analysis indicated that the Fe^{2+} ions have a higher concentration at the *M*(1) site than at *M*(2), and that the Na^+ site is approximately half-vacant, giving the chemical formula $Na_{0·56}Fe^{II}_{0·28}Ti^{IV}_{1·72}O_4$. Though some of the Fe^{2+} ions might be oxidized to Fe^{3+}, the amount should not be large, since the final difference Fourier maps are quite flat around the Na^+ and (Ti^{4+},Fe^{2+}) sites.

The $(Ti,Fe)O_6$ octahedra share edges, constructing double chains parallel to [010]. The chains are further joined laterally with each other by sharing corners of the octahedra to form a three-dimensional framework with ditrigonal tunnels running parallel to [010]. The *M*(1)—O distances range from 1·98 to 2·01 Å (mean 2·00 Å), while the *M*(2)—O distances are in the range from 1·95 to 2·04 Å (mean 1·98 Å). These values are in agreement with the (Ti,Fe)—O distances found in $Na_{0·90}Fe_{0·90}Ti_{1·10}O_4$ (Mumme & Reid, 1968) and freudenbergite (Ishiguro, Tanaka, Marumo, Ismail, Hirano & Sōmiya, 1978). In fact, the ionic radii given by Shannon & Prewitt (1969) suggest that the (Ti,Fe)—O distance in the present crystal should be longer than those in the above two crystals by only 0·005 and 0·013 Å respectively. It is notable that the Fe^{2+} ion with a larger ionic radius than Ti^{4+} is more concentrated at the *M*(1) site which has a slightly larger octahedral environment than *M*(2).

The Na—O distances range from 2·39 to 2·63 Å (mean 2·48 Å). Since the Na^+ ions lie in the wide tunnel spaces and approximately one half of their sites are vacant, this compound is expected to show ionic conduction by Na^+ ions in the [010] direction.

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References

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* **A26**, 71–83.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 73–74. Birmingham: Kynoch Press.

Ishiguro, T., Tanaka, K., Marumo, F., Ismail, M. G. M. U., Hirano, S. & Sōmiya, S. (1978). *Acta Cryst.* **B34**, 255–256.

Li, C., Reid, A. F. & Saunders, S. (1971). *J. Solid State Chem.* **3**, 614–620.

Mumme, W. G. & Reid, A. F. (1968). *Acta Cryst.* **B24**, 625–631.

Reid, A. F., Perkins, H. K. & Sienko, M. J. (1968). *Inorg. Chem.* **7**, 119–126.

Reid, A. F. & Sienko, M. J. (1967). *Inorg. Chem.* **6**, 321–324.

Reid, A. F., Wadsley, A. D. & Sienko, M. J. (1968). *Inorg. Chem.* **7**, 112–118.

Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* **B25**, 925–946.

Tokonami, M. (1965). *Acta Cryst.* **19**, 486.

Acta Cryst. (1978). B**34**, 3348–3349

Lead Zirconium Sulphide

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Abstract. $PbZrS_3$, *Pnma*, $a = 9·0134\,(7)$, $b = 3·7660\,(2)$, $c = 13·9237\,(10)$ Å, $Z = 4$. Structure refinement based on neutron diffraction powder diagrams established the modified NH_4CdCl_3 structure of $PbZrS_3$. The compound is isostructural with $PbSnS_3$.

Introduction. We investigated the crystal structure of $PbZrS_3$ as a part of a research programme on the structural relations of compounds ABX_3, where *A* represents an alkaline or alkaline-earth metal, *B* a transition metal and *X* a halogen or S.

Sterzel & Horn (1970) reported the structures of $PbZrS_3$ and $PbHfS_3$, but their samples were contaminated with PbS. Their resulting X-ray powder pattern could be indexed like $PbSnS_3$ (Yamaoko & Okai, 1970), Table 1.

Table 1. *Crystal axes for* ABS_3

	a (Å)	*b* (Å)	*c* (Å)	Reference
$PbZrS_3$	9·031 (6)	3·770 (4)	13·919 (9)	Sterzel & Horn (1970), omitting their PbS pattern
$PbHfS_3$	8·989 (2)	3·738 (2)	13·924 (4)	
$PbZrS_3$	9·037 (5)	3·77 (2)	13·926 (5)	Yamaoko (1972)
$PbZrS_3$	9·0134 (7)	3·7660 (2)	13·923 (10)	This work
$PbSnS_3$	8·738	3·792	14·052	Jumas *et al.* (1972)
Sn_2S_3	8·864 (6)	3·747 (1)	14·020	Mootz & Puhl (1972)

Yamaoko (1972) reported the structure of $PbZrS_3$, prepared under a pressure of 20 kbar at 800–900 °C; the X-ray powder diagram is similar to that of Sn_2S_3 (Mootz & Puhl, 1967).

We prepared $PbZrS_3$ and $PbHfS_3$ by firing stoichiometric amounts of the binary sulphides in evacuated sealed quartz tubes at 800 °C for a week. The X-ray diffraction patterns of both compounds could be indexed leading to the space groups *Pnma* or $Pn2_1a$, in agreement with the data of Yamaoko (1972). Neutron diffraction powder data of $PbZrS_3$ were collected on a neutron diffractometer at the HFR reactor in Petten. The neutron wavelength was 2·570 Å. Soller slits with a horizontal divergence at 30′ were placed before the monochromator and in front of the BF_3 counter.

With neutron diffraction data in the range $5{\cdot}4 < 2\theta < 138°$, a structure refinement based on the Rietveld (1969) profile method has been carried out in space group *Pnma* by minimizing the residual function $\chi^2 = \sum_i w_i |y_i(\text{obs}) - (1/c)y_i(\text{calc})|^2$. The R factors are defined by:

$$R_{\text{nuclear}} = 100 \sum |I(\text{obs}) - \frac{1}{c} I(\text{calc})| / \sum I(\text{obs}),$$

$$R_{\text{profile}} = 100 \sum |y(\text{obs}) - \frac{1}{c} y(\text{calc})| / \sum y(\text{obs}),$$

$$R_{\text{weight}} = 100 \sqrt{[\sum w|y(\text{obs}) - \frac{1}{c} y(\text{calc})|^2 / \sum w|y(\text{obs})|^2]}.$$

I(obs), I(calc) = observed and calculated integrated intensity of each reflection, y(obs), y(calc) = observed and calculated profile data point, w = statistical weight allotted to each data point, c = scale factor.

Table 2. *Structural parameters for* $PbZrS_3$ *in space-group Pnma with overall isotropic temperature factor B*

		x	y	z
Pb	4(c)	0·5167 (3)	0·25	0·8261 (2)
Zr	4(c)	0·1669 (4)	0·25	0·0498 (3)
S(1)	4(c)	0·2738 (9)	0·25	0·2142 (6)
S(2)	4(c)	0·1637 (11)	0·25	0·4908 (6)
S(3)	4(c)	0·0113 (14)	0·25	0·8932 (6)

R_{nuclear} 4·55 R_{profile} 7·95 R_{weight} 10·08

B (Å^2) 0·70 (5) Residue 4·25

Table 3. *Interatomic distances* (Å)

Distances marked with an asterisk occur in pairs.

Pb–S(1)	2·728 (6)*	Zr–S(1)	2·481 (9)
	3·579 (8)*	Zr–S(2)	2·558 (7)*
Pb–S(2)	2·879 (9)	Zr–S(3)	2·599 (8)*
	3·383 (8)*		2·590 (10)
Pb–S(3)	3·055 (9)		

The coherent scattering lengths ($\times 10^{-12}$ cm^2) were 0·940 for Pb, 0·71 for Zr and 0·28 for S (Bacon, 1972). The results are shown in Tables 2 and 3. The space group $Pn2_1a$ gave no significantly better results.

Discussion. In the ABS_3 compounds with large radius of A a number of structures are realized; the (distorted) perovskites, the NH_4CdCl_3 structure and the $TlPbI_3$ ($NdYbS_3$) structure (Stoeger, 1977).

The structure of $PbZrS_3$, and most likely that of $PbHfS_3$, is strongly related to the NH_4CdCl_3 type (*Strukturbericht*, type *E* 24), containing columns of double edge-sharing octahedra linked by Pb ions in tricapped trigonal-prismatic coordination. However, two of the anions, S(1) and S(3), have poor charge compensation in this structure. This may result in smaller Pb—S(1) and longer Pb—S(3) distances, as is the case in $KCdBr_3$ (Natarajan Iyer, Faggiani & Brown, 1977). However, in $PbZrS_3$ the Pb is moved to S(2) and one pair of S(1), resulting in an asymmetric position of Pb in the prismatic coordination and a hole for a lone pair. This feature is also found in $PbSnS_3$ (Jumas, Ribes, Philippot & Maurin, 1972) and Sn_2S_3.

In contrast, the sulphides $AZrS_3$, with A = Ca, Sr, Eu and Ba (Lelieveld & IJdo, 1978) are all distorted perovskite-type structures.

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References

Bacon, G. E. (1972). *Acta Cryst.* A**28**, 357–358.
Jumas, J. C., Ribes, M., Philippot, E. & Maurin, M. (1972). *C. R. Acad. Sci.* **275**, 267–272.
Lelieveld, R. & IJdo, D. J. W. (1978). To be published.
Mootz, D. & Puhl, H. (1967). *Acta Cryst.* **23**, 471–476.
Natarajan Iyer, M., Faggiani, R. & Brown, I. D. (1977). *Acta Cryst.* B**33**, 127–128.
Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
Sterzel, W. & Horn, J. (1970). *Z. Anorg. Allg. Chem.* **376**, 254–260.
Stoeger, W. (1977). *Z. Naturforsch. Teil B*, **32**, 975–981.
Yamaoko, S. (1972). *J. Am. Ceram. Soc.* **55**, 111.
Yamaoko, S. & Okai, B. (1970). *Mater. Res. Bull.* **5**, 889–894.