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Compounds with Perovskite-Type Slabs.
IV. Ferroelectric Phase Transitions in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) and $Sr_2Ta_2O_7$

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Abstract

Ferroelectric phase transitions in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) and $Sr_2Ta_2O_7$ were investigated by the single-crystal X-ray diffraction technique. The structures of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) at 300, 573, 773 and 1073 K and $Sr_2Ta_2O_7$ at 123 K have been determined from three-dimensional X-ray diffraction data and refined to final R values of 0.047, 0.070, 0.087, 0.097 and 0.033 for 907, 748, 663, 598 and 520 observed reflexions, respectively. The structures above the Curie points, approximately 675 K for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) and 166 K for $Sr_2Ta_2O_7$, have the symmetries of the space group $Cmcm$. All atoms are on the mirror planes at $z = 0.25$ and 0.75. Below the Curie points, the structures lose the mirror planes at $z = 0.25$ and 0.75 and the metal atoms move along the c axis on the mirror planes at $x = 0$ and 0.5. The space group becomes $Cmc2_1$. A slight deformation of the O atom framework in a perovskite-type slab can be regarded as a small rotation of $(Ta,Nb)O_6$ octahedra around axes parallel to the a axis. A distinct difference in the temperature dependence of the thermal parameters of the metal atoms in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) was found below and above the Curie point.

Introduction

Several ferroelectric $A_2B_2O_7$ compounds have been revealed to form a structural family related to the perovskite structure. The members include $Sr_2Ta_2O_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1976), $Sr_2Nb_2O_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1975; Scheunemann & Müller-Buschbaum, 1975a), $La_2Ti_2O_7$ (Scheunemann & Müller-Buschbaum, 1975b; Gasperin, 1975), $Ca_2Nb_2O_7$ (Scheunemann & Müller-Buschbaum, 1974; Ishizawa, Marumo, Iwai, Kimura & Kawamura, 1980) and $Nd_2Ti_2O_7$ (Scheunemann & Müller-Buschbaum, 1975c). The structures are composed of perovskite-type slabs stacked along the b axis. The slabs contain corner-shared BO_6 octahedra and A cations in twelve-coordination, and are linked by A cations lying at the boundaries of the slabs. These compounds have various polymorphs which are assumed to originate from a prototype structure whose space group is $Cmcm$ (Ishizawa *et al.*, 1980). The Curie temperatures (T_c) of these compounds are higher than 1500 K except for $Sr_2Ta_2O_7$ ($T_c = 166$ K) (Nanamatsu, Kimura & Kawamura, 1975). $Sr_2(Ta_{1-x}Nb_x)_2O_7$ forms a complete solid-solution system and T_c varies continuously from 166 K ($x = 0$; $Sr_2Ta_2O_7$) to 1615 K ($x = 1.0$; $Sr_2Nb_2O_7$) (Nanamatsu *et al.*, 1975). The space groups $Cmcm$ and $Cmc2_1$ were reported for the respective end members of the system at room temperature (Ishizawa *et al.*, 1975, 1976). Thus, the ferroelectric phase transition in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ was expected to accompany a structural change from $Cmcm$ to $Cmc2_1$ (Ishizawa *et al.*, 1976). Recently, new phases were found for $Sr_2Nb_2O_7$ below 493 K and for $Sr_2Ta_2O_7$ below 443 K (Yamamoto, Yagi, Honjo, Kimura & Kawamura, 1980). Studies related to the phase transition in $Sr_2Nb_2O_7$ were also carried out by Ohi, Kimura, Ishida & Kakinuma (1979) and Kojima,

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Ohi, Takashige, Nakamura & Kakinuma (1979). To obtain a better understanding of their phase transitions, it is necessary to elucidate the structural changes which occur with increasing or decreasing temperature. This study was therefore undertaken on crystals of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) and $Sr_2Ta_2O_7$, whose T_c's were in a suitable temperature range to investigate structural changes before and after the phase transitions with the high- or low-temperature X-ray diffraction technique.

Experimental

Single crystals of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) were kindly provided by Drs Kimura and Kawamura of Nippon Electric Company. They were made by the floating-zone technique on an image furnace. The value of x was determined to be 0.12 (4), though the initial value before zone melting was reported to be 0.2 (Nanamatsu et al., 1975). Chemical analyses of the crystal to determine the proportion of Nb were carried out at the Central Research Laboratory of Sumitomo Kinzoku Kozan Ltd, with the result $x = 0.14$ which agrees with the value $x = 0.12$ (4) within the limit of error. The Curie temperature of the substance was reported to be 675 K (Nanamatsu et al., 1975). Weissenberg photographs were taken at various temperatures up to 1200 K with Cu $K\alpha$ radiation, but no significant change in the diffraction symmetry was recognized on these photographs below and above T_c. No superlattice reflexions corresponding to those observed by Yamamoto et al. (1980) for $Sr_2Nb_2O_7$, and $Sr_2Ta_2O_7$ or those observed by Scheunemann & Müller-Buschbaum (1975a) for $Sr_2Nb_2O_7$ were detected on these photographs. The systematic absences, hkl for $h + k$ odd and $00l$ for l odd, restricted the space group to $Cmcm$, $Cmc2_1$ or $C2cm$. A four-circle diffractometer (Rigaku) equipped with a small specimen-heating apparatus (Ishizawa, Miyata, Minato & Iwai, 1978) was used for the determination of the cell dimensions and the collection of intensity data at 300, 573, 773 and 1073 K. The specimen was heated in a hot N_2 gas stream. The temperature of the specimen was kept constant within ±5 K. Two crystals of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) were used; one had dimensions 0.10 × 0.10 × 0.02 mm and was studied at 300 K, the other also had dimensions 0.10 × 0.10 ×

0.02 mm and was studied at high temperatures. It was supposed that the ferroelectric domains were not aligned in each specimen, since they were the fragments of as-grown crystals. Cell dimensions at each temperature were calculated from between 10 and 20 2θ values in the range $0.20 < \sin\theta/\lambda < 0.70$ Å^{-1} with the least-squares procedure. Crystal data for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) are given in Table 1. Intensities were collected with Mo $K\alpha$ radiation monochromatized with a graphite plate. The $2\theta-\omega$ scan technique was employed with a scan speed of 2° min^{-1} in ω. Numbers of independent reflexions whose $|F_o|$'s were larger than $3\sigma(|F_o|)$ were 907 at 300 K, 748 at 573 K, 663 at 773 K and 598 at 1073 K in the range $\sin\theta/\lambda < 0.91$ Å^{-1}. Intensities were corrected for Lorentz and polarization factors. Absorption corrections were also applied by taking into consideration the crystal shapes with the program $ACACA$ (Wuensch & Prewitt, 1965).

Intensity data of $Sr_2Ta_2O_7$ at 123 K were collected with the same specimen as was used in the structural investigation at room temperature (Ishizawa et al., 1976) on a four-circle diffractometer equipped with a cryostat using liquid N_2. Measurements were carried out with graphite-monochromated Mo $K\alpha$ radiation in the range $\sin\theta/\lambda < 0.71$ Å^{-1}. Crystal data for $Sr_2Ta_2O_7$ are given in Table 2. It was assumed that the ferroelectric phase in $Sr_2Ta_2O_7$ below 166 K is orthorhombic with the same extinction rules as for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$), the assumption being supported by the observed intensities. In all, 520 independent reflexions were obtained. Lorentz, polarization and absorption corrections were also applied in a similar way as for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$).

Refinement

Refinement of the structure of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) at each temperature was carried out with the full-matrix least-squares program $LINUS$ (Coppens & Hamilton, 1970). Since the Patterson maps were quite similar to that of the paraelectric $Sr_2Ta_2O_7$ at room temperature (Ishizawa et al., 1976), its positional parameters were used as the starting values for the

Table 2. *Crystal data for* $Sr_2Ta_2O_7$

Temperature	123 K	Room temperature
Crystal system	Orthorhombic	Orthorhombic
Space group	$Cmc2_1$	$Cmcm$
Cell dimensions		
a	3.940 (2) Å	3.937 (6) Å
b	27.15 (3)	27.198 (6)
c	5.692 (1)	5.692 (7)
Z	4	4

Table 1. *Crystal data for* $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$)

Temperature	300 K	573 K	773 K	1073 K
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Cmc2_1$	$Cmc2_1$	$Cmcm$	$Cmcm$
Cell dimensions				
a	3.961 (1) Å	3.967 (1) Å	3.967 (1) Å	3.975 (2) Å
b	27.110 (6)	27.247 (8)	27.325 (9)	27.393 (9)
c	5.687 (2)	5.705 (1)	5.723 (1)	5.739 (2)
Z	4	4	4	4

structure above T_c; parameters which were slightly displaced, in the same way as for the structure of ferroelectric $Sr_2Nb_2O_7$ at room temperature (Ishizawa *et al.*, 1975), were used as the starting values for the structure below T_c. The space group $C2cm$ was discarded for the ferroelectric structure since the spontaneous polarization occurs along the c direction (Nanamatsu *et al.*, 1975). Anisotropic temperature factors were used for the metal atoms and isotropic ones for the O atoms. Extinction corrections were also applied (Zachariasen, 1967) in the isotropic mode. The

Table 3. *Positional and thermal parameters ($\mathring{A}^2$) of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) with their estimated standard deviations in parentheses*

		300 K	573 K	773 K	1073 K
Sr(1)	x	0	0	0	0
	y	0.44707 (8)	0.4469 (2)	0.4469 (2)	0.4461 (3)
	z	0.748 (1)	0.746 (3)	0.75	0.75
	B^*	0.61	0.95	1.36	2.02
Sr(2)	x	0	0	0	0
	y	0.28911 (9)	0.2889 (2)	0.2895 (3)	0.2904 (5)
	z	0.229 (1)	0.248 (3)	0.25	0.25
	B^*	1.07	1.43	2.02	3.43
Ta(1)	x	0.5	0.5	0.5	0.5
	y	0.44445 (3)	0.44454 (6)	0.44459 (8)	0.44389 (9)
	z	0.25	0.25	0.25	0.25
	B^*	0.31	0.48	0.72	0.92
Ta(2)	x	0.5	0.5	0.5	0.5
	y	0.33964 (3)	0.33960 (7)	0.33971 (8)	0.3400 (1)
	z	0.7373 (4)	0.7359 (10)	0.75	0.75
	B^*	0.45	0.60	0.75	1.35
O(1)	x	0.5	0.5	0.5	0.5
	y	0.503 (1)	0.500 (3)	0.5	0.5
	z	0.514 (6)	0.49 (1)	0.5	0.5
	B	1.4 (4)	0.8 (5)	1.7 (6)	1.8 (7)
O(2)	x	0.5	0.5	0.5	0.5
	y	0.403 (1)	0.406 (2)	0.402 (1)	0.402 (1)
	z	0.524 (5)	0.53 (1)	0.517 (7)	0.523 (9)
	B	1.0 (3)	1.4 (8)	2.6 (6)	3.0 (6)
O(3)	x	0.5	0.5	0.5	0.5
	y	0.295 (1)	0.294 (1)	0.293 (1)	0.296 (1)
	z	0.511 (5)	0.510 (6)	0.506 (5)	0.516 (7)
	B	0.7 (4)	−0.3 (3)	1.2 (3)	2.3 (5)
O(4)	x	0	0	0	0
	y	0.454 (1)	0.456 (1)	0.459 (1)	0.460 (1)
	z	0.285 (4)	0.25 (2)	0.25	0.25
	B	1.1 (3)	0.8 (4)	1.2 (5)	1.3 (7)
O(5)	x	0	0	0	0
	y	0.352 (1)	0.348 (1)	0.350 (2)	0.341 (2)
	z	0.709 (4)	0.73 (1)	0.75	0.75
	B	1.1 (3)	1.2 (6)	2.9 (9)	3.0 (8)
O(6)†	x	0.5	0.5	0.5	0.5
	y	0.397 (1)	0.397 (2)	0.402 (1)	0.402 (1)
	z	0.015 (5)	−0.01 (1)	−0.017 (7)	−0.023 (9)
	B	1.1 (4)	1.4 (8)	2.6 (6)	3.0 (6)
O(7)‡	x	0.5	0.5	0.5	0.5
	y	0.292 (1)	0.293 (4)	0.293 (1)	0.296 (1)
	z	0.989 (7)	0.98 (2)	0.994 (5)	0.984 (7)
	B	1.5 (6)	4 (2)	1.2 (3)	2.3 (4)

* Calculated from anisotropic temperature factors by $B = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$.
† Equivalent to O(2) above T_c. Symmetry operation $x, y, \frac{1}{2} - z$.
‡ Equivalent to O(3) above T_c. Symmetry operation $x, y, \frac{1}{2} - z$.

Table 4. *Positional and thermal parameters of $Sr_2Ta_2O_7$ at 123 K with their estimated standard deviations in parentheses*

Sr(1)	x	0	O(3)	x	0.5
	y	0.44702 (5)		y	0.295 (1)
	z	0.757 (1)		z	0.509 (5)
	B^*	0.38		B	0.2 (2)
Sr(2)	x	0	O(4)	x	0
	y	0.28808 (5)		y	0.454 (1)
	z	0.245 (1)		z	0.292 (4)
	B^*	0.75		B	1.0 (3)
Ta(1)	x	0.5	O(5)	x	0
	y	0.44476 (2)		y	0.351 (1)
	z	0.25		z	0.785 (4)
	B^*	0.20		B	0.9 (2)
Ta(2)	x	0.5	O(6)	x	0.5
	y	0.33988 (2)		y	0.400 (1)
	z	0.7478 (6)		z	0.010 (5)
	B^*	0.22		B	1.4 (6)
O(1)	x	0.5	O(7)	x	0.5
	y	0.502 (1)		y	0.291 (1)
	z	0.495 (8)		z	0.986 (6)
	B	1.0 (2)		B	1.4 (7)
O(2)	x	0.5			
	y	0.401 (1)			
	z	0.523 (4)			
	B	0.5 (4)			

* Calculated from anisotropic temperature factors by $B = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$.

populations of the Nb atoms at two crystallographically independent octahedral sites, $B(1)$ and $B(2)$, were also included with the parameters to be refined on the assumption that both sites were fully occupied by Nb and Ta atoms. Atomic scattering factors and dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974). The final R values, assuming $Cmcm$ and $Cmc2_1$ for respective data sets, were 0.047, 0.070, 0.087 and 0.097 for structures at 300, 573, 773 and 1073 K, respectively. The refinement at 573 K, assuming $Cmc2_1$, showed a strong correlation between the O(3) and O(7) parameters, and converged to some unreasonable isotropic temperature factors for these atoms: a negative value for O(3) and a too large value for O(7). The site occupancy of Nb at the $B(1)$ site was determined to be 0.07 (2) as an average of 0.07 (1) at 300 K, 0.05 (2) at 573 K, 0.09 (2) at 773 K and 0.07 (1) at 1073 K. That of Nb at the $B(2)$ site was determined to be 0.16 (5) as an average of 0.12 (1), 0.13 (2), 0.21 (2) and 0.16 (2) at the respective temperatures. The value of x for the crystal was calculated to be 0.12 (4).

The refinement of the structure of $Sr_2Ta_2O_7$ at 123 K was undertaken in a similar way as for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$), with the space group $Cmc2_1$, giving a final R value of 0.033.

Final positional and thermal parameters are given in Table 3 for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) and in Table 4 for $Sr_2Ta_2O_7$.*

Discussion

The structure of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) at 300 K is shown in Fig. 1. All atoms are on the mirror planes at $x = 0$ and 0.5. The perovskite slabs formed by corner-shared $(Ta,Nb)O_6$ octahedra and twelve-coordinated $Sr(1)$ atoms are stacked along the b axis. $Sr(2)$ atoms are sited at the boundaries of the slabs, binding neighbouring slabs. The $Sr(2)$ atom is surrounded by eight O atoms within 3·5 Å. The distortion of the octahedral framework in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) at 300 K is fairly small in comparison with that of $Sr_2Nb_2O_7$ at room temperature (Ishizawa *et al.*, 1975), though both structures essentially belong to the same type having the space group $Cmc2_1$. The outer $B(2)O_6$ octahedra are more distorted and expanded than the inner $B(1)O_6$ octahedra, as is commonly observed in the structures of $A_2B_2O_7$ compounds with perovskite-type slabs. The populations of the Nb atoms at the $B(1)$ and $B(2)$ sites are 0·07 (2) and 0·16 (5), respectively. It is supposed that the BO_6 octahedra become more distorted with increasing Nb content in the $Sr_2(Ta_{1-x}Nb_x)_2O_7$ system.

The structural changes in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) and $Sr_2Ta_2O_7$ are shown in Figs. 2 and 3, respectively. Above T_c metal atoms are on the intersections of mirror planes parallel to (100) and those parallel to (001). Below T_c, they shift along the c axis on the mirror planes at $x = 0$ and 0·5, destroying the mirror symmetry with respect to the planes $z = 0.25$ and 0·75. The shifts of metal atoms from their positions at temperatures above T_c are given in Table 5, where the z parameter of $Ta(1)$ below T_c is fixed to 0·25, the value above T_c, to define the origin. Most of

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* Lists of structure factors, anisotropic thermal parameters and selected interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35643 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
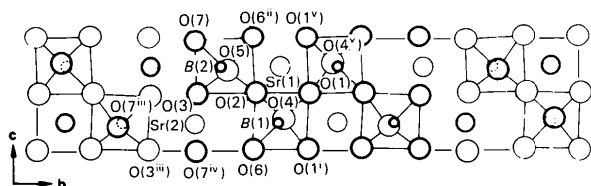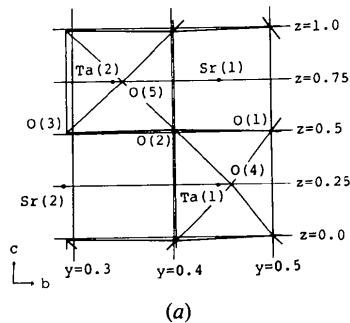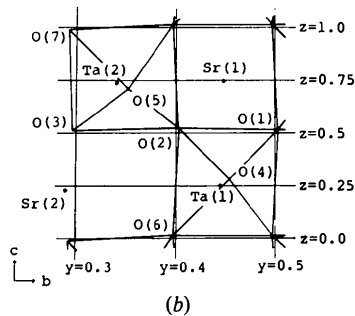

Fig. 1. The crystal structure of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) at 300 K projected on the (100) plane. The thick circles are at the level $x = 0.5$ and the thin ones are at the level $x = 0$. Symmetry operations are: none x,y,z; (i) x, $1 - y$, $z - \frac{1}{2}$; (ii) $x, y, z + 1$; (iii) $-x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x, y, z - 1$; (v) x, $1 - y$, $z + \frac{1}{2}$.

Fig. 2. The structures of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x \simeq 0.12$) at (a) 773 K and (b) 300 K projected on the (100) plane.
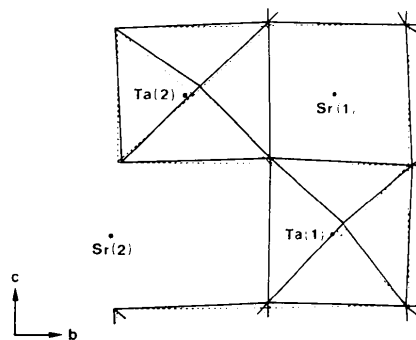

Fig. 3. The structures of $Sr_2Ta_2O_7$ at 123 K and room temperature shown by solid and broken lines, respectively.
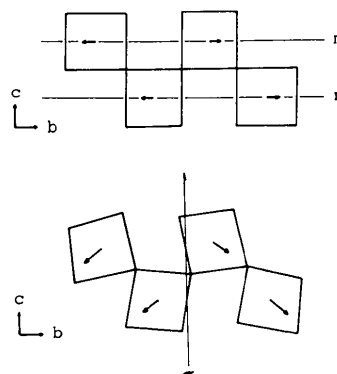

Fig. 4. The schematic features of the structural change between paraelectric (upper) and ferroelectric (lower) phases. Displacements of B atoms from the centres of respective octahedra are shown by arrows.

Table 5. *Displacements of metal atoms in the ferroelectric phases of* $Sr_2(Ta_{1-x}Nb_x)_2O_7$ *(x $\simeq$ 0·12) and* $Sr_2Ta_2O_7$ *from the positions in their paraelectric phases*

Values are the differences between the fractional coordinates at 773 K and those at respective temperatures for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12), and differences between the parameters at 123 K and those at room temperature for $Sr_2Ta_2O_7$.

| | $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12) | | | | $Sr_2Ta_2O_7$ | |
| | 300 K | | 573 K | | 123 K | |
	y	z	y	z	y	z
Sr(1)	−0·0002 (2)	0·002 (1)	0·0000 (2)	0·004 (3)	0·0002 (5)	−0·007 (1)
Sr(2)	0·0004 (3)	0·021 (1)	0·0006 (3)	0·002 (3)	0·0003 (5)	0·005 (1)
B(1)	0·00014 (8)	0	0·00005 (8)	0	0·0001 (2)	0
B(2)	0·00007 (8)	0·0127 (4)	0·00011 (8)	0·014 (1)	0·0000 (2)	0·0022 (6)

their displacements along the c axis exceed three times the respective estimated standard deviations. In the structure above T_c, O(1) is located at a centre of symmetry. O(4) and O(5) are on the mirror planes at $z = 0·25$ and $0·75$. O(2) and O(3) are located at positions very near the planes at $z = 0$ and $0·5$. The BO_6 octahedra in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12) at 300 K and $Sr_2Ta_2O_7$ at 123 K are rotated by approximately 2° around the axes parallel to a with respect to the orientation in the paraelectric phases. The schematic features of the structural change between the $Cmcm$ and $Cmc2_1$ phases are shown in Fig. 4.

Since the differences in the atomic coordinates between the ferroelectric and paralectric structures were small, it was examined whether the true space group could be selected with reasonable reliability at each temperature. The final R values, assuming the space groups $Cmcm$ and $Cmc2_1$, were 0·064 and 0·047 at 300 K, 0·075 and 0·070 at 573 K, 0·087 and 0·078 at 773 K and 0·097 and 0·091 at 1073 K for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12) and 0·036 and 0·033 at 123 K for $Sr_2Ta_2O_7$, respectively. Although smaller R values were obtained for $Cmc2_1$ models at all temperatures, the differences were insignificant for $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12) from Hamilton's (1965) significance test, except for the case at 300 K. For $Sr_2Ta_2O_7$, the test supported the $Cmc2_1$ model at the 99% significance level. Additional calculations relating to the existence of ferroelectric domains were carried out on the data of $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12) at 300 K. Two structural models, one based on the atomic coordinates given in Table 3 and the other based on those in Table 3 with their signs changed, were refined. The differences in their final R values and coordinates were insignificant. Therefore, the effect of domains on the final atomic parameters is presumed to be quite small. In $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12), a clue to distinguish between the paraelectric and ferroelectric phases was found in the temperature dependence of the thermal parameters for the metal atoms. Those of (Ta,Nb)(2) and Sr(2) are shown in Fig. 5 as examples. The gradients of U_{33} for the metal atoms clearly change
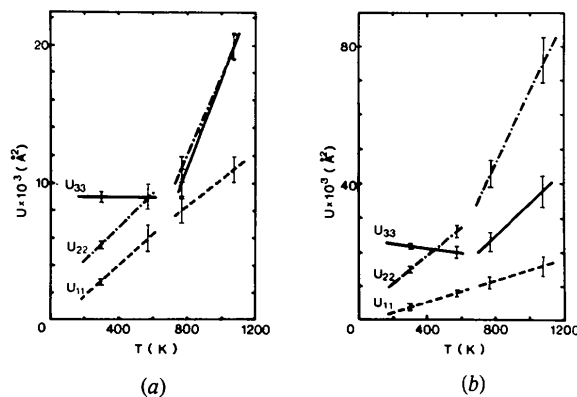

(a)   (b)

Fig. 5. Temperature dependence of thermal parameters U_{11}, U_{22} and U_{33} of (a) (Ta,Nb)(2) and (b) Sr(2) in $Sr_2(Ta_{1-x}Nb_x)_2O_7$ (x $\simeq$ 0·12).

at 673 ± 50 K, which corresponds to T_c of this substance.

$La_2Ti_2O_7$ (Gasperin, 1975), $Ca_2Nb_2O_7$ (Brandon & Megaw, 1970; Ishizawa *et al.*, 1980) and $Nd_2Ti_2O_7$ (Scheunemann & Müller-Buschbaum, 1975c) have monoclinic modifications with the space group $P2_1$. $Ca_2Nb_2O_7$, $Sr_2Nb_2O_7$ and $La_2Ti_2O_7$ (Scheunemann & Müller-Buschbaum, 1974, 1975a,b) have ortho-rhombic modifications with the space group $Pbn2_1$. Ferroelectric phase transition occurs above 1500 K in these compounds. $Ca_2Nb_2O_7$ is expected to be ferro-electric up to 2273 K, the melting temperature of this substance (Nanamatsu *et al.*, 1975). The structure of the $Pbn2_1$ modification can be obtained by stacking the structure of the unit cell of the $P2_1$ modification of $Ca_2Nb_2O_7$ or $La_2Ti_2O_7$ along the b axis with the operation of n glide symmetry (Ishizawa *et al.*, 1980). The transition between the two modifications is probably impossible since it needs a reconstruction of the octahedral framework in the perovskite-type slabs. On the other hand, the symmetries of these modifications are subgroups of $Cmc2_1$. The structures can be easily changed to those of the $Cmc2_1$ phases with small shifts of the constituent atoms. Thus, it is

reasonable to suppose that with increasing temperature these modifications undergo transitions to the $Cmc2_1$ phase, and further to the $Cmcm$ phase at T_c. The incommensurate phase found in $Sr_2Nb_2O_7$ below 493 K (Yamamoto et al., 1980) is considered to be an intermediate phase between $Cmc2_1$ and a lower-symmetry $P2_1$ or $Pbn2_1$ phase. Yamamoto et al. (1980) also observed weak superlattice reflexions in an electron diffraction study of $Sr_2Ta_2O_7$ below 443 K and suspected that the true space group of the substance at room temperature was $P2_1/m$. Such superlattice reflexions have not been observed during the X-ray study. Assuming that the true space group for $Sr_2Ta_2O_7$ is $P2_1/m$ at room temperature, it is supposed that the shifts of the atomic coordinates from the $Cmcm$ structural model are fairly small in comparison with the shifts between the $Cmcm$ and $Cmc2_1$ models discussed in this paper.

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