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## A note on the structure of non-ferroelectric lead metatantalate.

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Subbarao, Shirane & Jona, (1960), find two forms of lead metatantalate to exist: a rhombohedral form with $a_r = 7{\cdot}147$ Å, $\alpha_r = 94°\ 47'$ for material prepared below a temperature of 1150 °C.; and an orthorhombic form with

$$a_0 = 17{\cdot}68,\ b_0 = 17{\cdot}72,\ c_0 = 7{\cdot}754\ \text{Å}$$

for material prepared above 1150 °C. They report the orthorhombic form as ferroelectric with a Curie temperature of 265 °C., compared with 260 °C. measured by Smolenskii & Agranovskaya (1954), 240 °C. by Isupov (1957), and 150 °C. by Francombe & Lewis (1958). Their results disagree with those of Coates & Kay (1958), who found lead metatantalate to be non-ferroelectric but with a possible antiferroelectric transition at 70 °C. The purpose of this note is to state that our results refer to a third form quite distinct from the two forms noted by Subbarao, Shirane & Jona.

Our results were measured on ceramic discs of lead metatantalate, ($PbTa_2O_6$), prepared by firing together pressed discs of equi-molar amounts of either lead sulphate or lead oxide and tantalum pentoxide first for three hours at 1360 °C., then grinding and repressing with a final firing for 24 hours at 1420 °C. The same X-ray powder diffraction pattern was always obtained, and it cannot be indexed on the basis of either of the two cells given by Subbarao, Shirane & Jona, nor on the basis of any rhombohedral cell at all. However, the pattern does yield a pseudo-cubic tetragonal cell, with $a_t = 10{\cdot}9 \pm 0{\cdot}1$, $c_t = 11{\cdot}2 \pm 0{\cdot}1$ Å, calculated from the (800) and (008) reflexions. The cell is primitive.

Though no detailed structure analysis has been made, the fact that the pseudo-cubic cell contains eight formula-units and has a side of approximately 11 Å suggests that the structure is related to the pyrochlore type (with space group *Fd3m*) which is usually adopted by materials of the general formula $A_2B_2O_7$. Examples are $Cd_2Nb_2O_7$, with $a = 10{\cdot}37$ Å, and $Pb_2Nb_2O_7$, a rhombohedrally-distorted form with $a = 10{\cdot}70$ Å and $\alpha = 88°\ 25'$ (both given by Jona, Shirane & Pepinsky, 1955). The pyrochlore structure is a three-dimensional network of corner-sharing $BO_6$ octahedra, with the *A* ions and the seventh set of oxygens in the interstices between the octahedra. One might therefore expect it to be possible to remove part or all of the seventh set of oxygens, provided that an equivalent number of *A* ions is also removed, without destroying the stability of the structure, (Jona, Shirane & Pepinsky, 1955; Pyatenko, 1960). Jona, Shirane & Pepinsky suggest that the general formula should be written $A_{1+x}B_2O_{6+x}$, which gives $AB_2O_6$ when $x$ is zero. It is therefore possible for lead metatantalate to exist with a structure of the pyrochlore type or some close derivative of it. We believe that our material may well have such a structure.

### References

Coates, R. V. & Kay, H. F. (1958). *Phil. Mag.* Ser. 8, **36**, 1449.

Francombe, M. H. & Lewis, B. (1958). *Acta Cryst.* **11**, 696.

Isupov, V. A. (1957). *Izv. Akad. Nauk. S.S.S.R., Ser. Fiz.* **21**, 402.

Jona, F., Shirane, G. & Pepinsky, R. (1955). *Phys. Rev.* **98**, 903.

Pyatenko, Yu. A. (1960). *Soviet Physics, Cryst.* **4**, no. 2, 184.

Smolenskii, G. A. & Agranovskaya, A. I. (1954). *Dokl. Akad. Nauk. S.S.S.R.*, **97**, 237.

Subbarao, E. C., Shirane, G. & Jona, F. (1960). *Acta Cryst.* **13**, 226.

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## The space group of $MnAl_3$.

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Single-crystal specimens of $MnAl_3$ were prepared by the method described by Taylor (1960). The orthorhombic unit-cell dimensions were measured by X-ray rotation photographs and found to be:

$$a = 14{\cdot}79 \pm 0{\cdot}01,\ b = 12{\cdot}42 \pm 0{\cdot}01,\ c = 12{\cdot}59 \pm 0{\cdot}01\ \text{Å}\ ,$$

in agreement with the results of Hofmann (1938).

Systematic absences were consistent with space groups $Pn2_1a$ and *Pnma*: the intensity distributions in the three principal zones, however, resemble the hyper-symmetric distribution of Rogers & Wilson (1953) in that they lie well above the normal centric distribution: the space group is therefore probably *Pnma*.

Chemical analysis of the crystals gave a Mn content of 37·4 wt.%, the density of the crystals was $3{\cdot}90 \pm 0{\cdot}05$ g.cm.$^{-3}$: the unit-cell contents are therefore approximately 36 Mn and 124 Al atoms.

Rotation photographs about the *b* and *c* axis are very similar, indicating a strong pseudo-tetragonality. Marked layering perpendicular to these axes is evident.

No further work on this compound is contemplated.

### References

Hofmann, W. (1938). *Aluminium, Berlin*, **20**, 865.

Rogers, D. & Wilson, A. J. C. (1953). *Acta Cryst.* **6**, 439.

Taylor, M. A. (1960). *Acta Met.* **8**, 256.

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