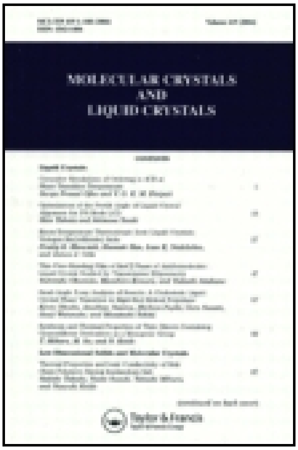

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SYNTHESIS AND STRUCTURE OF $LiTiZrX_4$ (X = S, Se, Te) LAYERED COMPOUNDS

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Abstract The $LiTiZrX_4$ compounds were slowly formed through a several days reaction between dispersed $TiZrX_4$ phase and LiC_4H_9. The obtained black crystaline powders are unstable in air . All these compounds exhibit structures close to that of TiX_4 and ZrX_4 .

INTRODUCTION

The intercalation behaviour of ternary selenide of transition metals seems to be less investigated than the binary diselenides. The chalcogenide $TiZrTe_4$ put in contact with a hexane solution of LiC_4H_9 gives $LiTiZrTe_4$.[1] It was interesting to study and explain, analogically to the above cases, the interactions of $TiZrSe_4$ and $TiZrS_4$ with LiC_4H_9 .

The preparation of the $LiTiZrX_4$ intercalates is performed through reaction between the ternary Titanium-Zirconium-Chalcogenides and a LiC_4H_9 solution in hexane. The $LiTiZrX_4$ compounds form slowly during a several days reaction. Another way to prepare the $LiTiZrX_4$ intercalats consist to start from the stoichiometric proportion of the four elements. The reaction in the solid state is carried on in an evacuated silica tube by heating for about 10 days up to 1173 K.

All the new compounds are significantly less stable at room temperature in air than the Silver-Titanium-Zirconium-Chalcogenides.[2] Therefore the powder samples of $LiTiZrX_4$ (X = S, Se, Te) were prepared using an epoxide polymer for embedding in order to prevent their decomposition during X-ray diffraction pattern recording.

X-RAY DIFFRACTION AND STRUCTURE

X-ray diffraction values observed and calculated for $LiTiZrX_4$ (X = S, Se, Te) have been published previously. The X-ray diffraction pattern together with the indexing and intensities are shown in Table 1, 2 and 3.

All the $LiTiZrX_4$ compounds show a small number of diffraction lines. However, for $LiTiZrTe_4$, it is possible to use two cells a hexagonal one with a=385.3±0.7 pm, c=2610.5±0.4 pm, z=2 and a monoclinic one with a=667.4±0.5 pm, b=385.3±0.7 pm, c=2610.5±0.4 pm, $\beta=91.32^{o}$, z=4.
For $LiTiZrSe_4$ it is also possible to index the phase diagram either with a hexagonal cell with a=635.0±1.3 pm, c=1212.0±2.4 pm, z=3 or a monoclinic one with a=631.0±0.98 pm, b=364.5±0.55 pm, $\beta=91.3^{o}$, z=4.
For $LiTiZrS_4$, it is not possible to index the diagram in the hexagonal symmetry. It can be done only in the monoclinic symmetry with a=612.0±0.8 pm, b=380.7±0.6 pm, c=2486.0±1.1 pm, $\beta=90.5^{o}$ and z=4.
$LiTiZrX_4$ consist in a layerlike structure of the CdJ_2 typ. Cationic sites alternatively occupied by Ti and Zr atoms yielding rows perpendicular to the (110) direction.

Figure 1 shows the molal volume change, in per cent, for $LiTiZrX_4$ chalcogenides in comparison with the corresponding ternary chalcogenides $TiZrX_4$ versus the X^{2-} radius.
Contrary to the two other $LiTiZrX_4$ phases the molal volume of $LiTiZrTe_4$ is nearly 3.5% smaller than for $TiZrTe_4$. This may be related to the large sites of the phase and the high polarisability of the Li^{+}- Te^{2-} bond.

Table 1. Spacings and intensities of the powder diffraction pattern of $LiTiZrTe_4$

I [%]	d_{exn} [pm]	Calc. d [pm]	hexagonal hk l	Calc. d [pm]	monoclin. hk l
19	645.83	652.62	004	650.03 642.89	10$\bar{1}$ 101
29	562.55	522.10	005	588.60	102
48	326.40	326.31	008	326.23	008
16	306.09	311.56	103	309.12	203
100	297.13	297.10	104	298.47 295.77	11$\bar{4}$ 10$\bar{8}$
11	267.76	264.78	106	267.71	20$\bar{6}$
42	233.64	233.30	108	223.88	214
12	218.17	218.91 217.54	109 00 12	218.45 217.63	302 119
18	192.79	192.65	110	192.97 192.65 192.62	30$\bar{7}$ 020 310
26	182.78	182.23	10 12	183.09 182.96	122 21 $\overline{10}$
9	163.75	163.96	203	164.16 163.54 163.50	30 $\overline{11}$ 11 $\overline{14}$ 223
9	162.48	162.77	10 14	162.51 162.08	40$\bar{4}$ 224
9	125.11	125.53 124.81	122;12$\bar{2}$ 123;12$\bar{3}$	125.18 125.11 125.03	51$\bar{3}$ 42$\bar{3}$ 22 $\overline{14}$

hexagonal	monoclinic
a=385.3±0.7 pm	a=667.4±0.5 pm
	b=385.3±0.7 pm
c=2610.5±0.4 pm	c=2610.5±0.4 pm
	β=91.32°
D =6.41 gcm^{-3}	D =6.41 gcm^{-3}
D_x=6.49 gcm^{-3}	D_x=6.49 gcm^{-3}
z=2	z=4
S.G.:P 6/m	S.G.:P 2/m

Table 2. Spacings and intensities of the powder diffraction pattern of $LiTiZrSe_4$

I [%]	d_{exn} [nm]	Calc d [pm]	hexagonal hk l	Calc. d [pm]	monoclin. hk l
20	618.86	605.80	002	621.84	004
10	317.29	317.49	110	315.60	110
10	306.61	307.12	111	306.64 306.74	107 11$\bar{2}$
10	294.73	302.90	004	294.25	410
100	281.16	281.21	112	281.43	10$\bar{8}$
80	271.21	274.95	200	269.16	20$\bar{5}$
10	227.95	227.28	203	228.18	213
20	223.61	221.75	105	223.98	21$\bar{4}$;20$\bar{8}$
20	203.43	203.59	204	202.73	303
40	182.95	183.30	300	182.83	11 11
20	175.71	175.45	302	175.73	30$\bar{7}$
20	170.25	171.38	214	170.01	10 14
10	159.64	158.74	220	159.71	114
10	151.77	152.52 151.45 151.32	310 008 311	151.75	10 $\overline{16}$
10	141.05	140.61	224	141.33	21 14
10	127.70	129.08	315	127.78 127.64	327 20 $\overline{18}$
10	126.53	126.16	320	126.62 126.39	32$\bar{8}$ 30 $\overline{16}$
10	123.74	123.51 123.94	322 119	123.78 123.67	21 17 30 16

a=635.0±1.3 pm c=1212.0±2.4 pm D =5.36 gcm^{-3} D_x=5.43 gcm^{-3} z=3 S.G.:P 6/m	a=631.0±0.98 pm b=364.5±0.55 pm c=2488±0.45 pm β=91.3° D_x=5.36 gcm^{-3} z=4 S.G.:P 2/m

Table 3. Spacings and intensities of the powder diffraction pater of $LiTiZrS_4$

I [%]	d_{exn} [pm]	Calc. d [pm]	monoclin. hk l
22	1083.95	1243.99	002
100	829.99	829.39	003
16	565.77	551.12	$10\bar{2}$
6	547.35	547.36	102
9	417.77	416.39	006
2	310.26	308.69	107
4	295.21	296.59	202
3	276.93	276.44	009
8	259.03	259.77	017
2	233.35	231.11	$10\ \overline{10}$
3	218.52	219.08	208
3	217.66	217.17	208
1	212.29	212.76	$10\ \overline{11}$
2	210.64	211.55	10 11
3	193.56	193.33	304
2	191.45	191.38	00 13
2	190.13	189.25	$21\bar{8}$
2	181.92	181.25	$10\ \overline{13}$
4	142.48	142.00	$41\bar{1}$

a=612.0±0.8 pm
b=380.7±0.6 pm
c=2486.0±1.1 pm
$\beta=90.5^{o}$
D =3.41 gcm^{-3}
D_x=3.14 gcm^{-3}
z=4
S.G.:P 2/m

PROPERTIES OF $LiTiZrX_4$

All the compounds are very unstable in air and generate the oxide hydrates of Ti and Zr as a result of hydrolysis. For $LiTiZrS_4$, the product of hydrolysis is, in the first step, H_2S, then sulfur. The decomposition of $LiTiZrSe_4$ and $LiTiZrTe_4$ gives amorphous Se and Te. It is very probable that, in the case of $LiTiZrS_4$, the decomposition takes place as follows:

$$2\,LiTiZrS_4 + 7/2\,O_2 + 5\,H_2O \rightarrow 2\,TiZrO_3(OH)_2 + 2\,LiOH + 3\,S_2 + 2\,H_2S$$

The electrical conductivity was measured in the 297 K to 428 K temperature range. The results of the above measurements show a very good electrical conduction at room temperature. The conductivity decreases with temperature increasing. However, it is lower than for the metals. The $LiTiZrX_4$ show, within the temperature range from 298 K to 450 K, the conductivity characteristic for metal [3], from $10^{-1}\,\Omega^{-1}cm^{-1}$ to $10^{-1}\,\Omega^{-1}cm^{-1}$.

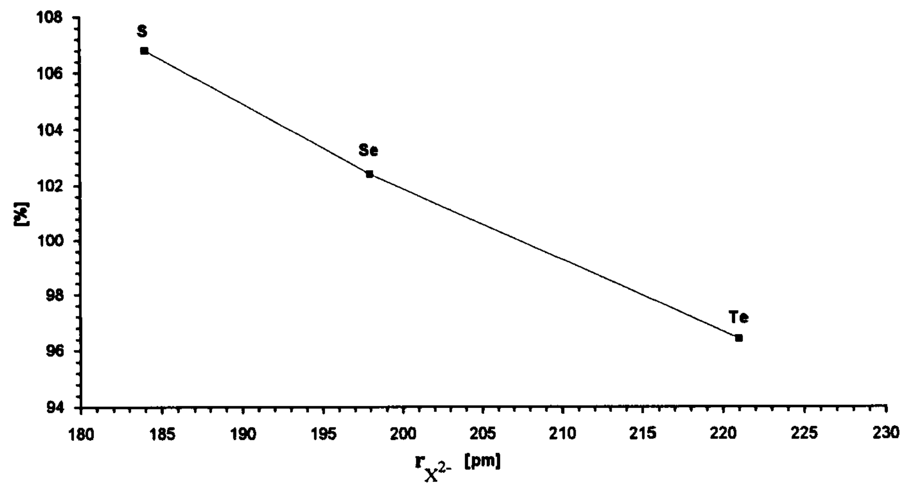

Fig. 1. Percentage change of the molal volume of $LiTiZrX_4$ in comparison with $TiZrX_4$ versus the X^{2-}-ion radius .

CONCLUSION

It is posible to prepare the $LiTiZrX_4$ compounds by two different methods: from the elements or from LiC_4H_9 and $TiZrX_4$ suspension in hexane. The cationic sites are alternatively occupied by Ti or Zr atoms rows perpendicular to the (110) direction. The intercalation by Li-ions causes c parameter enlarged. All the compounds show, within the temperature range from 298 K to 450 K, the conductivity characteristic for metals.

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