a (001) section, 0.200(2) mm thick, were made with a FTIR microscope.

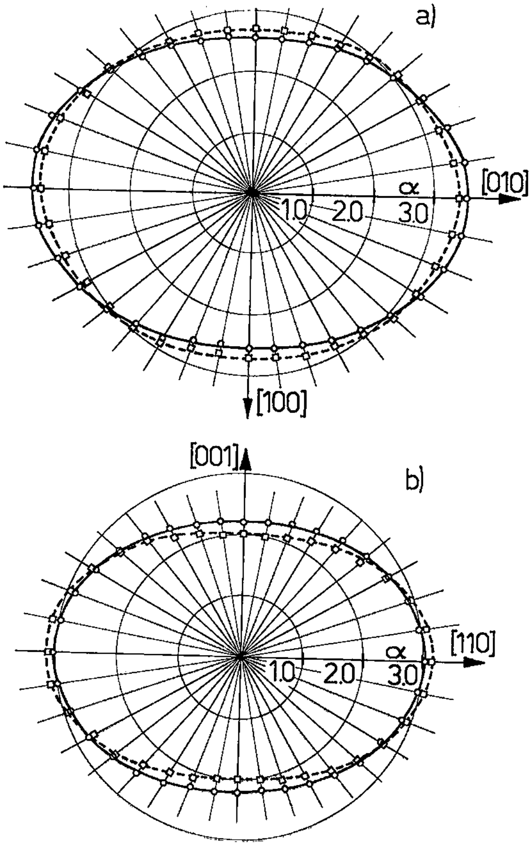

FIG. 3. Absorption coefficients α of the OH bands at 3394 cm^{-1} (small circles connected by lines) and 3326 cm^{-1} (squares connected by dashed lines) correlated to the rotation of the E vector of the polarized radiation in a (001) section (a), and in (110) (b).

TABLE 1. DETAILS CONCERNING THE COLLECTION AND REFINEMENT OF SINGLE-CRYSTAL X-RAY-DIFFRACTION DATA, SAN BENITO PEROVSKITE

a (Å)	5.380(1)	spacegroup	*Pbnm*
b (Å)	5.440(1)	Z	4
c (Å)	7.639(1)	crystal size (mm)	0.25x0.25x0.20
V (Å^3)	223.56(7)	data collection	0 - 40° θ
N_{refl}	1255	N_{par}	29
μ (mm^{-1})	5.81	*F* (000)	264
R_{int} (%)	2.6	Weights	$1/\sigma^2(F)$
all reflections		reflections with $F > 6\sigma$ (*F*)	
N_{unique}	695	N_{unique}	592
R (%)	3.3	*R* (%)	2.7
R_w (%)	4.0	R_w (%)	3.9
Goof	2.04	*Goof*	2.17
res. $e^-/Å^3$ *	-0.9 ; +1.2	*res.* $e^-/Å^3$ *	-0.8 ; +1.0

$R = \Sigma||F_{obs}| - |F_{calc}|| / \Sigma|F_{obs}|$
$R_w = (\Sigma w(|F_{obs}| - |F_{calc}|)^2 / \Sigma w|F_{obs}|^2)^{1/2}$
$Goof = (\Sigma w(|F_{obs}| - |F_{calc}|)^2 / (N_{refl} - N_{par}))^{1/2}$

* Largest residuals on a final difference Fourier map.

ω-scans did a few reflections show minor evidence of a "disoriented" crystal fragment. This was probably caused by the harsh separation-procedure during preparation (*i.e.*, mechanically induced lineage or mosaic structure).

X-ray intensities were collected on a CAD4 diffractometer using graphite monochromatized Mo*K*α radiation. Data were collected in one quadrant of reciprocal space out to θ = 40° using the 3.0° θ-scan mode. Cell constants, which were refined from 14 reflections with 15° < θ < 25°, and additional experimental parameters, are summarized in Table 1. Data reduction, including background and Lorentz-polarization corrections, was carried out with the SDP program system. An empirical absorption correction was applied using the ψ-scan technique. We used the program SHELXTL with neutral atom scattering factors in the structure refinement. The atomic parameters of Kay & Bailey (1957) were used as the initial starting set for the structure refinement, which finally converged to $R = 2.7$ % (Table 1). A table of structure factors is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

RESULTS AND DISCUSSION

Atomic positional parameters and anisotropic displacement parameters are presented in Table 2. The data essentially confirm the atomic positions determined by Kay & Bailey (1957), with minor deviations of up to 0.1 Å, and coincide (maximum deviations <0.01 Å) with the atomic positional parameters published for synthetic $CaTiO_3$ perovskite by Sasaki *et al.* (1987) and Buttner & Maslen (1992). The anisotropic displacement parameters are also comparable. Typically, the Ti and Ca atoms show almost isotropic behavior, whereas O1 and O2 are rather anisotropic. The predominance of U_{11} and U_{22} in O1 and of U_{33} in O2 is probably caused by a strong librational mode of the rigid TiO_6 octahedra with respect to the *c* axis. The refined unit-cell parameters are the smallest of any reported in recent investigations. Nevertheless, the data agree within 3σ with those of Sasaki *et al.* (1987).

The FTIR spectrum of perovskite in the region of the OH stretching fundamental consists of two strong bands with maxima centered at 3394 and 3326 cm^{-1}. As seen in Figure 2, satellite bands are extremely weak

TABLE 2. ATOMIC POSITIONAL PARAMETERS AND ANISOTROPIC DISPLACEMENT PARAMETERS OF SAN BENITO PEROVSKITE

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0	1/2	0	0.0059(2)	0.0052(2)	0.0045(2)	0.0000(1)	0.0000(1)	0.00025(9)
Ca	0.00648(8)	0.0356(1)	1/4	0.0082(2)	0.0083(2)	0.0079(2)	0.0016(2)	0	0
O1	0.5711(3)	-0.0161(3)	1/4	0.0082(6)	0.0086(7)	0.0045(5)	0.0002(5)	0	0
O2	0.2897(2)	0.2888(2)	0.0373(2)	0.0065(4)	0.0060(4)	0.0095(4)	0.0020(4)	-0.0008(3)	-0.0010(3)

Standard deviations in parentheses.

and could not be studied in detail. The two bands, which are characterized by a very similar pleochroic behavior, are attributed to structural OH groups. Figure 3 shows that in (001) sections, the bands have only a weak pleochroism; a somewhat stronger absorption occurs when the vector E of the polarized radiation vibrates parallel to [010]. In (110) sections, the bands at 3394 and 3326 cm^{-1} have a more distinct pleochroism, with a stronger component of absorption perpendicular to [001].

Unpolarized spectra measured in different regions of the crystal show that the band intensities are relatively constant, thus implying that the OH groups are uniformly distributed throughout. In view of these results, it seems unlikely that OH groups are concentrated at hidden twin planes. Estimating the analytical H_2O content on the basis of Lambert–Beer's law, the relation proposed by Paterson (1982) was used for the determination of the integral molar absorptivity ε_i. Since both bands at 3394 and 3326 cm^{-1} are attributed to one type of OH, a "mean" band maximum centered at 3360 cm^{-1} was assumed. The integral absorbance was measured with unpolarized radiation, and an anisotropy factor of ⅓ was taken into account. The resulting value of ε_i is 42000 $l \cdot mole^{-1} \cdot cm^{-2}$, and the corresponding H_2O content is calculated as 70 ppm.

The pleochroic scheme of the two OH absorption bands imposes certain constraints on the orientation of the OH dipoles. The relatively strong pleochroism in (110) requires a preferred orientation of the OH dipoles perpendicular to [001]. The moderate pleochroism of the bands in (001) implies an OH dipole direction essentially parallel to [110], which corresponds to the direction of the pseudo-cubic *a* axis. A crystal-chemically plausible model for the mode of OH incorporation in this sample of perovskite, based on the IR spectroscopic measurements, may be derived under the assumption of vacancies on the cation sites. Unfortunately, the small number of vacancies (equivalent to 70 ppm H_2O) cannot be proved by a refinement of the site occupancy. We further assume that the OH incorporation is critically influenced by the presence of minor elements replacing Ca or Ti [*e.g.*, $Ti^{4+} + O^{2-} \rightleftharpoons Fe^{3+} + (OH)^-$; $Ca^{2+} + O^{2-} \rightleftharpoons Na^+ + (OH)^-$], notably by the oxidation state of Fe, and by nonstoichiometry reflecting the general geochemical and thermodynamic environment of formation.

To facilitate the discussion, Figure 4 represents in a schematic diagram the most probable orientation of the OH dipoles. Owing to the pleochroic behavior of the bands in (110), the main component of the OH absorption is perpendicular to [001]. However, the component parallel to [001] demands a significant deviation of the OH vector direction from an alignment within the (001) plane. Under the assumption of a vacant Ca-site, an OH direction roughly pointing along [110] with the O2 oxygen atoms acting as donors would be consistent with the weakly pleochroic absorption behavior observed in (001). The deviation from the (001) plane is apparently caused by the repulsion of the proton by the cation in the occupied Ca-site beneath the OH dipoles, as shown in Figure 4. The separation of the two bands by 68 cm^{-1} is due to the two "different" O2-sites probably acting as hydrogen bond donors. On the basis of the relation diagram given by Nakamoto *et al.* (1955), the band positions at 3394 and 3326 cm^{-1} require weak hydrogen bridging. In addition, the relatively wide halfwidth of the bands is indicative of local displacements of the oxygen positions from their ideal coordinates.

The OH positions discussed are similar to those proposed by Meade *et al.* (1994) in high-pressure $MgSiO_3$ perovskite. The main differences are that the SiO_6 octahedra in $MgSiO_3$ are more tilted (thus building a more distorted perovskite structure) than the TiO_6 octahedra in $CaTiO_3$. Moreover, the IR bands are observed at 3483 and 3423 cm^{-1} in $MgSiO_3$, whereas they are at 3394 and 3326 cm^{-1} in $CaTiO_3$. Nevertheless, the separation of the bands and the alignment of the OH dipoles is similar in both perovskite-group structures. However, Meade *et al.* (1994) did not explicitly propose a vacant cation position, even though this seems necessary from geometric and electrostatic considerations.

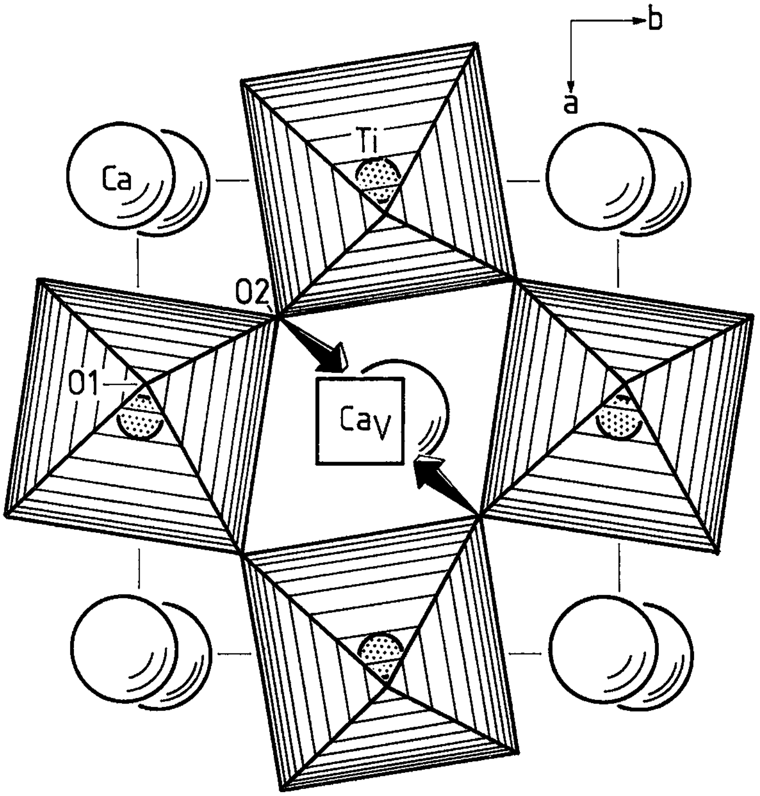

FIG. 4. Part of the perovskite structure showing a Ca-vacancy (Ca_V) and possible OH orientations represented by the two arrows.

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