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Study of the defect pyrochlores A(SbTe)O_6 (A = K, Rb, Cs, Tl)

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By solid-state reaction in air, four deficient pyrochlores A(SbTe)O_6 (A = K, Rb, Cs, Tl) have been prepared as pale polycrystalline powders. A(SbTe)O_6 are cubic with space group Fd$\bar{3}$m (No. 227), $Z = 8$, and a (nm) values varying from 1.01133(2) (A = K) to 1.01935(4) (A = Cs). The best discrepancy R factors were obtained for A at 32(e) positions and x positional parameters close to 1/8, origin at centre, $\bar{3}$m; antimony and tellurium distributed at random at 16(d); oxygen atoms at 48(f), with u positional parameters from 0.421 (A = Tl) to 0.430 (A = Cs). The coordination polyhedron of A has been considered as depending on the x positional parameter. The products of the thermal decomposition of A(SbTe)O_6 were examined by electron microscopy and could be identified as $A_3Sb_5O_{14}$ (A = Rb, Cs) and a pyrochlore phase that does not contain tellurium (A = Tl). The electric conductivity measurements led to σ ($\Omega^{-1}\,cm^{-1}$) values between 1.0×10^{-9} (A = K) and 9.7×10^{-6} (A = Cs) at 773 K.

1. Introduction

Within the wide family of materials known as pyrochlores, of general formula $A_2B_2O_6O'$, a particular case is constituted by the deficient compounds, $A\square B_2O_6\square$, in which both A and O′ positions are vacant or partially unoccupied.

Cubic AB_2O_6 pyrochlores can be described in space group Fd$\bar{3}$m, $Z = 8$, with the smaller B cations at 16(d) positions ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), origin at centre $\bar{3}$m; and the oxygen atoms at 48(f), ($u, \frac{1}{8}, \frac{1}{8}$) with $0.375 < u < 0.4375$. In previous papers [1, 2] the positions of the A atoms was thought to be 8(a), ($\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$); later on the occupancy of 32(e) positions, (x, x, x) close to $\frac{1}{8}$ was shown [3–5].

The defect pyrochlore structure can be described as a B_2O_6 framework of corner-shared octahedra that form channels parallel to all ⟨1 1 0⟩ directions in the crystal. The A ions reside in these channels occupying intermediate positions between 16(c) and 8(a), depending on their size, charge and polarizability. It is also noted that the resulting vacancies allow the diffusion of the A ions through the structure; hence, these compounds are potential ionic conductors [6, 7].

Recently, a procedure for calculating approximate u and x positional parameters for oxygen and A atoms, respectively, has been employed [5]. By this method, which was shown to give acceptable results for a number of AB_2O_6 compounds, the u_c value is computed by equating the (d)–(f) distance to the sum of ionic radii of B and O, for 6 and 8 coordinations respectively, according to $B\text{–}O = a(u^2 - u + 9/32)^{1/2}$, where a is the observed unit-cell parameter. For the calculation of the x parameter, a hard-sphere model was considered. With A placed at 32(e) positions there are three shorter distances to oxygen atoms, given by $(e)\text{–}(f) = a[3x^2 - (1 - 2u)x + u^2 - \frac{1}{2}u + 3/32]^{1/2}$. Thus, x can be derived by equating (e)–(f) to the sum of A and O ionic radii, A being regarded as sixfold coordinated.

Several families of deficient pyrochlores $A^I(B^VB^{VI})O_6$ have been described, with B^V = Nb, Ta, Sb and B^{VI} = W [8]; B^V = Nb, Ta and B^{VI} = Te [2]; B^V = Sb and B^{VI} = Mo [5]. As for $ASbTeO_6$ [9] the unit-cell parameter of $CsSbTeO_6$ was given in the pioneering work by Babel *et al.* [1].

In this paper the synthesis, structure, thermal decomposition and electric conductivity of the oxides A(SbTe)O_6 are reported. The coordination polyhedron of the A atom is discussed and the previously mentioned method [5] for the calculation of u and x parameters is applied.

2. Experimental procedure

2.1. Preparation of the samples

A(SbTe)O_6(A = K, Rb, Cs, Tl) were prepared by solid-state reaction from ground mixtures of the analytical-grade reagents shown in Table I. An excess of TeO_2 (15%) was provided to offset its partial volatilization. The samples were heated in air at the temperatures indicated in Table I, for 24 h each except for shorter high-temperature heatings. After each thermal treatment the samples were quenched, weighed, ground and examined by X-ray diffraction.

2.2. Experimental techniques

X-ray diffraction patterns were obtained by using a

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TABLE I Preparative conditions, colour and crystallinity of defect pyrochlores $A(SbTe)O_6$

Sample No.	Atom A	Reagents	Molar ratio	Temperature (K)	Colour	Crystallinity†
1	K	$KSb(OH)_6$, $Te(OH)_6$	1:1	473, 973	Light grey	c
2	K	K_2CO_3, TeO_2, Sb_2O_3	1:2.3:1	823, 973, 1073, 1123	Light grey	ccc
3	Rb	$RbNO_3$, $Te(OH)_6$, Sb_2O_3	2:2:1	723, 973	Grey	c
4	Rb	$RbNO_3$, TeO_2, Sb_2O_3	2:2.3:1	823, 973, 1123, 1173*, 1193*	Pale yellow	ccc
5	Cs	$CsNO_3$, $Te(OH)_6$, Sb_2O_3	2:2:1	723, 973	Black	c
6	Cs	$CsNO_3$, TeO_2, Sb_2O_3	2:2.3:1	823, 973, 1123, 1173*, 1193*	Green-grey	cc
7	Tl	$TlNO_3$, $Te(OH)_6$, Sb_2O_3	2:2:1	723, 973	Green-grey	c
8	Tl	Tl_2O_3, TeO_2, Sb_2O_3	1:2.3:1	823, 973, 1023*	Brown-grey	c

*Thermal treatments lasting 1 h; the remaining treatments were performed during one day.
†c = low, cc = medium, ccc = high.

Siemens Kristalloflex 810 generator and a D-500 goniometer, with Cu*K*α radiation. Details of the analysis of X-ray diffraction data and collection of intensities have been described elsewhere [5]. The calculation of the intensities for each compound was performed with the program Lazy Pulverix [10], using arbitrarily chosen values for the Debye–Waller factors: 0.008, 0.0034, 0.0036 nm^2 for oxygen, tellurium and antimony and 0.0070, 0.0051, 0.0032 and 0.0020 nm^2 for potassium, rubidium, caesium and thallium, respectively. The intensities were computed for the x positional parameters of the A atom ranging between 0.090 and 0.125, and for those of the u oxygen positional parameter between 0.410 and 0.437. The x and u final observed parameters were those leading to the smallest R factor, defined as $R = \Sigma|I_0^{1/2} - I_c^{1/2}|/\Sigma I_c^{1/2}$ where $I_0 = kI_0'$ and $k = \Sigma I_c/\Sigma I_0$; I_0 and I_c are observed and calculated intensities, respectively.

The thermal analysis was carried out in a Setaram MTB 10 – 8 at heating speeds ranging from 2 to $10\,K\,h^{-1}$.

Electrical conductivity measurements were performed by a.c. impedance complex plane analysis over a frequency range of 10 to 10^6 Hz. The compounds were pressed in pellets of 10 mm diameter and 3 to 6 mm thickness, to an apparent density of about 80% theoretical. The polished surfaces of the discs were covered with platinum paint. A Solartron 1174 impedance analyser controlled by a Commodore 4032 computer was employed. The measurements were made with a temperature interval of 100 K up to 1023 K; the data during both heating and cooling were collected.

The infrared (IR) spectra were recorded in a Perkin-Elmer 283 spectrophotometer between 200 and $4000\,cm^{-1}$, using KBr disks.

The scanning electron micrographs were obtained in a Jeol 35 CF microscope, provided with a Link microprobe that allowed qualitative analysis of the samples.

3. Results

3.1. Chemical characterization

The products were obtained as polycrystalline powders, coloured as indicated in Table I. The analysis of the weight losses after each thermal treatment led to the chemical composition $A(SbTe)O_6$ for all the samples. The qualitative analyses, made by means of a microprobe coupled to an electron microscope, showed the presence of the expected elements in each case. The IR spectra did not show the characteristic bands corresponding to OH vibrations, confirming that the products were not hydrated.

3.2. X-ray diffraction studies

All the products gave X-ray diffraction patterns characteristic of cubic pyrochlores, space group $Fd\bar{3}m$ (No. 227), $Z = 8$. Samples 2, 4, 6 and 8 (Table I) were chosen to perform structural studies due to their higher crystallinity. Table II includes the observed interplanar d spacings as well as observed, I_0, and calculated, I_c, intensities. For $Fd\bar{3}m$, $Z = 8$, origin at centre ($\bar{3}m$), the best discrepancy R factors between I_0 and I_c were obtained for A at 32(e) positions, antimony and tellurium randomly distributed at 16(d), and oxygen at 48(f). The final values of $x_{obs.}$ and $u_{obs.}$ positional parameters for A and O atoms, respectively, are shown in Table III, together with the values of a, V, D_c and final R. The parameters $x_{calc.}$ and $u_{calc.}$, also included in Table III, have been calculated following the method described above [5], from the sums of Shannon's ionic radii [11] considering as coordination numbers for A, B and O, respectively, the values 6, 6 and 3.

Table IV gives the observed distances, A–O1, A–O2, A–O3 and B–O, as well as those calculated, $A–O_{calc.}$, $B–O_{calc.}$, from the sums of ionic radii.

There are three kinds of oxygen that can be considered as coordinated to the A atom, as shown in Fig. 1, in which the A = Rb coordination polyhedron

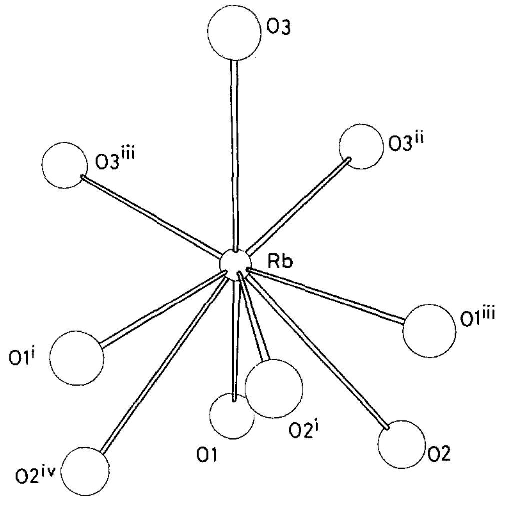

Figure 1 Rubidium coordination polyhedron in the pyrochlore $Rb(SbTe)O_6$. Symmetry code; (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $x + \frac{1}{4}, \frac{1}{2} - y, z - \frac{1}{4}$; (iii) $z + \frac{1}{2}, x - \frac{1}{2}, y$; (iv) $1 - z, 1 - x, 1 - y$.

TABLE II X-ray diffraction data for the deficient pyrochlores A(SbTe)O_6(A = K, Rb, Cs, Tl)

hkl	A = K			A = Rb			A = Cs			A = Tl		
	d_0(nm)	I_0	I_c	d_0(nm)	I_0	I_c	d_0(nm)	I_0	I_c	d_0(nm)	I_0	I_c
111	0.586	659.6	923.2	0.589	280.6	391.0	0.592	131.2	123.7	0.588	25.2	7.8
220	0.3581	11.2	11.5	0.3596	81.6	83.2	0.3613	172.2	188.5	0.3590	253.7	284.7
311	0.3052	963.8	1000.0	0.3070	1006.3	1000.0	0.3080	989.1	1000.0	0.3060	918.2	1000.0
222	0.2922	723.6	738.7	0.2938	532.4	536.0	0.2949	380.9	382.5	0.2930	343.5	295.6
400	0.2530	99.8	107.3	0.2545	42.3	41.9	–	–	7.7	–	–	0.5
331	0.2322	75.7	86.0	0.2335	21.3	21.9	–	–	0.2	–	–	4.6
422	–	–	0.4	0.2077	3.6	9.3	0.2082	38.6	45.9	0.2072	58.4	74.0
511, 333	0.19458	283.0	284.1	0.1957	283.4	284.4	0.19622	307.6	303.7	0.1954	282.4	278.5
440	0.17873	434.4	436.5	0.1797	382.9	379.4	0.18020	359.6	353.6	0.1795	332.4	322.2
531	0.17090	192.3	175.4	0.17188	74.3	78.9	0.17236	–	17.7	0.1718	–	7.0
620	0.15992	11.3	10.7	0.16077	29.0	26.1	0.16116	59.6	54.8	0.16037	46.5	46.6
533	0.15420	129.6	122.3	0.15507	128.9	121.3	0.15541	135.4	126.6	0.15470	111.3	114.3
622	0.15246	313.4	289.5	0.15328	228.4	206.9	0.15365	164.4	150.6	0.15306	135.7	105.2
444	0.14597	59.8	52.4	0.14678	34.6	28.6	–	–	9.8	–	–	4.0
551, 711	0.14159	118.8	112.6	0.14240	58.3	56.9	0.14280	12.0	16.3	0.14210	11.8	8.0
642	–	–	3.1	0.13589	14.2	12.7	0.13620	43.3	40.5	0.13554	26.9	31.6
553, 731	0.13163	206.8	193.6	0.13240	187.7	178.2	0.13268	217.9	197.7	0.13208	160.5	150.6
800	0.12641	56.2	54.9	0.12711	51.4	46.5	0.12743	44.9	47.0	0.12684	36.1	34.6
733	0.12356	12.3	11.4	–	–	5.2	–	–	0.1	–	–	0.8
660, 822	–	–	5.3	–	–	6.0	0.12011	13.9	15.9	–	–	8.6
751, 555	0.11677	89.2	72.3	0.11742	76.2	65.7	0.11770	85.3	80.1	0.11717	68.9	55.9
662	0.11599	120.0	116.0	0.11665	87.0	87.3	0.11693	66.2	60.6	0.11640	57.9	55.1
840	0.11307	99.0	79.9	0.11369	49.6	47.5	–	–	16.0	0.11351	13.2	13.8
753, 911	0.11100	66.6	55.2	–	29.4	26.8	–	–	5.2	–	–	4.9
931	0.10600	60.4	57.5	0.10659	51.2	50.9	0.10685	61.2	63.1	0.10637	37.7	32.1
844	0.10320	108.2	96.7	0.103787	83.1	78.2	0.10402	83.2	83.4	0.10356	55.6	58.4
933, 771, 755	0.10163	52.2	45.1	0.102203	26.3	25.6	–	–	5.0			
10, 20, 862	–	–	2.3	–	–	3.4	–	19.8	19.0			
951, 773	0.09776	78.2	70.5	0.098309	63.2	59.3	0.098551	34.1	74.3			
1022, 666	0.09731	120.9	104.2	0.097858	80.8	73.6	0.098091	27.9	53.0			
953	0.09429	37.1	36.7	0.094840	–	22.7	–	–	4.4			
775, 1111	–	44.3	47.4	0.091691	39.5	40.3	0.091908	42.1	47.0			
880	0.089390	45.3	41.9	0.089889	35.0	32.3	0.090097	35.1	35.7			
955, 1131, 971	0.088362	85.1	57.4	0.088855	53.8	53.1	–	–	11.9			
1133, 973	0.085780	116.9	99.3	0.086260	80.9	81.6	0.086456	89.2	93.7			
1062	0.085473	208.4	173.5	0.085953	129.9	114.4	0.086150	101.7	84.7			
1200, 884	–	140.8	117.4	–	78.4	76.3	–	–	28.4			
1151, 777	0.083414	79.4	63.0	0.083881	38.7	43.4	–	–	11.6			
957, 1153	0.081229	131.3	122.1	0.081687	90.0	87.5	0.081880	124.2	117.8			
1240	0.079953	170.0	161.3	0.080399	97.6	111.7	0.080590	125.4	125.5			

is plotted. As for the B atom, it has six oxygens at equal B–O distances, conforming a slightly distorted octahedron.

3.3. Thermal analysis

$KSbTeO_6$ decomposes above 1173 K, giving rise to an amorphous phase which could not be identified. Rubidium, caesium and thallium pyrochlores decompose at about 1273 K. In order to study the products of decomposition, samples of A(SbTe)O_6 (A = Rb, Cs, Tl) were heated at 1273 K for 24 h. Typical micrographs of the products obtained by electron microscopy are shown in Fig. 2. In every case the microprobe indicated the absence of tellurium.

For A = Rb, an orthorhombic phase of composition $Rb_3Sb_5O_{14}$ was identified, constituted by transparent well-shaped single crystals (Fig. 2a). The unit cell parameters of this phase, previously reported [12], are *a* = 2.441, *b* = 0.736, *c* = 0.720 nm. The observed weight loss, 48.3%, agrees with that calculated, 49.4%, for the process $5RbSbTeO_6 \rightarrow Rb_3Sb_5O_{14}$.

For A = Cs, although the X-ray diffraction pattern of the final decomposition product is quite different from that of $Rb_3Sb_5O_{14}$, the observed weight loss of 50.1% suggests the formula $Cs_3Sb_5O_{14}$ for that phase, since that calculated for the conversion $5CsSbTeO_6 \rightarrow Cs_3Sb_5O_{14}$ is 48.5%.

TABLE III Crystal data for the deficient pyrochlores A(SbTe)O_6 (with e.s.d. in parentheses)

Atom A	*a* (nm)	*V* (nm^{-3})	D_c ($Mg\,m^{-3}$)	*u*		*x*		*R*
				Obs.	Calc.	Obs.	Calc.	
K	1.01133(2)	1.03438(6)	4.94	0.425	0.426	0.109	0.091	0.053
Rb	1.01699(2)	1.05184(6)	5.44	0.428	0.428	0.107	0.104	0.035
Cs	1.01935(5)	1.0592(1)	6.00	0.430	0.429	0.114	0.118	0.044
Tl	1.01472(6)	1.0448(2)	6.99	0.421	0.427	0.104	0.103	0.059

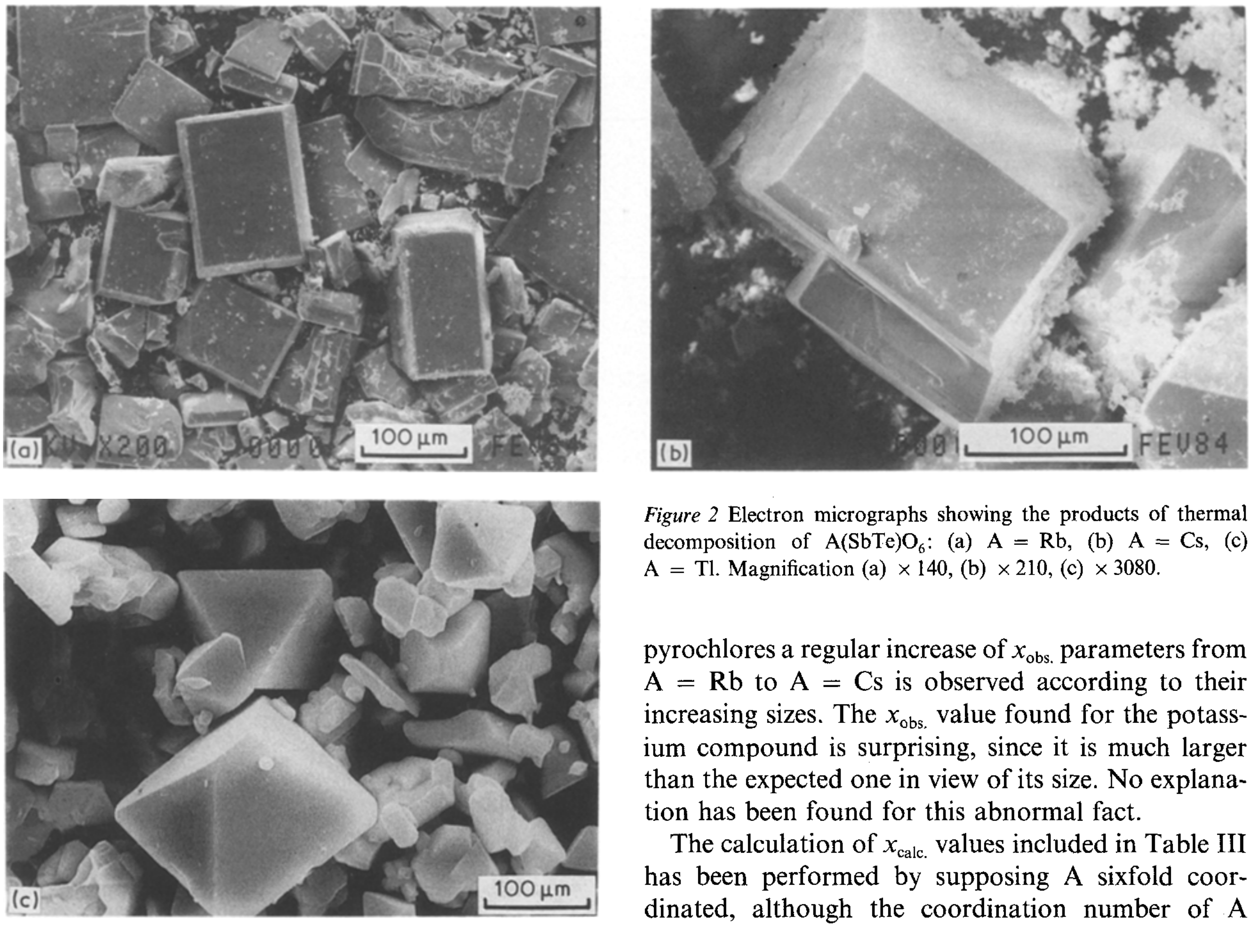

Figure 2 Electron micrographs showing the products of thermal decomposition of $A(SbTe)O_6$: (a) A = Rb, (b) A = Cs, (c) A = Tl. Magnification (a) × 140, (b) × 210, (c) × 3080.

As for $TlSbTeO_6$, the thermal treatment led to a pyrochlore phase which did not contain tellurium, probably related to that described by Piffard and Tournaux [13]. Fig. 2c shows an octahedron-shaped single crystal corresponding to this phase.

3.4. Conductivity measurements

$KSbTeO_6$ showed a very low conductivity, about $10^{-9}\,\Omega^{-1}\,cm^{-1}$ at 773 K. For rubidium, caesium and thallium pyrochlores log (σT) against $1/T$ plots are shown in Fig. 3. The activation energies were obtained from four to eight high-temperature experimental points, fitted by least squares to the equation $\log(\sigma T) = \log\sigma_0 - E_a/kT$.

The values of E_a were 1.24, 0.75 and 1.20 eV for the rubidium, caesium and thallium compounds, respectively.

4. Discussion of some structural aspects

As mentioned before, the actual position occupied by A atoms in 32(e) sites depends roughly on their ionic size, for cations with the same charge. For $A(SbTe)O_6$ pyrochlores a regular increase of $x_{obs.}$ parameters from A = Rb to A = Cs is observed according to their increasing sizes. The $x_{obs.}$ value found for the potassium compound is surprising, since it is much larger than the expected one in view of its size. No explanation has been found for this abnormal fact.

The calculation of $x_{calc.}$ values included in Table III has been performed by supposing A sixfold coordinated, although the coordination number of A atoms seems not to be well defined, as can be deduced from the observed distances listed in Table IV. In fact, the coordination polyhedron of A depends strongly on the x parameter value, as shown in Fig. 4. In this case the variation of A–O distances with x for one of the pyrochlores arbitrarily chosen, $RbSbTeO_6$, is represented.

For x equal or close to zero, the A atom can be considered as coordinated only to six oxygens 3(01) + 3(02), conforming a corrugated hexagon normal to the threefold axis [1 1 1]. With increasing x, A–O3 distances become shorter in such a way that O3 begins to take part of the coordination sphere of A. Finally, for x equal to 1/8 (position 8(a)), A occupies the centre of a wide cage conformed by 18 oxygens, 6 of them at relatively short distances (3(01) + 3(03)), and 12 at larger distances (3(02) + nine additional oxygens, which are not shown).

According to the observed x values for the pyrochlores $A(SbTe)O_6$, the three O3 oxygens clearly belong to the A coordination sphere, A–O3 being of the same order, even shorter than A–O2. Thus, the A polyhedron can be described as constituted by three closer oxygens 3(01), undoubtedly "bonded" to A, plus six (3(02) + 3(03)) at relatively large distances,

TABLE IV Observed and calculated interatomic distances for $A(SbTe)O_6$ pyrochlores

Atom A	$(A–O)_{calc.}$ (nm)	$(A–O)_{obs.}$ (nm)			$(B–O)_{calc.}$ (nm)	$(B–O)_{obs.}$ (nm)
		A–O1	A–O2	A–O3		
K	0.274	0.288	0.341	0.320	0.194	0.194
Rb	0.288	0.291	0.341	0.327	0.194	0.194
Cs	0.303	0.300	0.351	0.323	0.194	0.194
Tl	0.286	0.281	0.336	0.323	0.194	0.196

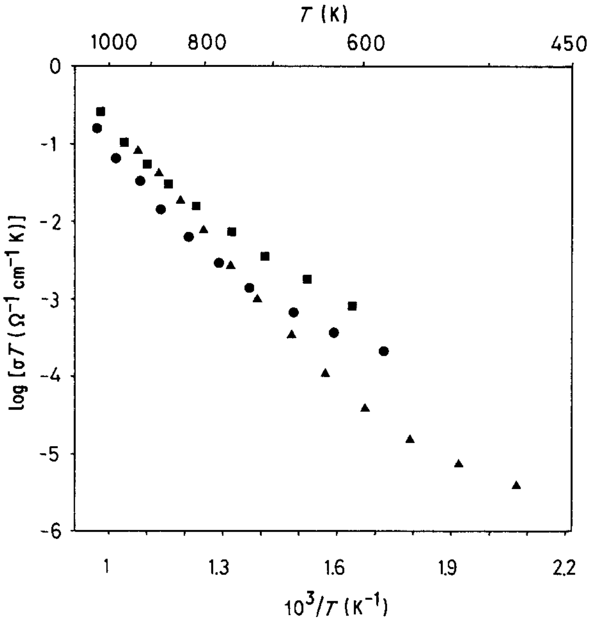

Figure 3 Log (σT) against $1/T$ for $A(SbTe)O_6$ pyrochlores: (●) A = Rb, (■) A = Cs, (▲) A = Tl.

involving much weaker A–O interactions. The actual A position in $RbSbTeO_6$ is shown in Fig. 4, for $x = 0.107$. The A coordination number being larger than 3 but hardly as large as 9, the figure of 6 gives good results when performing calculations from tabulated ionic radii.

In the paper mentioned above [5] u and x parameters were calculated for a number of defect pyrochlores, assuming A sixfold coordinated, and compared with those obtained experimentally, observing average differences of 1.1 and 4.4% for u and x respectively. As for $A(SbTe)O_6$ (A = K, Rb, Cs, Tl) there exists a good agreement between observed and calculated values of the u parameter (average difference of 0.5%). With the exception of the potassium compound, whose abnormal $x_{obs.}$ value has been commented on before, $x_{obs.}$ and $x_{calc.}$ agree closely for the remaining pyrochlores, with an average error of 2.5%.

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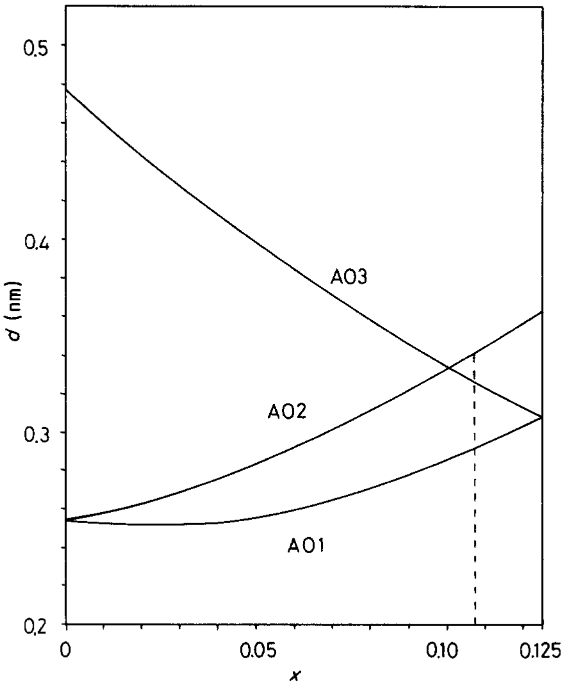

Figure 4 Rb–O calculated distances d against the rubidium positional parameter x.

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