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Electron and X-Ray Diffraction Study of $K_2SrTi_{10}O_{22}$

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The single-phase compound $K_2SrTi_{10}O_{22}$ was prepared by solid-state reaction. It crystallizes in the monoclinic system, space group $C2/m$ with a = 15.314(2), b = 3.7865(6), and c = 15.439(2) Å, β = 102.68(1)°, and Z = 2. The structure was determined from 1674 reflections collected on a Enraf–Nonius CAD4 automatic diffractometer with Mo$K\alpha$ radiation. The final R index and weighted R_w index are 0.057 and 0.061, respectively. $K_2SrTi_{10}O_{22}$ belongs to the family of titanates $(A_2Ti_6O_{13})_n$–$A'Ti_4O_9$ with A = Na, K, Rb, A' = Ba, Sr, Pb, and n = 1, 2, 3, . . . , first described by Raveau *et al.*, with n = 1. The covalent framework is built up of the intergrowth of two types of structural units: $A_2Ti_6O_{13}$ and hypothetical $A'Ti_4O_9$. Both units are characterized by zigzag ribbons of, respectively, 2 × 3 and 2 × 2 edge-sharing octahedra joined by corners sharing to form tunnels along the [001] direction. The tunnels accommodate the K^+ cation on the A' site, whereas the A site is occupied by Sr^{2+}/K^+ cations. Electron diffraction study shows diffuse streaks parallel to the (a^*, c^*) plane leading to a doubling of the b parameter. This suggests a one-dimensional ordering of K atoms and vacancies along the b axis, on the one hand, and Sr/K atoms on the other hand.

Introduction

In the last decade, Raveau *et al.* have described a new family of titanates $(A_2Ti_6O_{13})_n$–$A'Ti_4O_9$ with A = Na, K, Rb, A' = Ba, Sr, Pb, and n = 1, 2, 3, . . . , (*1*). For n = 1, the structure is built up from the intergrowth along the c axis of two structural units: $A_2Ti_6O_{13}$ and the hypothetical $A'Ti_4O_9$. The structure of $A_2Ti_6O_{13}$ was first determined by Anderson and Wadsley (*2*).

Titanates with the formula $A_2Ti_6O_{13}$ with A = Na, K, Rb, Ba exhibit an analogous covalent framework, which may be described as triple zigzag ribbons of octahedra sharing common edges (*3–5*). The ribbons are joined by corners, leading to a sheet parallel to the (b, c) plane; two adjacent sheets share an octahedral corner to form a tunnel in which A cations are inserted. The same type of sheets, but with triple ribbons replaced by double ribbons, has been found in the hypothetical $A'Ti_4O_9$ structure. To our knowledge, only X-ray powder diffraction and electron microscopy studies have been performed on these compounds.

The structural characterization of intergrowth phases $(A_2Ti_6O_{13})_n$–$A'Ti_4O_9$ with (A, A') = (K, Sr) has been undertaken in order to specify the structure previously mentioned (*1*), as well as to elucidate the arrangement of potassium and strontium cations within the tunnels. In this paper, we report the refinement and description of the crystal structure for the phase with n = 1: $K_2SrTi_{10}O_{22}$.

Experimental

$K_2SrTi_{10}O_{22}$ was prepared by conventional solid-state reaction of intimately mixed powders using stoichiometric amounts of K_2CO_3, $SrCO_3$, and TiO_2 (anatase). The mixture was first heated in a platinum crucible at 1273 K for 4 hr in order to remove CO_2, then at 1673 K for 2 days. The single crystals obtained grow in the form of

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TABLE I

$K_2SrTi_{10}O_{22}$: CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA

Space group	$C2/m$
a (Å)	15.314(2)
b (Å)	3.7865(6)
c (Å)	15.439(2)
β(°)	102.68(1)
V (Å^3)	873.4(4)
Z	2
Formula weight (g)	996.8
D_{calc} (g/cm^3)	3.795
μ (cm^{-1})	78.1
Equipment	Nonius CAD4 diffractometer
Radiation (Å)	Mo$K\alpha$, λ = 0.71069
Scan mode	$\omega - 2\theta$
Scan angle (°)	$\Delta\omega = 1.0 + 0.35$ tg θ
Recording angular range (θ°)	1.5–35.0
Number of independant data observed with $\sigma(I)/I <$ 0.33 used in refinement	1674
Number of variables	111
$R = \sum (\|\|F_o\| - \|F_c\|\|)/\sum \|F_o\|$	0.057
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$ with $w = 1/(1 + [F_{obs} - F_{av})/F_{max}]^2)$	0.061
Extinction parameter refined g	1.78(2) × 10^{-6}

colorless thin needles elongated along the [010] direction.

A preliminary analysis was performed using a scanning electron microscope Jeol 35C equipped with a Tracor EDX system. A transmission electron diffraction study was carried out with Philips CM 30 operating at 300 kV. The samples were prepared as powders on amorphous holey carbon-coated polymer films supported by a copper grid. The powder samples were ground in an agate mortar with a few droplets of methanol which were allowed to evaporate.

The X-ray powder diffraction investigation was performed on an Inel curve detector using a 0.2-mm-diameter capillary and Cu$K\alpha_1$ radiation (λ = 1.54059 Å). The cell parameters refined by a least-squares method are given in Table I. The powder pattern (Table II) includes observed and calculated interplanar distances of the reflection planes along with the experimental intensities.

TABLE II

$K_2SrTi_{10}O_{22}$: X-RAY POWDER DIFFRACTION DATA

hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_0	hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_0
200	7.464	7.470	40	$80\bar{7}$	1.595	1.594	13
$20\bar{2}$	6.002	6.003	35	$71\bar{7}$	1.562	1.562	22
003	5.014	5.020	10	423	1.554	1.554	45
$40\bar{2}$	3.685	3.684	22	408	1.549	1.549	18
110	3.671	3.670	13	$91\bar{1}$	1.544	1.544	10
$20\bar{5}$	3.034	3.034	100	$91\bar{4}$	1.520	1.519	19
310	3.013	3.014	65	$62\bar{2}$	1.517	1.517	15
$31\bar{2}$	2.937	2.936	67	$100\bar{4}$	1.506	1.507	44
113	2.886	2.889	49	0010	1.506	1.506	44
403	2.723	2.724	64	911	1.483	1.483	13
$11\bar{4}$	2.697	2.702	11	$31\bar{1}\bar{0}$	1.425	1.425	12
$60\bar{2}$	2.536	2.536	34	2010	1.418	1.417	15
600	2.486	2.490	9	$42\bar{7}$	1.398	1.397	40
$40\bar{7}$	2.070	2.071	95	623	1.394	1.393	38
603	2.057	2.058	77	518	1.358	1.358	13
$51\bar{5}$	2.028	2.028	15	821	1.307	1.307	8
315	2.001	2.001	10	$111\bar{4}$	1.295	1.295	19
020	1.894	1.893	80	$60\bar{1}\bar{2}$	1.235	1.235	12
$60\bar{7}$	1.840	1.840	11	1201	1.219	1.219	15
801	1.805	1.805	26	$111\bar{7}$	1.215	1.215	7
$51\bar{7}$	1.742	1.742	24	428	1.199	1.199	17
$22\bar{4}$	1.685	1.685	18	$102\bar{4}$	1.179	1.179	28
713	1.644	1.644	25	1006	1.175	1.175	11
$22\bar{5}$	1.606	1.606	27				

The X-ray single-crystal data were collected with a four-circle Enraf–Nonius CAD4 diffractometer operating under the conditions given in Table I. For the data reduction, structure solution, and refinement, the SDP-plus program chain (1982 version) of Enraf–Nonius, written by Frenz (*6*), was used. Owing to the small value of the calculated linear absorption coefficient (μ = 78.1 cm^{-1}) and of the crystal size, no absorption correction was performed.

Initial positions of the framework atoms were deduced from the basic structure (*1*). Refinement was carried out by the full-matrix least-squares method. The positional parameters of K and Sr were determined from successive difference Fourier maps. Anisotropic temperature factors were then assigned to all atoms. The final stage of refinement with corrections for secondary extinctions and anomalous dispersion converges to final $R = 0.057$ and $R_w = 0.061$. The final Fourier difference map shows an electronic residue of $\pm 2.8\ e^-/Å^3$ on the 2*d* (1/2, 0, 1/2) site position, which suggests that the compound is not fully ordered. An explanation will be proposed from electron diffraction results. Table III gives the final atomic coordinates and thermal parameters (a structure factors table will be sent upon request).

Description and Discussion of the Structure

The covalent framework is built up from the intergrowth of two types of structural units, $A_2Ti_6O_{13}$ and the hypothetical $A'Ti_4O_9$. Both units are characterized by zigzag ribbons of, respectively, 2 × 3 and 2 × 2 edge-sharing octahedra joined by shared corners to form tunnels along the [010] direction (Fig. 1). A list of bond distances and angles with their standard deviations is given in Tables IVa and IVb. It can be seen from this table that all distances are in good agreement with those generally observed in titanates.

TABLE III

$K_2SrTi_{10}O_{22}$: Fractional Atomic Coordinates and Isotropic Thermal Parameters

Atom	Position	*x*	*y*	*z*	*B* (Å²)
Ti(1)	4*i*	0.24465(8)	0.00	0.16382(8)	0.46(2)
Ti(2)	4*i*	0.13837(8)	0.00	0.36066(8)	0.58(2)
Ti(3)	4*i*	0.09821(8)	0.00	0.75648(8)	0.54(2)
Ti(4)	4*i*	0.20306(8)	0.00	0.56551(8)	0.51(2)
Ti(5)	4*i*	0.16575(7)	0.00	0.96285(8)	0.50(2)
Sr[a]	4*i*	0.44209(7)	0.00	0.83945(9)	1.46(2)
K(1)[a]	4*i*	0.44209(7)	0.00	0.83945(9)	1.46(2)
K(2)[b]	4*i*	0.4833(2)	0.00	0.4507(2)	0.83(4)
O(1)	4*i*	0.3001(3)	0.00	0.0422(3)	0.69(8)
O(2)	4*i*	0.0214(4)	0.00	0.2928(4)	1.5(1)
O(3)	4*i*	0.3763(3)	0.00	0.2297(3)	0.72(8)
O(4)	4*i*	0.0651(4)	0.00	0.8785(4)	0.94(8)
O(5)	4*i*	0.3354(4)	0.00	0.6348(4)	0.80(8)
O(6)	4*i*	0.2662(3)	0.00	0.4429(3)	0.63(7)
O(7)	4*i*	0.1841(4)	0.00	0.2467(4)	0.97(8)
O(8)	4*i*	0.1033(3)	0.00	0.4704(3)	0.86(8)
O(9)	4*i*	0.1357(3)	0.00	0.0704(3)	0.92(8)
O(10)	4*i*	0.1417(4)	0.00	0.6499(3)	0.98(8)
O(11)	4*i*	0.2274(3)	0.00	0.8459(3)	0.61(7)

[a] Fractional occupancies for Sr: $p[Sr] = 0.25$; for K(1): $p[K(1)] = 0.25$, $p[Sr] + p[K(1)] = 0.5$.
[b] Fractional occupancy for K(2): $p[K(2)] = 0.25$.

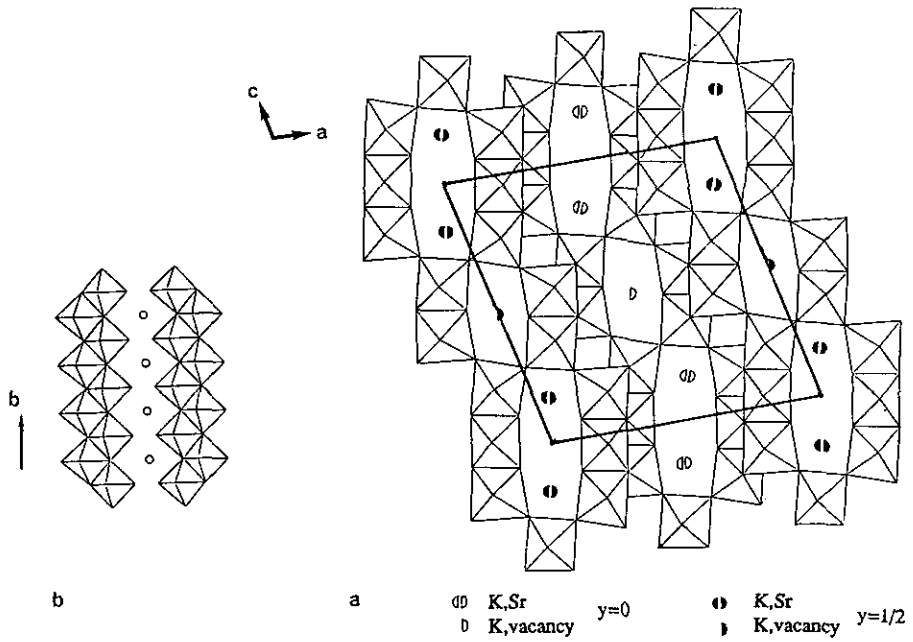

FIG. 1. (a) Structure of $K_2SrTi_{10}O_{22}$ in projection onto [010]: 2 × 2 and 2 × 3 edge-sharing octahedra joined by corners sharing to form tunnels along [010] direction. (b) Sheet formation by edge-sharing octahedra.

The K/Ti and Sr/Ti ratios, obtained from the crystal structure determination of $K_2SrTi_{10}O_{22}$, are in good agreement with the EDX preliminary analysis which gave K/Ti = 0.19(2) and Sr/Ti = 0.11(2). As shown in Table III, the 4*i* site (0.4421, 0, 0.8395) is statistically occupied by 50% of potassium and 50% of strontium atoms, whereas 50% of potassium atoms and 50% of vacancies are distributed on the position 4*i* (0.4832, 0, 0.4507). This indicates that K^+ cations are preferentially pinned on the second site. The biggest cation, i.e. K^+ (rK^+ = 1.38 Å compared with rSr^+ = 1.18 Å), is located in the narrowest tunnel, for which the available space is, however, the largest (Fig. 2).

In order to elucidate the electronic residue (± 2.8 $e^-/Å^3$) at the position 2*d* (1/2, 0, 1/2), electron diffraction studies have been performed. Typical electron diffraction patterns of the [001] and [100] zone axis are shown in Figs. 3 and 4, respectively. In Fig. 3, diffuse streaks parallel to a^* are observed between the Bragg spots. Diffuse streaks parallel to c^* can also be observed in Fig. 4.

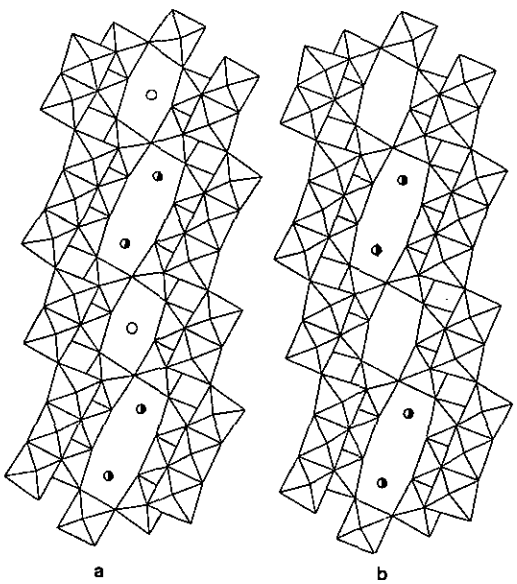

FIG. 2. Model of cell with a doubled b parameter (a) y = 0, occupation of 4*i* sites: 50% of potassium and 50% of strontium on (0.4421, 0, 0.8395), 100% of potassium on (0.4832, 0, 0.4507); (b) y = 1/2, occupation of 4*i* sites: 50% of potassium and 50% of strontium on (0.4421, 1/2, 0.8395), 100% of vacancies on (0.4832, 1/2, 0.4507).

TABLE IVa

$K_2SrTi_{10}O_{22}$: SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR THE COORDINATION POLYHEDRA

			$Ti(1)O_6$ octahedron			
Ti(1)	O(1)	O(3)	O(7)	O(9)	O(11)	O(11)
O(1)	2.224(6)					
O(3)	84.4(2)	2.049(5)				
O(7)	170.5(2)	105.1(2)	1.737(6)			
O(9)	78.4(2)	162.8(2)	92.1(2)	1.952(5)		
O(11)	116.1(2)	80.2(1)	102.6(2)	96.3(1)	1.951(1)	
O(11)	116.1(2)	80.2(1)	102.6(2)	96.3(1)	151.3(2)	1.951(1)
			$Ti(2)O_6$ octahedron			
Ti(2)	O(2)	O(5)	O(5)	O(6)	O(7)	O(8)
O(2)	1.866(5)					
O(5)	100.8(1)	1.931(1)				
O(5)	100.8(1)	156.6(2)	1.931(1)			
O(6)	176.8(3)	79.5(1)	79.5(1)	2.087(4)		
O(7)	89.1(2)	85.6(2)	85.6(2)	94.1(2)	2.031(6)	
O(8)	94.4(3)	93.7(2)	93.7(2)	82.4(2)	176.5(2)	1.886(5)
			$Ti(3)O_6$ octahedron			
Ti(3)	O(2)	O(3)	O(3)	O(4)	O(10)	O(11)
O(2)	1.824(6)					
O(3)	101.9(1)	1.933(1)				
O(3)	101.9(1)	156.0(2)	1.933(1)			
O(4)	87.5(3)	89.0(2)	89.0(2)	2.055(6)		
O(10)	98.6(3)	89.7(2)	89.7(2)	174.0(2)	1.905(6)	
O(11)	165.4(2)	78.1(1)	78.1(1)	77.8(2)	96.2(2)	2.150(5)
			$Ti(4)O_6$ octahedron			
Ti(4)	O(5)	O(6)	O(6)	O(6)	O(8)	O(10)
O(5)	2.074(5)					
O(6)	83.4(2)	2.306(6)				
O(6)	79.2(1)	78.2(2)	1.959(1)			
O(6)	79.2(1)	78.2(2)	149.4(2)	1.959(1)		
O(8)	160.3(2)	105.9(2)	96.6(1)	96.6(1)	1.873(5)	
O(10)	103.7(2)	102.9(2)	102.9(2)	102.9(2)	96.0(2)	1.766(6)
			$Ti(5)O_6$ octahedron			
Ti(5)	O(1)	O(1)	O(1)	O(4)	O(9)	O(11)
O(1)	2.152(5)					
O(1)	78.1(1)	1.968(1)				
O(1)	78.1(1)	147.7(2)	1.968(1)			
O(4)	168.4(3)	99.5(1)	99.5(1)	1.787(5)		
O(9)	104.5(2)	99.1(2)	99.1(2)	108.4(2)	1.818(6)	
O(11)	117.5(1)	78.7(2)	78.7(2)	81.9(2)	169.7(2)	2.213(6)

TABLE IVb

$K_2SrTi_{10}O_{22}$: SELECTED INTERATOMIC DISTANCES (Å) FOR Sr AND K

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
Sr		2.925(5)	3.190(6)	2.644(4)	3.225(5)	
K(1)		2.927(5)	3.191(6)	2.644(3)	3.227(5)	
K(2)		3.237(6)	3.447(6)		3.325(7)	3.300(6)
	O(7)	O(8)	O(9)	O(10)	O(11)	
Sr	2.821(4)		2.767(4)		3.311(5)	
K(1)	2.821(4)		2.765(4)		3.310(5)	
K(2)		2.743(5)		2.890(4)		

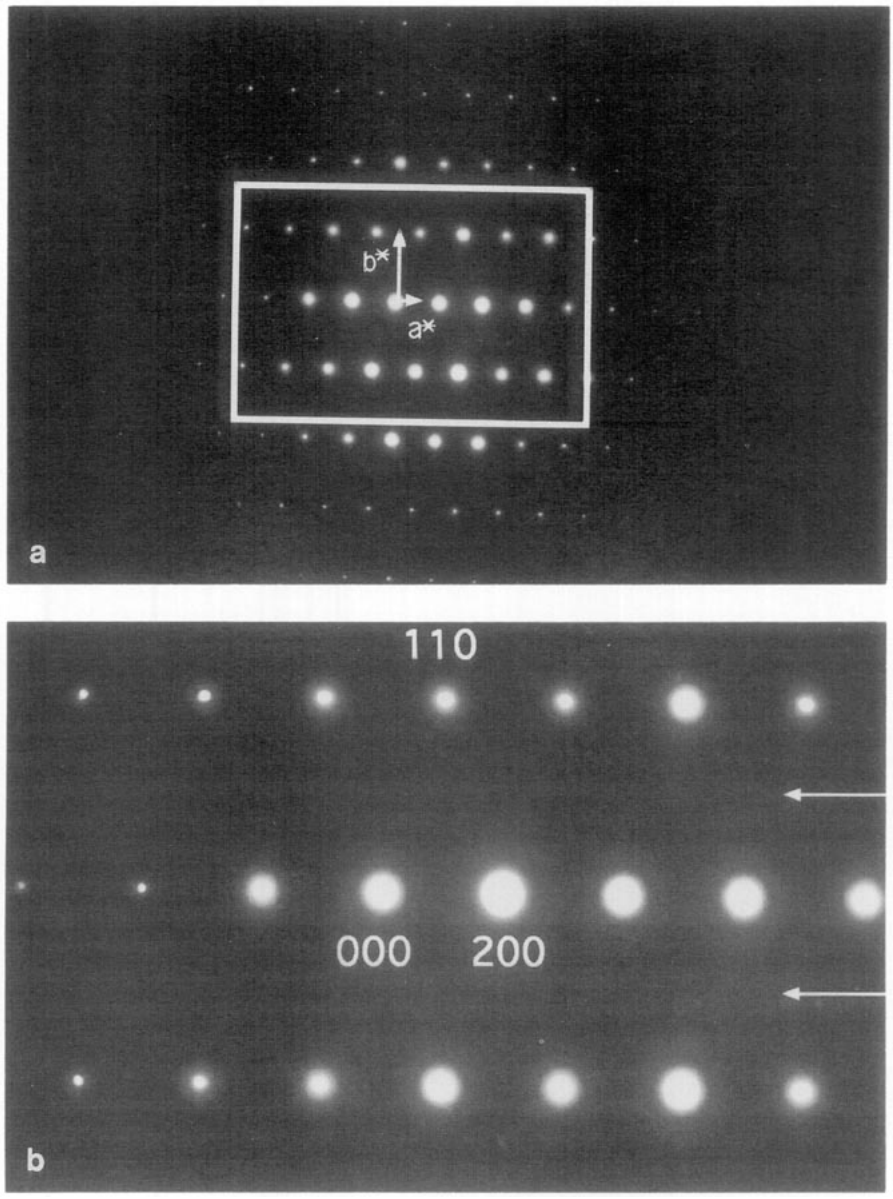

FIG. 3. (a) Electron diffraction pattern of the [001] zone axis. (b) Arrows: observation of diffuse streaks parallel to a^*.

In a first approximation, the positions of diffuse lines are consistent with a doubling of the b parameter with respect to the average cell ($b \approx 3.78$ Å).

This suggests the existence of an intratunnel order of Sr^{2+} and K^+ cations along b. A model can be proposed in which the distribution of A and A' cations within the tunnels is described by a $2b$ occupancy order of the site $2d$ (1/2, 0, 1/2), but with a disorder in the (a, c) plane from one tunnel to the other.

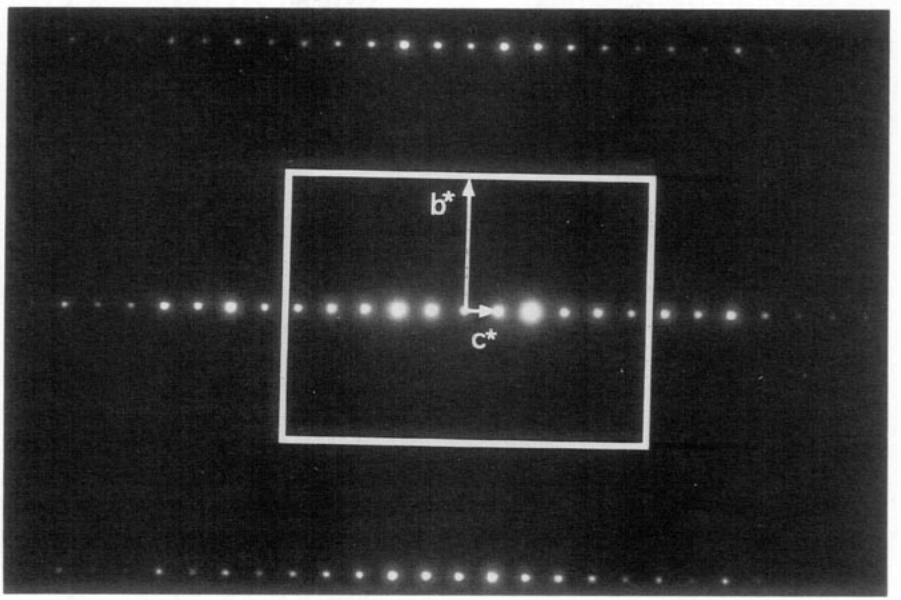

FIG. 4. Electron diffraction pattern of the [100] zone axis. Observation of very diffuse streaks parallel to c^*.

Conclusion

The occupancies of potassium and strontium sites do not correspond to those previously announced. The 4*i* site of $A_2Ti_6O_{13}$ is fully occupied, half by potassium and half by strontium atoms. The 4*i* site of the hypothetical $A'Ti_4O_9$ is occupied by 50% of potassium atoms. The one-dimensional ordering along the *b* axis of K atoms and vacancies in one tunnel and Sr/K in the other tunnel explain the diffuse streaks parallel to the (a^*, c^*) plane observed in electron diffraction patterns.

References

1. M. HERVIEU, G. DESGARDIN, AND B. RAVEAU, *J. Solid State Chem.* **30,** 375 (1979).
2. S. ANDERSON AND A. D. WADSLEY, *Acta Crystallogr.* **15,** 194 (1962).
3. H. CID-DRESDNER AND M. J. BUERGER, *Z. Kristallogr.* **117,** 411 (1962).
4. J. SCHMACHTEL AND HK. MÜLLER-BUSCHBAUM, *Z. Anorg. Allg. Chem.* **435,** 243 (1977).
5. M. HERVIEU, P. GERMAIN, G. DESGARDIN, AND B. RAVEAU, *Mater. Res. Bull.* **14,** 267 (1979).
6. B. FRENZ, "Enraf–Nonius Structure Determination Package," Delft Univ. Press, Delft (1982).