JOURNAL OF SOLID STATE CHEMISTRY 80, 227–234 (1989)

Synthesis, X-Ray Diffraction Study, and Ionic Conductivity of New AB_2O_6 Pyrochlores

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Received July 18, 1988; in revised form January 24, 1989

The oxides $A(Ti_{0.5}Te_{1.5})O_6$ (A = K, Rb, Cs, Tl), $A(Ti_{0.5}W_{1.5})O_6$ (A = Rb, Cs, Tl), and $Cs(B_{0.5}W_{1.5})O_6$ (B = Zr, Hf) have been obtained as polycrystalline powders giving X-ray diffraction patterns characteristic of defect cubic pyrochlores, space group $Fd\bar{3}m$ (No. 227), $Z = 8$. The best discrepancy R factors, from 0.0265 for $Rb(Ti_{0.5}Te_{1.5})O_6$ to 0.0554 for $Cs(Zr_{0.5}W_{1.5})O_6$, were obtained for the B cations randomly distributed at 16(d), A ions at one quarter of 32(e), and oxygen atoms at 48(f) positions. A linear relationship is observed between the a unit cell parameters and the ionic radii of the A cations, as well as the average ionic radii of the B atoms. The results of electrical resistivity measurements for $A(Ti_{0.5}Te_{1.5})O_6$ (A = K, Rb, Cs, Tl) are given.

Introduction

During the last 20 years, some cubic deficient pyrochlores of general formula AB_2O_6, with A cations much larger than B, have been investigated (*1–4*). These oxides can be described in the space group $Fd\bar{3}m$ (No. 227), $Z = 8$, with the center ($\bar{3}m$) as origin, the smaller B atoms at 16(d) positions, 1/2 1/2 1/2, the oxygen atoms at 48(f), u 1/8 1/8, $0.375 < u < 0.4375$, and A cations at one quarter of 32(e) sites, x x x. Depending on the size, charge, and polarizability of the A cations, the x positional parameter can vary from $x = 0$ to $x = 0.125$, values which correspond to the 16(c) and 8(a) positions, respectively.

The authors recently suggested (*5*) a simple method for estimating u and x positional parameters. We have also shown (*6*) that for intermediate x values, between 0 and 0.125, the coordination polyhedron of the A cations is formed by three closer oxygen atoms and six additional oxygens at fairly longer distances. In this article we report our attempts to synthesize the $A(Ti_{0.5}Te_{1.5})O_6$ and $A(B_{0.5}W_{1.5})O_6$ (A = K, Rb, Cs, Tl; B = Ti, Ge, Zr, Sn, Hf) compounds; the X-ray diffraction study of the nine pure phases we obtained, $A(Ti_{0.5}Te_{1.5})O_6$, A = K, Rb, Cs, Tl; $A'(Ti_{0.5}W_{1.5})O_6$, A' = Rb, Cs, Tl, and $Cs(B_{0.5}W_{1.5})O_6$, B = Zr, Hf; and the

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0022-4596/89 $3.00

results of electrical resistivity measurements of four of these oxides.[1]

Experimental

Polycrystalline samples of the compositions indicated in Table I were prepared by solid-state reactions from stoichiometric mixtures of analytical-grade WO_3 or TeO_2, MO_2 (M = Ti, Ge, Zr, Sn, Hf), and K_2CO_3, ANO_3 (A = Rb, Cs) or Tl_2O_3. For sample No. 5, $Zr(NO_3)_4$ was used instead of ZrO_2. The samples were ground and heated in air at 773 K for 24 hr (samples Nos. 9 and 11 at 723 K) and finally at the temperatures and for the times indicated in Table I. After each thermal treatment the products were quenched, weighed, ground, and examined by X-ray diffraction.

TABLE I

PREPARATIVE CONDITIONS, IDENTIFIED PHASES, AND CELL DIMENSION OF THE $A(B_{0.5}B'_{1.5})O_6$ PYROCHLORES

No.	Compositions	Temperature (K)-time (hr)	Phases	a (Å)
1	$K(Ti_{0.5}Te_{1.5})O_6$	873-24	P	10.0597(3)
2	$Rb(Ti_{0.5}Te_{1.5})O_6$	923-24	P	10.0903(2)
3	$Cs(Ti_{0.5}Te_{1.5})O_6$	923-24	P	10.1346(2)
4	$Tl(Ti_{0.5}Te_{1.5})O_6$	873-24	P	10.0930(3)
5	$K(Ti_{0.5}W_{1.5})O_6$	1123-24	$P + X$	10.20
6	$Rb(Ti_{0.5}W_{1.5})O_6$	1123-24	P	10.2426(2)
7	$Cs(Ti_{0.5}W_{1.5})O_6$	1123-24	P	10.2710(3)
8	$Tl(Ti_{0.5}W_{1.5})O_6$	1073-24	P	10.2459(1)
9	$Rb(Zr_{0.5}W_{1.5})O_6$	793-168	$P + A$	10.39
10	$Cs(Zr_{0.5}W_{1.5})O_6$	1173-96	P	10.4109(5)
11	$Rb(Hf_{0.5}W_{1.5})O_6$	793-168	$P + D$	10.28
12	$Cs(Hf_{0.5}W_{1.5})O_6$	1173-96	P	10.3906(3)
13	$Rb(Sn_{0.5}W_{1.5})O_6$	793-48	$P + E$	10.27
14	$Rb(Ge_{0.5}W_{1.5})O_6$	793-48	$P + Y$	10.16

Note. A, Rb_2ZrO_3; D, $Rb_2Hf_3O_7$; E, Rb_2SnO_3; X, Y, unidentified materials; P, pyrochlore.

X-ray diffraction patterns were obtained by using a Siemens Kristalloflex 810 generator, a D-500 goniometer provided with a graphite monochromator, and Cu$K\alpha$ radiation (λ = 1.540598 Å). The patterns for identification purposes were made at a scanning rate of 5°(2θ) min^{-1}. The more accurate d-spacing measurements were performed at 0.1°(2θ) min^{-1}, from 13° to 156°(2θ), using W, a = 3.16524(4) Å, as an internal standard. Unit cell parameters were refined from the 2θ values of the last seven observed reflections. I'_o were measured by step-scanning from 13° to 156°(2θ) with increments of 0.02°(2θ) and a counting time of 1 sec each step, the goniometer being controlled by a DACO-MPV2 computer, which carried out the integration of the diffraction peaks and the background correction.

The program LAZY PULVERIX (7) was employed in the calculation of the intensities, using arbitrarily chosen values for Debye–Waller factors, 0.80 $Å^2$ for oxygen and 0.02 $Å^2$ for Tl, and the following values, which were obtained interpolating the respective atomic masses between those of oxygen and Tl: 0.67, 0.49, 0.34, 0.13, and 0.11 $Å^2$ for Ti, Zr, Te, Hf, and W; and 0.70, 0.51, and 0.32 for K, Rb, and Cs, respectively. The intensities were computed for the x positional parameter of the A atom ranging between 0.085 and 0.125, and for the u oxygen positional parameter between 0.420 and 0.438. The chosen x and u values were those leading to the smallest R factor, defined as $R = (\Sigma|I_o^{1/2} - I_c^{1/2}|)/\Sigma I_o^{1/2}$, where $I_o = kI'_o$, and $k = \Sigma I_c/\Sigma I_o$. The number of observed reflections employed in the refinement was 35 for $K(Ti_{0.5}Te_{1.5})O_6$ and $Rb(Ti_{0.5}W_{1.5})O_6$, 33 for $A(Ti_{0.5}W_{1.5})O_6$ (A = Cs, Tl) and $Cs(Zr_{0.5}W_{1.5})O_6$, 32 for $Rb(Ti_{0.5}Te_{1.5})O_6$, 34 for $Cs(Ti_{0.5}Te_{1.5})O_6$, 29 for $Cs(Hf_{0.5}W_{1.5})O_6$, and 26 for $Tl(Ti_{0.5}Te_{1.5})O_6$.

The impedance measurements were made on cylindrical disks of 5 mm diameter and 1 or 2 mm thickness to a compactness of about 75%. Blocking electrodes were formed by sputtering Pt into the planar surfaces of the disks. The impedance was mea-

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[1] Supplementary material available: X-ray diffraction data (observed and calculated d-spacings and intensities) for each of the nine defect pyrochlores $A(Ti_{0.5}W_{1.5})O_6$ (A = Rb, Cs, Tl), $Cs(B_{0.5}W_{1.5})O_6$ (B = Zr, Hf), and $A'(Ti_{0.5}Te_{1.5})O_6$ (A' = K, Rb, Cs, Tl).

sured in the frequency range 1 to 10^6 Hz using a computer-controlled Solartron 1170 frequency response analyzer. The measurements were carried out at temperatures ranging from 473 to 823 K.

Results and Discussion

1. X-Ray Diffraction Study

The compounds identified by X-ray diffraction in the products of thermal treatments are indicated in Table I. In samples 1, 2, 3, 4, 6, 7, 8, 10, and 12, pure and very crystalline $A(B_{0.5}B'_{1.5})O_6$ pyrochlore oxides were isolated, but the presence of unidentified materials and that of Rb and B (B = Zr, Hf, Sn) mixed oxides was also observed in samples 5, 9, 11, 13, and 14. In the case of sample 9 only traces of a pyrochlore phase were obtained by reaction between $RbNO_3$, ZrO_2, and WO_3. $Rb(Zr_{0.5}W_{1.5})O_6$ could only be prepared from $Zr(NO_3)_4$ and it appeared impurified by Rb_2ZrO_3.

The compounds of W were obtained as white powders, and the oxides $A(Ti_{0.5}Te_{1.5})O_6$ were beige (A = K), brown (A = Rb, Tl), or grey (A = Cs). All these samples gave good X-ray diffraction patterns characteristic of defect cubic pyrochlores AB_2O_6, space group $Fd\bar{3}m$ (No. 227), $Z = 8$.

The best discrepancy factors, R, between observed and calculated intensities were obtained for B and B' statistically distributed ($B:B' = 1:3$) at 16(d), A at one quarter of 32(e) positions, and oxygen atoms at 48(f) sites. The final values of x and u positional parameters together with the values for cell dimensions, calculated densities, and final R factors are shown in Table II.

The x and u positional parameters, which were calculated as indicated elsewhere (*5*) from the sums of Shannon's ionic radii (*8*) for coordination numbers 6, 6, and 3 for A, B, and O, respectively, acceptably agree with those observed.

The coordination polyhedron around the B and B' atoms is an almost regular octahedron, as expected for u values close to 0.4375. As for the A atoms, their coordination depends on the x parameter value (*6*). For the oxides studied here, A cations can be considered as coordinated to nine oxygen atoms, three at a distance which is close to the sum of ionic radii (O1), and six (O2, O3) which, although at larger distances, can be considered as bonded to A. Table III gives the observed A–O1, A–O2, A–O3, and B,B'–O distances as well as those calculated from the sums of ionic radii, A–O_c, and B,B'–O_c. Figure 1 shows a view of the unit cell of one of the studied pyrochlores, namely $Cs(Ti_{0.5}Te_{1.5})O_6$.

The unit cell a parameter for the pyro-

TABLE II

CRYSTAL DATA (WITH STANDARD DEVIATIONS IN PARENTHESES) FOR THE PYROCHLORES $A(B_{0.5}B'_{1.5})O_6$

A	B	B'	a (Å)	V (Å^3)	D_c (Mg m^{-3})	x	u	R
K	Ti	Te	10.0597(3)	1018.02(9)	4.57	0.107	0.427	0.0309
Rb	Ti	Te	10.0903(2)	1027.34(6)	5.13	0.113	0.427	0.0265
Cs	Ti	Te	10.1346(2)	1040.93(6)	5.67	0.121	0.425	0.0385
Tl	Ti	Te	10.0930(3)	1028.16(9)	6.66	0.106	0.428	0.0273
Rb	Ti	W	10.2426(2)	1074.56(6)	5.95	0.106	0.437	0.0383
Cs	Ti	W	10.2710(3)	1083.52(9)	6.48	0.112	0.435	0.0362
Tl	Ti	W	10.2459(1)	1075.60(3)	7.41	0.095	0.437	0.0479
Cs	Zr	W	10.4109(5)	1128.4(2)	6.48	0.110	0.437	0.0554
Cs	Hf	W	10.3906(3)	1121.8(1)	7.03	0.108	0.437	0.0461

TABLE III

OBSERVED AND CALCULATED INTERATOMIC DISTANCES (Å) FOR THE $A(B_{0.5}B'_{1.5})O_6$ PYROCHLORES

				A–O_o				
A	B	B'	A–O_c	A–O1	A–O2	A–O3	B,B'–O_c	B–B'–O_o
K	Ti	Te	2.74	2.868	3.375	3.229	1.931	1.924
Rb	Ti	Te	2.88	2.931	3.457	3.173	1.931	1.930
Cs	Ti	Te	3.03	3.000	3.568	3.081	1.931	1.946
Tl	Ti	Te	2.86	2.879	3.376	3.261	1.931	1.927
Rb	Ti	W	2.88	3.014	3.447	3.401	1.961	1.922
Cs	Ti	W	3.03	3.056	3.523	3.323	1.961	1.935
Tl	Ti	W	2.86	2.922	3.324	3.531	1.961	1.923
Cs	Zr	W	3.03	3.100	3.552	3.412	2.020	1.954
Cs	Hf	W	3.03	3.075	3.521	3.428	2.015	1.950

chlores of the $A(B_{0.5}B_{1.5})O_6$ family is plotted versus the radii of the A ions and the average radii of the B and B' cations in Figs. 2a and 2b, respectively. The correlation factors, 0.994 and 0.999, respectively, confirm the dependence of the unit cell parameter on the ionic size of both cations. However, the a values found for $Tl(Ti_{0.5}Te_{1.5})O_6$ and $Tl(Ti_{0.5}W_{1.5})O_6$ are slightly larger than expected. This can be attributed to the Tl (*I*) $6s^2$ nonbonded pair, which *occupies* a significant volume.

Table IV includes the unit cell parameters for 54 pyrochlores and the radii (*8*) of the A cations and the average B,B' cations, as well as the corresponding references. The values of the a parameters for pyrochlores with the same alkali metal as the A cation and a B sublattice of variable size (which are 10 compounds for A = K, 18 for A = Rb, 15 for A = Cs, and 11 for A = Tl) proceed from at least five papers, in which differences of the a values for the same compound as large as those indicated at the footnote of Table IV can be found. Nevertheless, the correlation factors of a as a linear function of the B size are 0.989, 0.925, 0.948, and 0.974, for A = K, Rb, Cs, and Tl,

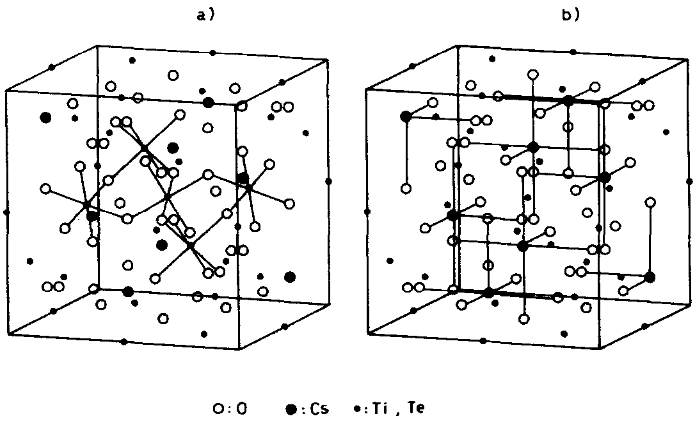

FIG. 1. A view of the unit cell of the pyrochlore $Cs(Ti_{0.5}Te_{1.5})O_6$ showing the coordination of: (a) Ti and Te atoms, (b) Cs atoms (only the shorter A–O1 and A–O3 distances are shown).

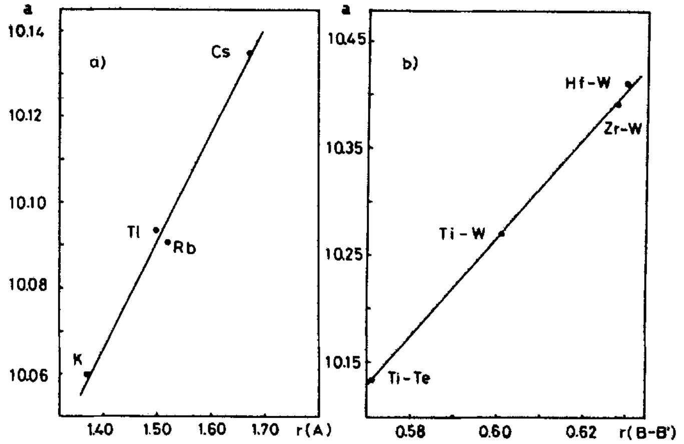

FIG. 2. Unit cell parameter a (Å) vs: (a) ionic radii of A cation for $A(Ti_{0.5}Te_{1.5})O_6$ (A = K, Rb, Cs, Tl), (b) ionic radii of B and B' cations for $Cs(B_{0.5}B'_{1.5})O_6$ (B = Ti, Zr, Hf, B' = Te, W).

respectively. Similar correlation factors are found when the four examples with different A cations (K, Rb, Cs, Tl) and the same B sublattice are considered: 0.994 for the set TiTe studied in this paper; 0.925 for CrW (*9*); 0.918 for FeW (*9*); 0.942 for NbTe (*3*); 0.951 for NbW (*3*); 0.966 for SbTe (*6*); 0.958 for SbW (*10*); 0.929 for TaTe; and 0.980 for TaW (*3*). Thus, some linear dependence of a from both cationic radii, those of A and of B,B', although not as clear as Fig. 2 shows, can be concluded.

2. *Conductivity Measurements*

$A(Ti_{0.5}Te_{1.5})O_6$ (A = K, Cs, Tl) showed an average conductivity, about 10^{-4} Ω^{-1} cm^{-1} at 773 K, and that of $Rb(Ti_{0.5}Te_{1.5})O_6$ was lower, 8.63×10^{-6} Ω^{-1} cm^{-1} at 773 K. The impedance diagrams did not show two semicircles (bulk and grain boundary contributions) and one straight line (electrode effect) but only a flattened semicircle due to the overlapping of both bulk and grain boundary impedances. The conductivity values were derived from the intersection of the semicircle with the x axis. For these four pyrochlore oxides, $\log(\sigma T)$ plotted versus $1/T$, is shown in Fig. 3. The activation energies were obtained from the experimental points corresponding to temperatures of 600 to 800 K, fitted by least-squares to the equation

$$\log(\sigma T) = \log \sigma_0 - E_a/kT.$$

The values (eV) were 1.63, 1.17, 1.15, and 1.19 for the K, Rb, Cs, and Tl compounds, respectively.

None of these compounds seem to exhibit pure ionic conductivity but rather a mixture of both ionic and electronic. This is supported by both the absence of electrode effect in the impedance diagrams and the magnitude of activation energy values, larger than expected for pure electronic conductivity.

It is worthwhile to compare the conductivity values found in these phases with those of other similar pyrochlore phases published by different authors. The compounds $ATaWO_6$ (A = Na, Tl) and $TlNbWO_6$ were studied 10 years ago (*11*), and more recently (*12*) conductivity values for $TlMWO_6$ (M = Nb, Ta) have been reported as well. The nature of the octahedra framework in the $A(Ti_{0.5}Te_{1.5})O_6$ family should favor, in principle, a higher ionic mobility due to the higher polarizability of the cations involved; however, there is an-

TABLE IV

Unit Cell Parameters, a (Å), for the Pyrochlores $A(B_pB'_{2-p})O_6$, and Cationic Radii, r (Å), for Coordination Number 6

No.	A	B	B'	p	a	r_A	$\bar{r}_{B,B'}$	Reference
1	K	Al	W	0.33	10.1690	1.38	0.589	(*9*)
2	K	Ti	Te	0.50	10.0597	1.38	0.571	This work
3	K	Cr	W	0.33	10.2270	1.38	0.603	(*9*)
4	K	Fe	W	0.33	10.2520	1.38	0.608	(*9*)
5	K	Nb	Te	1.00	10.2450	1.38	0.600	(*3*)
6	K	Nb	W	1.00	10.3400	1.38	0.620	(*3*)
7	K	Sb	Te	1.00	10.1133	1.38	0.580	(*6*)
8	K	Sb	W	1.00	10.2340	1.38	0.600	(*10*)
9	K	Ta	Te	1.00	10.2480	1.38	0.600	(*3*)
10	K	Ta	W	1.00	10.3360	1.38	0.620	(*3*)
11	Rb	Li	W	0.20	10.2880	1.52	0.616	(*2*)
12	Rb	Mg	W	0.25	10.2920	1.52	0.615	(*2*)
13	Rb	Al	W	0.33	10.1760	1.52	0.589	(*9*)
14	Rb	Ti	Te	0.50	10.0903	1.52	0.571	This work
15	Rb	Ti	W	0.50	10.2426[a]	1.52	0.601	This work
16	Rb	Cr	W	0.33	10.2320[b]	1.52	0.603	(*9*)
17	Rb	Fe	W	0.33	10.2560	1.52	0.608	(*9*)
18	Rb	Co	W	0.25	10.2860	1.52	0.618	(*2*)
19	Rb	Cu	W	0.25	10.2770	1.52	0.616	(*2*)
20	Rb	Zn	W	0.25	10.2900	1.52	0.618	(*2*)
21	Rb	Ga	W	0.33	10.2230	1.52	0.603	(*9*)
22	Rb	Nb	Te	1.00	10.2550	1.52	0.600	(*3*)
23	Rb	Nb	W	1.00	10.3660	1.52	0.620	(*3*)
24	Rb	Sb	Mo	1.00	10.2562	1.52	0.595	(*5*)
25	Rb	Sb	Te	1.00	10.1699	1.52	0.580	(*6*)
26	Rb	Sb	W	1.00	10.2450	1.52	0.600	(*10*)
27	Rb	Ta	Te	1.00	10.2550	1.52	0.600	(*3*)
28	Rb	Ta	W	1.00	10.3540[c]	1.52	0.620	(*3*)
29	Cs	Al	W	0.33	10.1890	1.67	0.589	(*9*)
30	Cs	Ti	Te	0.50	10.1346	1.67	0.571	This work
31	Cs	Ti	W	0.50	10.2710	1.67	0.601	This work
32	Cs	Cr	W	0.33	10.2640	1.67	0.603	(*9*)
33	Cs	Fe	W	0.33	10.2890	1.67	0.608	(*9*)
34	Cs	Ga	W	0.33	10.2380	1.67	0.603	(*9*)
35	Cs	Zr	W	0.50	10.4109	1.67	0.630	This work
36	Cs	Nb	Te	1.00	10.3000	1.67	0.600	(*3*)
37	Cs	Nb	W	1.00	10.3800[d]	1.67	0.620	(*1*)
38	Cs	Sb	Mo	1.00	10.3000	1.67	0.595	(*5*)
39	Cs	Sb	Te	1.00	10.1935	1.67	0.580	(*6*)
40	Cs	Sb	W	1.00	10.2790	1.67	0.600	(*10*)
41	Cs	Hf	W	0.50	10.3906	1.67	0.628	This work
42	Cs	Ta	Te	1.00	10.2930	1.67	0.600	(*3*)
43	Cs	Ta	W	1.00	10.3810	1.67	0.620	(*3*)
44	Tl	Ti	Te	0.50	10.0930	1.50	0.571	This work
45	Tl	Ti	W	0.50	10.2459	1.50	0.601	This work
46	Tl	Cr	W	0.33	10.2340	1.50	0.603	(*9*)
47	Tl	Fe	W	0.33	10.2640	1.50	0.608	(*9*)
48	Tl	Ga	W	0.33	10.2240	1.50	0.603	(*9*)

TABLE IV—*Continued*

No.	*A*	*B*	*B'*	*p*	*a*	r_A	$\bar{r}_{B,B'}$	Reference
49	Tl	Nb	Te	1.00	10.2570	1.50	0.600	(*3*)
50	Tl	Nb	W	1.00	10.3670	1.50	0.620	(*3*)
51	Tl	Sb	Te	1.00	10.1472	1.50	0.580	(*6*)
52	Tl	Sb	W	1.00	10.2440	1.50	0.600	(*10*)
53	Tl	Ta	Te	1.00	10.2560	1.50	0.600	(*3*)
54	Tl	Ta	W	1.00	10.3600	1.50	0.620	(*3*)

[a] 10.235: Ref. (*2*).
[b] 10.222: Ref. (*2*).
[c] 10.361: Ref. (*2*).
[d] 10.39: Ref. (*3*).

other determinant factor which offsets the former one. This is the size of the channels inside the structure, smaller in the family object of this work. Actually, the cell parameters for the tungsten pyrochlores are around 10.4 Å, while in the tellurium compounds they range from 10.06 to 10.23 Å. If the conductivity values and cell parameters of three thallium pyrochlores are compared (Table V) a much larger activation energy for the tellurium compound can be found. This is probably due to the higher energy necessary to pass through smaller bottlenecks. On the other hand, when the conductivity values for the tellurium pyrochlores are considered, a higher mobility is observed for the potassium, cesium, and thallium. This can be understood in terms of polarizability for Cs and Tl, because they are bigger cations; i.e., their electron distribution can be adjusted more easily along the paths. The transport of potassium can simply be due to its smaller ionic radius which fits better to the structure channels. The rubidium polarizability and size being midway could be responsible for the lower mobility of Rb among the tellurium pyrochlore family.

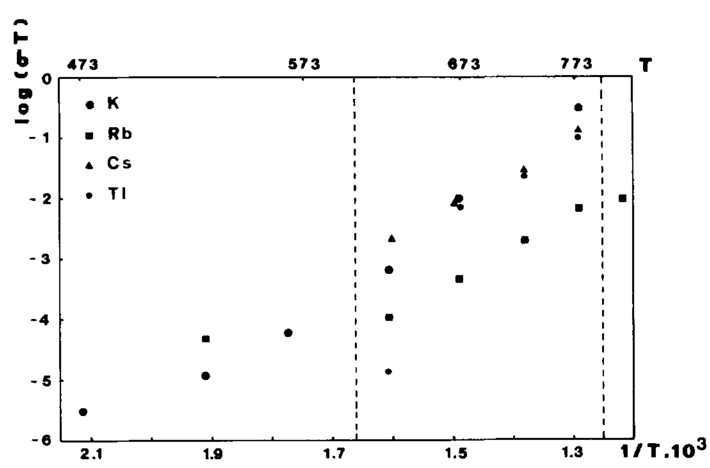

FIG. 3. Log (σT) vs $1/T$ for $A(Ti_{0.5}Te_{1.5})O_6$ pyrochlores (A = K, Rb, Cs, Tl) (σ in Ω^{-1} cm^{-1}; T in K). Dashed lines show the experimental points considered for determining the activation energy.

TABLE V

COMPARISON OF CELL PARAMETERS AND CONDUCTIVITY VALUES FOR Tl PYROCHLORES

Compound	a (Å)	E_a (eV)	$\sigma_{673\text{ K}}$ (Ω^{-1} cm^{-1})	Reference
$TlNbWO_6$	10.37	0.56	$1.1.10^{-4a}$	(*11*)
$TlTaWO_6$	10.35	0.35	$1.9.10^{-4a}$	(*12*)
$TlTaWO_6$	10.36	0.37	$7.1.10^{-5a}$	(*12*)
$TlTi_{0.5}Te_{1.5}O_6$	10.09	1.19	$9.4.10^{-6}$	This work

[a] Extrapolated values.

Acknowledgments

The authors acknowledge one fellowship (A.C.) and the aid of the Consejo Superior de Investigaciones Científicas. One of them (X.T.) thanks the Basque Government for financial support.

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