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New compounds of the K_2NiF_4 type.

By S. N. Ruddlesden and P. Popper, *The British Ceramic Research Association, Stoke-on-Trent, England*

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In the course of our investigations of new A_2BO_4 compounds whose equivalent ABO_3 compounds form perovskites, details of which will be published elsewhere, three compounds were found with the K_2NIF_4-type structure. These are Sr_2TiO_4, Ca_2MnO_4 and $SrLaAlO_4$. It may be noted that their tolerance factors, expressed in terms of the radii of the ions concerned as

$$t = (r_A + r_O)/\sqrt{2}.(r_B + r_O),$$

lie between 0·95 and 0·985. The absence of the K_2NiF_4-type structure in compounds with lower tolerance factors suggests that, contrary to the perovskite case, the radius of the A ion cannot be reduced much below that satisfying the geometrical condition for touching spheres ($t = 1$). The A_2BO_4 compounds were formed by firing the appropriate oxide, or carbonate, mixture and examined using Co $K\alpha$ radiation and a 9 cm. powder camera. Line intensities were estimated by visual comparison with a calibrated strip on which lines of known intensity were superimposed on backgrounds of varying intensity.

The K_2NiF_4 structure has been described by Balz & Plieth (1955), who showed its relation to the perovskite structure. They also suggested that Sr_2TiO_4 had the K_2NiF_4 type of structure, whilst Ba_2TiO_4 has the K_2SO_4 structure. The unit cell of K_2NiF_4 is tetragonal, body-centred with $a = 4{\cdot}00$, $c = 13{\cdot}07$ Å and atomic positions, according to Balz & Plieth:

$$0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}+$$

1 Ni at $0,0,0$;
2 K at $0,0,z$; $0,0,\bar{z}$;
4 F at $0,0,z$; $0,0,\bar{z}$; $\tfrac{1}{2},0,0$; $0,\tfrac{1}{2},0$.

The parameter values are given as $z_F = 0{\cdot}151$ and $z_K = 0{\cdot}352$. The relative intensities of powder diffraction lines of A_2BO_4 compounds with this structure have been calculated with the approximation $z_O = \frac{1}{2} - z_A = 0{\cdot}15$ and neglecting temperature and absorption effects. A refinement of the parameters has not been attempted.

The structure of Sr_2TiO_4 has been confirmed and Ca_2MnO_4 and $SrLaAlO_4$ are found to be isostructural with it. In the latter case Sr and La are assumed randomly distributed in the A positions, since no extra lines due to their ordering were found. A number of extra lines were, however, found which could be attributed to the presence of the perovskite $LaAlO_3$. Unreacted SrO would not be easily detected, owing to its rapid hydrolysis. The lattice parameters of these compounds were found to be

	a (Å)	c (Å)
Sr_2TiO_4	3·88	12·60
Ca_2MnO_4	3·67	12·08
$SrLaAlO_4$	3·75	12·5

The calculated and observed line positions and intensities are compared in Tables 1–3.

We should like to express our thanks to Dr T. A.

Table 1. Sr_2TiO_4: *X-ray powder diffraction data*

Spacings are calculated for a tetragonal unit cell, with $a = 3{\cdot}88$, $c = 12{\cdot}60$ Å

hkl	d_c (Å)	d_o (Å)	I_c	I_o
002	6·30	~6·26	2	2
101	3·71	3·72	8	10
004	3·15	3·16	8	10
103	2·85	2·86	100	100
110	2·73	2·74	68	70
112	2·52	2·52	7	5
105	2·12	2·11	3	5
006	2·10	2·10	19	20
114	2·07	2·07	29	30
200	1·94	1·95	38	40
202	1·86	—	0	—
211	1·72	1·73	2	2
116	1·67	1·67	18	10
204	1·65	1·66	4	5
107	1·63	1·63	4	5
213	1·61	1·61	32	30
008	1·58	1·57	2	2
215	1·431	—	1	—
206	1·427	1·425	18	20
220	1·372	1·375	7	15
118	1·368	1·367	2	2
222	1·341	—	0	—
109	1·318	1·317	4	2
301	1·287	—	0	—
0,0,10	1·260	1·259	1	2
224	1·258		2	
217	1·250	1·250	4	5
303	1·237	1·238	7	5
310	1·228	1·229	10	10
208	1·223	1·225	3	5
312	1·206	—	1	—
305	1·151	1·150	0	10
226	1·150		10	
1,1,10	1·147	1·144	6	15
314	1·144		7	
1,0,11	1·100	1·099	3	5
219	1·090	1·090	3	2
321	1·073	—	0	—
316	1·060	1·059	12	8
2,0,10	1·058		3	
307	1·051	1·051	2	2
0,0,12	1·050		1	
323	1·043	1·044	14	15
228	1·034	1·036	3	5
325	0·990	0·991	1	2
1,1,12	0·981	—	2	—
400	0·971	0·971	9	10
318	0·968	—	4	—
402	0·960	—	0	—
2,1,11	0·956	0·956	10	15
309	0·950	—	5	—
1,0,13	0·941	0·940	3	2
411	0·940		1	
2,2,10	0·928	0·929	6	2
404	0·927	—	3	—
327	0·924	0·924	8	2
2,0,12	0·924		7	
413	0·919	0·919	32	10
330	0·915	0·916	12	2
332	0·905	—	1	—
0,0,14	0·901	—	14	—

Table 2. Ca_2MnO_4: *X-ray powder diffraction data*

Spacings are calculated for a tetragonal unit cell, with $a = 3{\cdot}67$, $c = 12{\cdot}08$ Å

hkl	d_c	d_o	I_c	I_o
002	6·04	~6·03	55	~50
101	3·51	3·51	12	~ 2
004	3·02	—	0	—
103	2·71	2·71	100	100
110	2·60	2·59	87	90
112	2·39	—	3	—
105	2·02	2·01	11	50
006	2·01		31	
114	1·97	1·97	22	10
200	1·83	1·83	59	50
—	—	1·80	—	2
202	1·76	1·76	5	2
211	1·63	—	1	—
116	1·59	1·59	24	20
204	1·57	—	0	—
107	1·56	—	0	—
213	1·52	1·52	35	30
008	1·51		5	
215	1·358	1·356	6	40
206	1·356		30	
118	1·306	—	3	—
220	1·298	1·298	8	10
222	1·269	—	2	—
109	1·261	1·257	6	2
301	1·218	—	0	—
0,0,10	1·209	—	0	—
224	1·192	—	0	—
217	1·190	—	0	—
303	1·171	1·168	9	5
208	1·167		9	
310	1·160	1·160	14	10
312	1·140	—	0	—
1,1,10	1·095	—	5	—
305	1·091	—	2	—
226	1·090	1·090	19	10
314	1·084	1·084	5	2
1,0,11	1·051	1·051	6	5
219	1·038	1·038	6	5
321	1·015	—	0	—
2,0,10	1·008	—	1	—
0,0,12	1·006	—	3	—
316	1·005	1·006	23	20
307	0·998	—	0	—
323	0·986	0·987	22	10
228	0·984	0·984	11	5
1,1,12	0·938	0·938	5	5
325	0·938		7	
318	0·920	0·919	14	5
400	0·917	0·918	27	10
2,1,11	0·913	0·913	35	15
402	0·907	—	5	—
309	0·904	—	26	—
1,0,13	0·901	—	0	—

In addition to the above lines, a weak pattern of CaO was observed.

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Table 3. $SrLaAlO_4$: *X-ray powder diffraction data*

Spacings are calculated for a tetragonal unit cell, with $a = 3{\cdot}75$, $c = 12{\cdot}5$ Å

hkl	d_c	d_o	I_c	I_o
002	6·25	—	1	—
101	3·59	3·56	34	25
004	3·13	3·12	19	20
103	2·79	2·77	100	100
110	2·65	2·63	67	60
112	2·44	2·43	1	2
006	2·08	2·08	17	30
105	2·08		1	
114	2·02	2·02	42	50
200	1·88	1·87	35	30
202	1·80	—	0	—
211	1·67	1·66	7	10
116	1·64	1·64	13	10
107	1·61	1·62	10	10
204	1·61	1·61	9	10
008	1·57	1·57	2	5
213	1·56	1·56	32	30
206	1·39	1·40	13	25
215	1·39		0	
118	1·35	1·35	1	10
220	1·33	1·32	10	10
109	1·30	—	4	—
222	1·30	—	0	—
0,0,10	1·25	1·26	2	5
301	1·24	1·24	1	2
217	1·22	1·23	9	20
224	1·22		4	
208	1·20	1·21	3	10
303	1·20	1·20	7	10
310	1·19	1·18	10	15
312	1·17	—	2	—
1,1,10	1·13	1·14	9	20
226	1·12	1·12	10	10
305	1·12		0	
314	1·11	1·11	13	20
1,0,11	1·09	1·10	3	20
219	1·07	—	3	—
0,0,12	1·04	1·05	1	10
2,0,10	1·04		6	
321	1·04		1	
316	1·03	1·03	14	20
307	1·03	1·03	4	10
228	1·01	1·01	3	10
321	1·01	1·01	16	30
1,1,12	0·97	—	1	—
325	0·96	—	0	—
318	0·95	—	3	—
2,1,11	0·94	0·94	11	80
400	0·94		78	
1,0,13	0·93	0·93	8	10
309	0·93		6	
402	0·93		0	
2,0,12	0·91	0·91	7	5
2,2,10	0·91		18	
411	0·91		8	
327	0·90	0·90	45	25
404	0·90		19	
0,0,14	0·90		13	

In addition to the above lines a very weak pattern of $LaAlO_3$ was observed.

Reference

Balz, D. & Plieth, K. (1955). *Z. Elektrochem.* **59**, 545.