

Structural Study of the Low-Temperature Phase Transition in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$

BY M. ICHIKAWA

Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan

AND T. GUSTAFSSON AND I. OLOVSSON

Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden

(Received 22 January 1992; accepted 13 April 1992)

Abstract

The X-ray structure of tricaesium deuteriumbiselenate, $\text{Cs}_3\text{D}(\text{SeO}_4)_2$, $M_r = 686.7$, has been studied at 25, 190 and 297 K with particular attention being paid to the low-temperature phase transition at $T_{c3} = 180$ K. The structure of $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ has also been studied at 297 K. The data were refined in the monoclinic space group $C2/m$, $Z = 2$, at 297 and 190 K, and in $P2_1/m$, $Z = 2$, at 25 K (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). For $\text{Cs}_3\text{D}(\text{SeO}_4)_2$, $R(F^2) = 0.0365$ for 1801 unique reflections at 297 K, $R(F^2) = 0.0389$ for 1787 unique reflections at 190 K and $R(F^2) = 0.0405$ for 3514 unique reflections at 25 K. For $\text{Cs}_3\text{H}(\text{SeO}_4)_2$, $R(F^2) = 0.0637$ for 1265 unique reflections at 297 K. Temperature effects on the structure are mainly noticeable in the Cs—O bond distances of the oxygen coordination polyhedra of Cs (0.016 Å per 100 K on average). Accompanying the T_{c3} transition, the space group changes from $C2/m$ to $P2_1/m$, and the two SeO_4 groups in the dimer become non-equivalent with one adopting HSeO_4^- character and the other SeO_4^{2-} character. As a result, the dimers have a net dipole moment and are arranged in an antipolar way, similar to $\text{K}_3\text{D}(\text{SO}_4)_2$. An examination of the room-temperature structure of $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ and other $M_3\text{H}(\text{XO}_4)_2$ -type crystals reveals that the non-H atoms lie in approximately the same position in both cases and that the only major difference is that half of the hydrogens in other $M_3\text{H}(\text{XO}_4)_2$ -type crystals are involved in hydrogen-bonded dimers which are formed with two different adjacent selenate groups. The successive transitions in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ are characterized as an order–disorder transition of the donor-oxygen atom at T_{c1} , reorganization of the hydrogen bonds at T_{c2} and an order–disorder transition of the proton at T_{c3} .

1. Introduction

Tricaesium hydrogenbiselenate $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ (abbreviated to TCHSe) and its deuterated analogue

$\text{Cs}_3\text{D}(\text{SeO}_4)_2$ (TCDSe) are members of a family of hydrogen-bonded compounds with the general formula $M_3\text{H}(\text{XO}_4)_2$ ($M = \text{K, Rb, Cs}$, and $X = \text{S, Se}$), the crystal structures of which are presently being systematically studied. For further information on the characteristics of, and interest in, these compounds, see Ichikawa, Gustafsson & Olovsson (1992). All $M_3\text{H}(\text{XO}_4)_2$ -type crystals have the same trigonal ($R\bar{3}m$) superionic and paraelastic phase (I) above the transition temperature T_{c1} (range 339–456 K). TCHSe and TCDSe, however, are unique in the following respects:

(1) TCHSe and TCDSe have an extra intermediate ferroelastic phase (II) above T_{c2} , between the room-temperature (RT) ferroelastic phase (III) and the high-temperature phase (I) (Komukae, Osaka, Kaneko & Makita, 1985).

(2) While the space group of the RT phase of all other members is the same ($A2/a$), recent optical and structural studies reveal that the space group of TCHSe in the RT phase (III) is $C2/m$ (Merinov, Baranov, Tregubchenko & Shuvalov, 1988; Merinov, Bolotina, Baranov & Shuvalov, 1988).

(3) Quite recently the intermediate phase (II) has been shown to be monoclinic ($A2/a$), the same as the RT phase of other members (Merinov, Baranov & Shuvalov, 1990).

(4) The transition temperature T_{c3} of TCDSe at 180 K, between the RT phase (III) and the low-temperature (LT) phase (IV), is the highest among the members (*cf.* 20–90 K for the other members) and it falls in the normal temperature range observed in hydrogen-bonded ferroelectric crystals such as KH_2PO_4 (Komukae *et al.*, 1985; Ichikawa, Gustafsson & Olovsson, 1991).

In order to understand the nature of the successive phase transitions in $M_3\text{H}(\text{XO}_4)_2$ -type crystals, we considered it to be of great interest to investigate the similarities and differences between the $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ [and $\text{Cs}_3\text{D}(\text{SeO}_4)_2$] crystal and the other members, and also between the different phases of $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ [$\text{Cs}_3\text{D}(\text{SeO}_4)_2$], since their mutual relationship does not seem to have been fully explored. To this end, in

particular focusing on the LT phase transition at T_{c3} , the X-ray structure of Cs₃D(SeO₄)₂ has been investigated at 297 and 190 K (above T_{c3}) and at 25 K (below T_{c3}), together with that of Cs₃H(SeO₄)₂ at 297 K.

2. Experimental

Single crystals of Cs₃H(SeO₄)₂ were prepared by cooling, from around 313 K, a saturated aqueous solution containing excess selenic acid. A specimen of dimensions 0.11 × 0.06 × 0.10 mm was cut from a ferroelastic single-domain part of the batch. The lattice constants are from Ichikawa & Sato (1987) and are given in Table 1. The preparation of Cs₃D(SeO₄)₂ single crystals is described by Ichikawa *et al.* (1991) and the specimen used was a hexagonal plate with a ferroelastic single domain and with a width of 0.25 mm and thickness of 0.06 mm; the unit-cell parameters are taken from Ichikawa *et al.* (1991) and are given in Table 1.

The data were collected using Mo $K\alpha$ radiation (0.71073 Å) and a Huber four-circle X-ray diffractometer with a closed-cycle helium refrigerator (Samson, Goldish & Dick, 1980). The temperature was measured by silicon sensors installed in the cold-station extender (T_A) and in the φ shaft of the diffractometer (T_B). The temperature at the specimen (T_S) was calibrated against the transition temperatures of KH₂PO₄ (123 K) and KMnF₃ (81 and 187 K). The stability of the temperature during the measurement was within 1 K. The accuracy of the temperature of the crystal is estimated to be within 2 K.

Data collection was carried out at 297 K for Cs₃H(SeO₄)₂. Intensity measurements were carried out in the ω - 2θ scan mode. The step width was 0.015° in ω with a minimum number of 70 steps plus the α_1 - α_2 splitting. The measuring time varied from 0.5 to 2.0 s step⁻¹ in the range $2 < 2\theta < 70^\circ$ for $-17 \leq h \leq 14$, $-10 \leq k \leq 0$, $-12 \leq l \leq 13$ (max. $\sin\theta/\lambda = 0.8069 \text{ \AA}^{-1}$). For Cs₃D(SeO₄)₂ the data collection was carried out in the order 190, 25 and 297 K. Intensity measurements were carried out in the ω - 2θ scan mode. The step width was 0.010° with a minimum number of 74 steps plus the α_1 - α_2 splitting. The measuring time varied from 0.3 to 2.0 s step⁻¹ in the range $2 < 2\theta < 80^\circ$ for $-19 \leq h \leq 0$, $-11 \leq k \leq 11$, $-14 \leq l \leq 15$ (max. $\sin\theta/\lambda = 0.9044 \text{ \AA}^{-1}$). Five standard reflections monitored every 3 h were used to check the stability of the measurements. The intensities and their standard deviations were corrected for variations by the method of McCandlish, Stout & Andrews (1975). For TCHSe, the correction factors were 1.0–0.958 and for TCDS_e, 1.0–0.985 at 297 K, 1.0–1.012 at 190 K, 1.0–1.041 at 25 K. The data set was corrected

Table 1. Crystallographic data

The unit-cell dimensions were determined in the papers cited below, although no values are quoted there. Monoclinic, $Z = 2$, $F(000) = 596$. Cs₃D(SeO₄)₂, Mo $K\alpha$ ($\lambda = 0.70930 \text{ \AA}$); Cs₃H(SeO₄)₂, Ag $K\alpha$ ($\lambda = 0.56087 \text{ \AA}$).

Number and 2θ range (°) of reflections used	Cs ₃ D(SeO ₄) ₂ *			Cs ₃ H(SeO ₄) ₂ †
	25 K 26 (55–59)	190 K 26 (54–59)	297 K 26 (54–58)	295 K 40 (20–22)
a (Å)	10.7906 (11)	10.8465 (7)	10.8911 (9)	10.8921 (15)
b (Å)	6.3264 (3)	6.3551 (2)	6.3830 (3)	6.3864 (9)
c (Å)	8.3669 (20)	8.4040 (12)	8.4483 (16)	8.4441 (12)
β (°)	112.215 (27)	112.385 (16)	112.454 (21)	112.422 (12)
V (Å ³)	528.78 (22)	535.64 (13)	542.42 (17)	542.98 (12)
D_x (g cm ⁻³)	4.312	4.257	4.204	4.200

* Ichikawa *et al.* (1991).

† Ichikawa & Sato (1987).

for background effects (Lehmann & Larsen, 1974) and Lorentz, polarization and absorption effects (for TCHSe, transmission factors 0.2654–0.4405, for TCDS_e, 0.0475–0.3176 at 297 K, 0.0452–0.3138 at 190 K, 0.0440–0.3110 at 25 K). Other experimental details are summarized in Table 2.

The space group of Cs₃D(SeO₄)₂ is $C2/m$ above the LT transition at T_{c3} [the same as Cs₃H(SeO₄)₂ (Merinov, Bolotina *et al.*, 1988)] and $P2_1/m$ or $P2_1$ below T_{c3} (Ichikawa *et al.*, 1991). In order to check the possibility of cell doubling below the T_{c3} transition, a Q scan was carried out at 25 K along the a^* , b^* and c^* axes and $[hh0]$, $[0kk]$, $[h0h]$ and $[hhh]$ directions. No evidence of cell doubling or tripling was found.

The refinement (on F^2) of both the TCHSe and TCDS_e data started with the RT TCHSe structure reported by Merinov, Bolotina *et al.* (1988). All atoms except hydrogen were refined with anisotropic displacement parameters; the H atom with an isotropic displacement parameter. For the 25 K data, refinement was performed in the space group $P2_1/m$, with a fixed isotropic displacement parameter for D. The residual peaks in the final $\Delta\rho$ map were larger in this case compared to the other three data sets [the largest positive and negative peaks are seen around Cs(1)]. This might indicate a small degree of disorder and could be the reason for the larger wR value, but detailed examination is left for the future. Refinement was also carried out in the alternative space group $P2_1$, but no significant improvement was achieved.

A type-(I) isotropic extinction parameter with Lorentzian distribution resulted in the best agreement between observed and calculated data for the four data sets. Some reflections were omitted at the later stages of the refinement (see Table 2). Details of the refinements are given in Table 2.

All calculations were performed using the program system described by Lundgren (1983) and the struc-

Table 2. *Experimental details*

	25 K	Cs ₃ D(SeO ₄) ₂ 190 K	297 K	Cs ₃ H(SeO ₄) ₂ 297 K
μ (mm ⁻¹)	17.04	16.82	16.60	16.60
Total number of reflections measured and used	7279	3478	3507	1351
Number of unique reflections	3514	1787	1801	1265
R_{int}	0.0194	0.0259	0.0225	0.0322
Final least-squares refinement				
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$
Weights	$1/\sigma^2(F^2)$	$1/\sigma^2(F^2)$	$1/\sigma^2(F^2)$	$1/\sigma^2(F^2)$
Excluded reflections	1* + 12†	2* + 15†	2* + 6†	1* + 2†
Number of parameters	77	40	40	40
Isotropic secondary-extinction parameter	0.18 (1) × 10 ⁴	0.53 (1) × 10 ⁴	0.96 (6) × 10 ³	0.30 (1) × 10 ⁴
$R(F^2)$	0.0405	0.0389	0.0365	0.0637
wR	0.0877	0.0484	0.0582	0.0733
S	3.60	1.76	1.94	2.22
Max. Δ/σ	0.02	0.003	0.02	0.05
Final $\Delta\rho$ map				
Max. and min. $\Delta\rho$ (e Å ⁻³)	5.94, -6.52	1.43, -1.39	1.61, -0.67	1.44, -2.57

* Extinction.

† Multiple reflection.

ture was drawn using ORTEPII (Johnson, 1976). Atomic scattering factors and mass attenuation coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

3. Results and discussion

Final positional and (equivalent) isotropic displacement parameters at 297, 190 and 25 K are given in Table 3.* The projection of the structure along b is shown in Fig. 1. Temperature dependencies of selected interatomic distances and angles are given in Table 4.

3.1. General features of the structure

The structure of Cs₃D(SeO₄)₂, which is isomorphous with Cs₃H(SeO₄)₂, is built up of hydrogen-bonded SeO₄ dimers and Cs—O polyhedra (Fig. 1). There are two kinds of Cs atoms: Cs(1) occupies a special position on a twofold axis; Cs(2) lies in a general position. Both types of Cs atoms are surrounded by ten O atoms, as in other $M_3H(XO_4)_2$ -type crystals. The Cs(1)—O bond lengths are shorter than the Cs(2)—O bond lengths by about 0.02 Å on average (0.021 Å for TCHSe and 0.018 Å for TCDSe). This trend is analogous to that observed in Rb₃D(SeO₄)₂ (Ichikawa *et al.*, 1992), although less prominent in the Cs compound. The two SeO₄²⁻ ions

Table 3. *Fractional coordinates and equivalent isotropic displacement parameters (Å²)*

The equivalent isotropic displacement factor is of the form:

$$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	$B_{\text{eq}}(B)$
Cs ₃ H(SeO ₄) ₂				
297 K				
Cs(1)	0	0	0	2.16
Cs(2)	0.19761 (3)	0	0.60724 (5)	2.30
Se	0.42702 (5)	0	0.23495 (7)	1.65
O(1)	0.48639 (25)	0.21103 (42)	0.69056 (32)	2.96
O(2)	0.39058 (42)	0	0.02072 (48)	2.59
O(3)	0.28813 (37)	0	0.26199 (58)	3.05
H	0.5	0	0	8.7 (3.9)
Cs ₃ D(SeO ₄) ₂				
297 K				
Cs(1)	0	0	0	2.20
Cs(2)	0.19761 (1)	0	0.60725 (2)	2.34
Se	0.42686 (2)	0	0.23473 (3)	1.80
O(1)	0.48646 (12)	0.21134 (15)	0.69104 (15)	2.99
O(2)	0.39049 (20)	0	0.02109 (20)	2.79
O(3)	0.28748 (16)	0	0.26264 (26)	3.21
D	0.5	0	0	9.7 (2.4)
190 K				
Cs(1)	0 (1)	0	0	1.35
Cs(2)	0.19775 (1)	0	0.60691 (1)	1.38
Se	0.42695 (1)	0	0.23541 (2)	0.98
O(1)	0.48589 (8)	0.21251 (11)	0.69003 (11)	1.82
O(2)	0.39012 (14)	0	0.02034 (14)	1.69
O(3)	0.28684 (12)	0	0.26336 (18)	1.90
D	0.5	0	0	5.2 (1.4)
25 K				
Cs(1)	0.25909 (2)	0.25	-0.00105 (2)	0.68
Cs(21)	0.44858 (2)	0.25	0.60871 (2)	0.61
Se(1)	0.67699 (3)	0.25	0.23682 (4)	0.69
O(11)	0.76588 (13)	0.46352 (19)	0.31393 (18)	0.45
O(21)	0.64006 (20)	0.25	0.02292 (26)	0.67
O(31)	0.53877 (19)	0.25	0.27255 (29)	0.88
D	0.782 (6)	0.25	-0.012 (10)	15
Cs(22)	0.05256 (2)	0.25	-0.60372 (2)	0.59
Se(2)	-0.17527 (3)	0.25	-0.23536 (4)	0.70
O(12)	-0.26293 (13)	0.46441 (19)	-0.30645 (18)	0.69
O(22)	-0.13602 (20)	0.25	-0.01625 (26)	0.64
O(32)	-0.03346 (19)	0.25	-0.26030 (28)	0.74

* Lists of anisotropic displacement parameters, interatomic distances and angles, structure factors and a c -axis projection of the structure have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55127 (78 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0279]

in the hydrogen-bonded dimers are related by a twofold axis, with hydrogen either on the twofold axis or in two disordered positions about it.

The systematic trends in the bond distances and angles of the SeO₄ tetrahedra are analogous to those in Rb₃D(SeO₄)₂ (Ichikawa *et al.*, 1992); for a detailed discussion this paper should be consulted. It is noted that at RT the O(2)—O(3) distance is larger than the O(1)—O(2) distance and rather close to other O—O distances involving O atoms without an attached proton, in contrast to the regular HSeO₄⁻ group. This is because the O(2)—Se—O(3) angle is considerably larger than the O(1)—Se—O(2) angle (Table 4). This trend is also observed in the case of Rb₃D(SeO₄)₂.

The trend in the equivalent isotropic displacement parameters B_{eq} which was pointed out for the case of Rb₃D(SeO₄)₂ is also observed in the present results: $B_{eq}(\text{Se}) < B_{eq}(\text{Cs}) < B_{eq}(\text{O})$ (except at 25 K). The relation $B_{eq}[\text{Cs}(1)] < B_{eq}[\text{Cs}(2)]$ is also noted. This trend is also consistent with the observation that $[\text{Cs}(1)\text{—O}]_{av} < [\text{Cs}(2)\text{—O}]_{av}$ (details are given in Table 6, deposited). These relations are characteristic of all $M_3\text{H}(\text{XO}_4)_2$ -type crystals so far studied. The disk-shaped anisotropy of the displacement parameters for O(2) and O(3) is also analogous to that observed for Rb₃D(SeO₄)₂ (Ichikawa *et al.*, 1992).

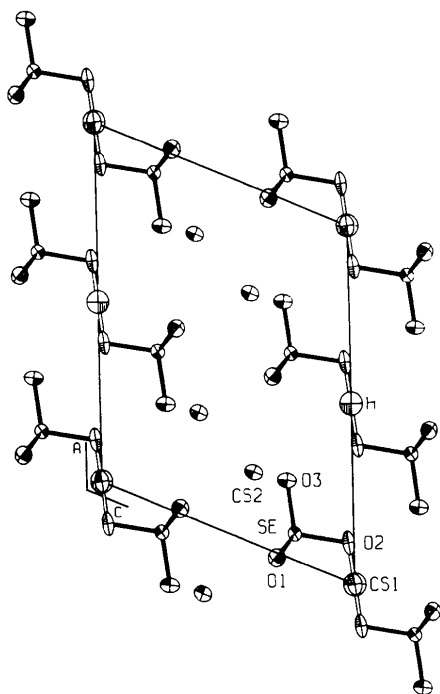


Fig. 1. The *b*-axis projection of the RT structure of Cs₃H(SeO₄)₂. Displacement ellipsoids are scaled to include 50% probability. The isotropic displacement parameter for hydrogen is arbitrarily given the value 4.0 Å².

3.2. Comparison between the room-temperature results

The present results for Cs₃H(SeO₄)₂ at 297 K agree well with those at 295 K obtained by Merinov, Bolotina *et al.* (1988): the differences in the bond distances and angles are generally $\leq \sigma$ with a maximum value of 1.7σ .

In order to study the isotope effect a comparison was also made between the bond distances and angles of Cs₃D(SeO₄)₂ at 297 K and those of Cs₃H(SeO₄)₂ at 297 K and at 295 K as observed by Merinov, Bolotina *et al.* (1988). Our TCDSe and TCHSe data gave differences of less than 2.3σ (a detailed comparison is made in Table 6, deposited). The differences may be due to errors in the results since the effects on the distances and angles, other than on the hydrogen-bonded distance, are only indirect and should be very small. These results are consistent with the lattice-constant results, where no significant isotope effect could be found (Ichikawa *et al.*, 1991). The hydrogen-bonded distance O(2)⋯O(2ⁱⁱ) at RT in TCHS is 2.538 (8) Å (this work) and 2.535 (9) Å (Merinov, Bolotina *et al.*, 1988), which is shorter than that in TCDSe [2.543 (4) Å]. This trend agrees with earlier empirical results (Olovsson & Jönsson, 1976; Ichikawa, 1978). However, the isotope effect, 0.005 (9) Å (our data) and 0.008 (10) Å [comparison with the data of Merinov, Bolotina *et al.* (1988)] is hardly significant compared to the standard deviations.

3.3. Temperature dependence and phase transition at T_{c3}

Temperature changes in the structure are mainly noticeable in the Cs—O bond distances of the oxygen coordination polyhedra of Cs (0.016 Å per 100 K on average) [*cf.* 0.015 Å per 100 K for Rb—O in Rb₃D(SeO₄)₂ on average (Ichikawa *et al.*, 1992)]. These changes may explain the temperature dependence of the lattice constants. No noticeable temperature dependence could be seen for the other bond distances and angles.

The space group changes from $C2/m$ to $P2_1/m$ on passing through the T_{c3} transition with decreasing temperature. The structural changes accompanying the T_{c3} transition are clearly in contrast to Rb₃D(SeO₄)₂, but are similar to those in K₃D(SO₄)₂ where breaking of the *A*-centering is clearly seen and the space group changes from $A2/a$ to $P2_1/a$ (Noda, Watanabe, Kasatani, Terauchi & Gesi, 1991). The atoms located in the mirror plane in the RT phase (III) are still in the mirror plane, but as a result of the disappearance of the twofold axis, the Cs(1) atom no longer lies on a twofold axis and Cs(2) splits into Cs(21) and Cs(22). The D atom, which was on the twofold axis (or more plausibly, occupied two

Table 4. Selected bond distances (Å) and angles (°)

Bond distances have not been corrected for thermal motion. The corresponding values for $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ at 295 K obtained by Merinov, Bolotina *et al.* (1988) are also given for comparison. Symmetry code: (i) $1+x, y, z$; (ii) $1-x, -y, -z$.

	$\text{Cs}_3\text{D}(\text{SeO}_4)_2$				$\text{Cs}_3\text{H}(\text{SeO}_4)_2$	
	25 K		190 K	297 K	297 K	295 K
SeO₄ ion						
Se(1)—O(11) ($\times 2$)	1.641 (2)	Se(1)—O(1) ($\times 2$)	1.631 (1)	1.629 (1)	1.628 (3)	1.628 (4)
—O(21)	1.679 (1)	—O(2)	1.696 (1)	1.694 (2)	1.698 (4)	1.703 (5)
—O(31)	1.628 (2)	—O(3)	1.624 (1)	1.623 (2)	1.614 (4)	1.623 (6)
Average	1.647		1.645	1.643	1.642	1.646
Se(2)—O(12) ($\times 2$)	1.631 (2)					
—O(22)	1.719 (3)					
—O(32)	1.621 (2)					
Average	1.651					
O(11)—Se(1)—O(11)	110.8 (1)	O(1)—Se(1)—O(1)	111.8 (1)	111.9 (1)	111.8 (2)	112.0 (2)
—O(21) ($\times 2$)	106.7 (1)	—O(2) ($\times 2$)	106.0 (1)	106.0 (1)	106.1 (1)	106.1 (2)
—O(31) ($\times 2$)	111.6 (1)	—O(3) ($\times 2$)	112.5 (1)	112.4 (1)	112.4 (1)	112.5 (2)
O(21)—Se(1)—O(31)	109.3 (1)	O(2)—Se(1)—O(3)	107.5 (1)	107.7 (1)	107.5 (2)	107.0 (2)
Average	109.5		109.4	109.4	109.4	109.4
O(12)—Se(2)—O(12)	112.4 (1)					
—O(22) ($\times 2$)	105.3 (1)					
—O(32) ($\times 2$)	113.5 (1)					
O(22)—Se(1)—O(32)	105.8 (1)					
Average	109.3					
O(11)—O(11)	2.701 (3)	O(1)—O(1)	2.701 (1)	2.698 (2)	2.695 (5)	2.698 (5)
—O(21) ($\times 2$)	2.664 (3)	—O(2) ($\times 2$)	2.658 (1)	2.653 (2)	2.658 (4)	2.663 (6)
—O(31) ($\times 2$)	2.704 (3)	—O(3) ($\times 2$)	2.705 (1)	2.702 (2)	2.694 (4)	2.704 (6)
O(21)—O(31)	2.697 (4)	O(2)—O(3)	2.677 (2)	2.678 (3)	2.670 (6)	2.675 (8)
Average	2.689		2.684	2.681	2.678	2.685
O(12)—O(12)	2.712 (3)					
—O(22) ($\times 2$)	2.664 (3)					
—O(32) ($\times 2$)	2.720 (2)					
O(22)—O(32)	2.664 (4)					
Average	2.691					
Hydrogen bond						
O(21)⋯O(22 ⁱ)	2.558 (4)	O(2)⋯O(2 ⁱⁱ)	2.534 (3)	2.543 (4)	2.538 (8)	2.535 (9)

disordered positions close to the twofold axis), shifts along the $\text{O}(2)\cdots\text{O}(2^{\text{ii}})$ hydrogen bond. Thus $\text{Se}(1)\text{O}_4$ in the $\text{H}(\text{SeO}_4)_2^{3-}$ ion becomes closer to an SeO_4^{2-} ion and $\text{Se}(2)\text{O}_4$ becomes closer to an HSeO_4^- ion. Table 4 clearly shows that the bond distances and angles in $\text{Se}(1)\text{O}_4$ shift in such a way as to reduce the distortion and those in $\text{Se}(2)\text{O}_4$ shift so as to increase the distortion. As a result the dimer has a net dipole moment, since the deviation of the Se atom from the center of the O atoms is larger in HSeO_4 than in SeO_4 (Ichikawa, 1987, 1988). The dipole moment vectors lie in the mirror plane, but they are arranged antiparallel along the a axis, parallel along the b axis, and antiparallel to each other between two adjacent arrays of the dipole-moment vectors in the (100) plane. As a whole the LT structure is antipolar and could be antiferroelectric. It is, however, still uncertain whether the LT phase really is antiferroelectric, since neither a ferroelectric nor an antiferroelectric hysteresis loop has been observed, not only in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ but also in other $M_3\text{H}(\text{XO}_4)_2$ -type crystals (Gesi, 1980; Komukae *et al.*, 1985; Baranov, Merinov, Tregubchenko, Shuvalov & Shchagina, 1988). If we compare the primitive cell of the LT phase (IV) and the RT phase (III), a cell doubling

occurs in the LT phase (IV). This is similar to $\text{K}_3\text{D}(\text{SO}_4)_2$ (Noda *et al.*, 1991).

3.4. Relation between room-temperature structures of $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ and other $M_3\text{H}(\text{XO}_4)_2$ -type crystals

The RT structures of $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ and other $M_3\text{H}(\text{XO}_4)_2$ -type crystals are similar in certain respects, but clearly differ in other respects. Although the mutual relation of their unit cells was discussed by Ichikawa *et al.* (1991), the relationship between the atomic arrangements does not seem to have been fully clarified. For this reason, the corresponding projections for both types of structure have been examined. In Fig. 2(a) the projection of the RT structure along $-\frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c}$ is given for $\text{Rb}_3\text{D}(\text{SeO}_4)_2$; this corresponds to the c -axis projection of $\text{Cs}_3\text{D}(\text{SeO}_4)_2$, which is shown in Fig. 2(b). It is seen that the atomic positions for non-H atoms are approximately the same in both structures (*cf.* also Fig. 4, deposited). The main difference is that half of the H atoms in the Rb compound are involved in hydrogen-bonded dimers which are formed with two different adjacent selenate groups; this breaks the C base centering which is valid for TCHSe (Fig. 2).

three equivalent positions around the hexagonal *c* axis (Baranov, Makarova, Muradyan, Tregubchenko, Shuvalov & Simonov, 1987; Merinov *et al.*, 1990). This implies that the H atom also jumps from one site to another, following the O(2) atom, *i.e.* one hydrogen bond breaks and another is formed. The transition at T_{c1} can thus be characterized as an order-disorder transition not only of hydrogen but also of the donor-oxygen atom in the hydrogen-bonded system.

In phase (II), where as stated earlier the space group is the same ($A2/a$) as that in the RT phase of the other members, all H atoms are disordered around the center of symmetry (see Fig. 2*a*). At the T_{c2} transition, half of the H atoms break hydrogen bonds and form alternative hydrogen bonds so as to form a dimer between two different adjacent selenate groups. As a result of this, non-H atoms shift their positions slightly, all atoms except O(1) lie in a mirror plane, and H atoms become disordered around a twofold axis in phase (III) (see Fig. 1). On passing through T_{c3} , the proton becomes ordered, as a result of which the twofold axis and the *C* base centering disappear and the primitive cell becomes doubled in phase (IV).

The authors wish to thank Mr Hilding Karlsson for his skilful technical assistance throughout this work. The work was partly supported by the International Scientific Program (Joint research) (63044002), and a Grant-in-Aid for Co-operative Research (02302021) from the Ministry of Education, Science and Culture, Japan, and a Grant-in-Aid from the Nippon Sheet Glass Foundation for Materials Science Research.

Acta Cryst. (1992). **B48**, 639–644

Electron Difference Density and Vibration Tensors in SrTiO₃

BY R. H. BUTTNER AND E. N. MASLEN

Department of Physics, University of Western Australia, Nedlands 6009, Australia

(Received 16 August 1991; accepted 21 April 1992)

Abstract

Multiple data sets for strontium titanate SrTiO₃: $M_r = 183.51$, cubic, $Pm\bar{3}m$, $a = 3.9092(4)$ Å, $V = 59.740(3)$ Å³, $Z = 1$, $D_x = 5.101$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 26.489$ mm⁻¹, $F(000) = 84$, $T = 298$ K, refinement indices range $R = 0.013$ – 0.028 ,

0108-7681/92/050639-06\$06.00

References

- BARANOV, A. I., MAKAROVA, I. P., MURADYAN, L. A., TREGUBCHENKO, A. V., SHUVALOV, L. A. & SIMONOV, V. I. (1987). *Sov. Phys. Crystallogr.* **32**, 400–407.
- BARANOV, A. I., MERINOV, B. V., TREGUBCHENKO, A. V., SHUVALOV, L. A. & SHCHAGINA, N. M. (1988). *Ferroelectrics*, **81**, 187–191.
- BARANOV, A. I., TREGUBCHENKO, A. V., SHUVALOV, L. A. & SHCHAGINA, N. M. (1987). *Sov. Phys. Solid State*, **29**, 1448–1449.
- GESI, K. (1980). *J. Phys. Soc. Jpn.* **48**, 886–889.
- ICHIKAWA, M. (1978). *Acta Cryst.* **B34**, 2074–2080.
- ICHIKAWA, M. (1987). *Acta Cryst.* **B43**, 23–28.
- ICHIKAWA, M. (1988). *J. Mol. Struct.* **177**, 441–448.
- ICHIKAWA, M., GUSTAFSSON, T. & OLOVSSON, I. (1991). *Solid State Commun.* **78**, 547–551.
- ICHIKAWA, M., GUSTAFSSON, T. & OLOVSSON, I. (1992). *Acta Cryst.* **C48**, 603–607.
- ICHIKAWA, M. & SATO, S. (1987). Unpublished work.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KOMUKAE, M., OSAKA, T., KANEKO, T. & MAKITA, Y. (1985). *J. Phys. Soc. Jpn.* **54**, 3401–3405.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- LUNDGREN, J.-O. (1983). *Crystallographic Computer Programs*. Report UUIC-B13-4-05. Institute of Chemistry, Univ. of Uppsala, Sweden.
- MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
- MERINOV, B. V., BARANOV, A. I. & SHUVALOV, L. A. (1990). *Sov. Phys. Crystallogr.* **35**, 200–203.
- MERINOV, B. V., BARANOV, A. I., TREGUBCHENKO, A. V. & SHUVALOV, L. A. (1988). *Sov. Phys. Dokl.* **33**, 715–716.
- MERINOV, B. V., BOLOTINA, N. B., BARANOV, A. I. & SHUVALOV, L. A. (1988). *Sov. Phys. Crystallogr.* **33**, 824–827.
- NODA, Y., WATANABE, Y., KASATANI, H., TERAUCHI, H. & GESI, K. (1991). *J. Phys. Soc. Jpn.* **60**, 1972–1977.
- OLOVSSON, I. & JÖNSSON, P.-G. (1976). *The Hydrogen Bond*, Vol. II, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, ch. 8. Amsterdam: North Holland.
- SAMSON, S., GOLDISH, E. & DICK, C. J. (1980). *J. Appl. Cryst.* **13**, 425–432.

$wR = 0.012$ – 0.028 for 91 unique reflections. Seven structure refinements from five different flux-grown crystals of SrTiO₃ are compared. The specimens selected showed mild to modest extinction. In all cases the mean-square vibration amplitude for the Ti atom along the Ti–O bond markedly exceeds that for the O atom. The amplitudes of the cations are

© 1992 International Union of Crystallography