rounding off the discontinuity in Wilchinsky's theory but converging in a most satisfactory way to a common intersection at $\varphi = 90°$ and at the level of the curve for the solid sample.

Many questions, such as the dependance of the effect thus measured on wavelength of primary and secondary radiation (important if the result is to be used for diffraction), the analogous effect for specimens used in transmission, influence of a non-transparent binder etc., can be studied conveniently by using fluorescence. It is hoped that continued research by the present empirical method will some time give a sufficiently clear picture of particle absorption to enable one to make a reliable estimate of the effect in quantitative X-ray work.

The extra-fast goniometer drive was constructed by K. Lowitzsch. His assistance, as well as helpful discussions with Dr W. Parrish and several colleagues at the Philips laboratories, are hereby gratefully acknowledged.

Reference

Wilchinsky, Z. W. (1951). *Acta Cryst.* **4**, 1.

Acta Cryst. (1956). **9**, 683

Polymorphim in lead metaniobate.*

By M. H. Francombe, *Research Laboratories of The General Electric Company Limited, Wembley, England*

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X-ray diffraction powder studies of sintered ceramic specimens of lead metaniobate ($PbNb_2O_6$) have shown that this compound can adopt a structural form distinct from the orthorhombic, ferroelectric structure reported by Goodman (1953). This second structure is produced in specimens which have been fired in air at temperatures near 1200° C. Ceramic preparations made under these conditions are light fawn in colour and show no evidence of ferroelectric behaviour.

From 19 cm. camera X-ray powder photographs the crystal structure of the new polymorphic form is seen to be a deformed perovskite type. The deformation is rhombohedral, the simplest structure cell possessing the dimensions

$$a_R = 6{\cdot}206 \text{ Å},\ \alpha_R = 58°\ 18'.$$

To display more clearly the relationship to the idealized perovskite structure a larger, pseudo-cubic cell may be chosen with dimensions

$$a'_R = 8{\cdot}664 \text{ Å},\ \alpha'_R = 88°\ 30'.$$

This can be visualized as consisting of eight distorted simple perovskite-type cells. In ⟨100⟩ directions, referred to the multiple-type cell, Pb^{2+} ions alternate with vacancies on the *A* sites, and thus {222} planes contain only oxygen ions and unfilled Pb^{2+} sites.

Interplanar spacings, *hkl* indices (referred to hexagonal axes) and peak intensity values (derived from powder photograph microdensitometer data and from data obtained with a Philips X-ray diffractometer) are listed in Table 1.

Turning now to the orthorhombic, ferroelectric lead metaniobate reported by Goodman (1953), we have prepared ceramic samples of this form by using firing temperatures in excess of 1250° C. By fusing these products in platinum boats at about 1350° C. columnar crystals of up to 2–3 mm. in length were obtained. Crystals thus prepared in air and in a PbO atmosphere

Table 1. *X-ray powder diffraction data for rhombohedral form of* $PbNb_2O_6$

(19 cm. camera, Cu $K\alpha$ radiation)

hkl	*d* (Å)	*I*
200	5·250	14
201	4·890	4
204	3·103	100
220	3·023	81
400	2·619	7
224	2·376	3
322	2·225	4
404	2·167	28
420	1·981	3
008	1·922	9
208	1·804	6
424	1·761	28
600	1·746	14
109	1·688	1
119	1·643	2
228	1·623	20
408	1·549	4
507	1·517	8
442	1·479	1
620	1·453	1
606	1·444	1
622	1·427	1
428	1·379	4
624	1·359	10
540	1·342	1
527	1·333	2
800	1·310	2
608 802	1·293	6
1,1,12	1·252	2
2,0,12	1·246	5
804	1·240	4
641	1·199	1
448	1·189	3
901	1·160	2
4,0,12	1·152	4
644	1·148	8
815	1·138	6
822	1·131	2
727	1·105	2
4,4,10	1·077	5
10,0,2	1·038	2
729	1·024	1
4,0,14	1·012	2
10,0,4	1·009	2
660	1·006	2
842 828	0·983	4
0,0,16	0·962	3
844	0·959	4
6,4,10	0·947	2
934	0·939	1
5,2,14	0·919	1
8,2,10 2,2,16	0·917	4
8,0,12	0·915	6

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* Communication from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.

were green and pale yellow in colour respectively. The former crystals were found to have lost 2–3% in weight while the latter had gained 2–3%, during firing.

When examined under the microscope crystals of both colour were found to be biaxial. X-ray single-crystal rotation photographs showed the structure to be orthorhombic, but a simpler structure cell than that reported by Goodman (1953) fitted the data. For both green and yellow crystals the calculated dimensions were

$$a = 17{\cdot}51,\ b = 17{\cdot}81,\ c = 7{\cdot}73\ \text{Å}\,,$$

compared with Goodman's values

$$a_0 \sim 25,\ b_0 \sim 25,\ c_0 \sim 7\ \text{Å}\,.$$

The measured density was approximately 6·6 g.cm.$^{-3}$, and this suggests that the new unit cell contains 20 molecules, compared with the 40 molecules proposed for the larger cell.

Permittivity values were also measured at various temperatures for slices cut from some of the larger yellow crystals. Sharp maxima, of the order of 15,000, were obtained in the permittivity/temperature curves at 570° C. (the Curie temperature found by Goodman (1953)) for directions of measurement lying in the principal cleavage plane of the crystals. When similar measurements were made in a direction perpendicular to the cleavage plane no maxima were obtained.

Further studies of single crystals of orthorhombic lead niobate are being made by electrical, X-ray and optical methods, and it is hoped to describe the results in detail in a separate paper.

Reference

Goodman, G. (1953). *J. Amer. Ceram. Soc.* **36**, 368.

Acta Cryst. (1956). **9**, 684

The structure of TiF_3.*

By Stanley Siegel, *Argonne National Laboratory, Lemont, Illinois, U.S.A.*

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Ehrlich & Pietzka (1954) have reported the unit cell of TiF_3 as rhombohedral with $a = 5{\cdot}52_3$ Å and $\alpha = 58{\cdot}88°$. Our measurements indicate similar values:

$$a = 5{\cdot}519 \pm 0{\cdot}002\ \text{Å},\ \alpha = 59{\cdot}07 \pm 0{\cdot}07°\,.$$

Powder patterns recorded with Cu $K\alpha$ radiation ($\lambda\alpha_1\alpha_2 = 1{\cdot}5417$ Å) in a camera of 19 cm. diameter show the pseudo-cubic character of the cell. Several maxima are not resolved, and microphotometer tracings give weak indications only of the multiple nature of these lines.

The extinctions and structure reported here are consistent with the space group $R\bar{3}c$. The cell contains two molecules with

$$2\ \text{Ti in}\ 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\,,$$
$$\text{and}\ 6\ \text{F in}\ \pm(x, \tfrac{1}{2}-x, \tfrac{1}{4});\ \pm(\tfrac{1}{2}-x, \tfrac{1}{4}, x),$$
$$\pm(\tfrac{1}{4}, x, \tfrac{1}{2}-x),\ \text{with}\ x = -0{\cdot}183 \pm 0{\cdot}011\,.$$

TiF_3 is therefore isostructural with VF_3 reported by Jack & Gutmann (1951). Each titanium atom occupies the center of a slightly distorted octahedron formed by six fluorine atoms, with Ti–6 F = 1·97±0·02 Å. The fluorine atoms lie in planes normal to the [111] direction and an octahedron is formed from three fluorines in each plane on either side of a titanium atom. The normal distance between a titanium atom and a fluorine plane is 1·13 Å. The fluorine-to-fluorine distances within the octahedra are 2·78±0·02 and 2·79±0·02 Å.

The X-ray data are presented in Table 1. Reflections extending to $\sin^2\theta = 0{\cdot}93$ are observed on the film. However, maxima suitable for intensity purposes range up to $\sin^2\theta = 0{\cdot}40$ only.

Table 1. *Observed and calculated data*

hkl	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	$I_o^{\frac{1}{2}}$	$I_c^{\frac{1}{2}}$
110	0·03934	0·03959	110	154
211	0·07840	0·07808	46	45
$10\bar{1}$	0·07933	0·08028	32	34
210	0·1090	0·1091	40	49
222	0·1196	0·1154	10	7
200		0·1199		
220	0·1582	0·1584	81	75
$20\bar{1}$	0·1909	0·1905	22	23
321	0·1956	0·1957	68	66
$21\bar{1}$	0·1992	0·2001	50	54
332	0·2330	0·2320	21	20
310	0·2398	0·2384	37	33
$2\bar{1}\bar{1}$		0·2408		
320	0·2674	0·2675	14	16
422	0·3124	0·3123	35	39
$2\bar{2}0$	0·3213	0·3211	25	29
432	—	0·3400	*	—
421	—	0·3445	*	—
433	0·3475	0·3475	*	—
$31\bar{1}$	—	0·3500	*	—
$21\bar{2}$	—	0·3511	*	—
330	0·3572	0·3562	*	—
411		0·3562	*	—
$30\bar{1}$	0·3602	0·3607	*	—
431	0·3931	0·3926	20	21
$32\bar{1}$	0·3978	0·3991	14	15

* Not resolved in intensity.

The author wishes to thank Mr H. Selig for the TiF_3 preparations and Miss E. Gebert for computational aid.

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