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LETTER TO THE EDITOR

A New Titanium Perovskite Oxide, $Na_{2/3}Th_{1/3}TiO_3$

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A thorium titanium perovskite oxide $Na_{2/3}Th_{1/3}TiO_3$ was obtained by codoping with the alkaline metal ion Na^+. This phase has a cubic superstructure $2a_p$ (a_p = 3.8477(4) Å), which was attributed to the partial ordering of Na^+ and Th^{4+}. This is the first example of titanium perovskite oxides with a tetravalent ion at the A site.

Titanium perovskite oxides form a large family, $ATiO_3$, where A is a divalent or trivalent cation. The lanthanum defect phase $Ln_{2/3}TiO_{3-x}$ (Ln = La, Pr, Ce, or Nd) (1) can be obtained under reducing conditions at temperatures of 1300–1400°C. These compounds will decompose when heated in air at above 900°C. The Na^+ ion was found to stabilize this perovskite structure with the composition $Na_{1/2}Ln_{1/2}TiO_3$ (2, 3). The Ce-containing phase $Na_{1/2}Ce_{1/2}TiO_3$ was black (2), where Ce is trivalent. Studies of L_{III}-absorption spectra and magnetic susceptibility on this oxide confirmed the valence state of Ce (4). To our knowledge, no titanium perovskite oxides with a tetravalent cation at the A site have ever been registered. Here we report one such case, $Na_{2/3}Th_{1/3}TiO_3$.

The sample $Na_{2/3}Th_{1/3}TiO_3$ was synthesized by the stoichiometric amounts of Na_2CO_3, TiO_2, and ThO_2. The thoroughly mixed powder was pelletized and sintered at 850°C in air for 24 hr. It was then reground and sintered at 1100°C for 48 hr, followed by quenching to room temperature. The X-ray diffraction pattern shown in Fig. 1 was recorded between 5° and 120° at intervals of 0.02° with Cu$K\alpha$ radiation. The strong, narrow peaks correspond to a simple perovskite structure. A Rietveld refinement on this phase made with the DBWS-9411 version (5) gives the lattice parameter a = 3.8477(4) Å (R_{wp} = 13.8%, R_p = 10.0%, R_B = 7.8%, χ = 1.58). Occupancies for Na and Th were 0.67(1) and 0.32(1), respectively, which gives the approximate formula $Na_{2/3}Th_{1/3}TiO_3$ and the expected valence state 2 of the A site. Table 1 lists d values and observed and calculated intensity data for $Na_{2/3}Th_{1/3}TiO_3$.

The peaks indicated by asterisks in Fig. 1 are rather broad. However, they can be well indexed on a cubic supercell $2a_p$, which most probably is due to the ordering of Na^+ and Th^{4+}, as in the closely related phase $Li_{1/2}La_{1/2}TiO_3$ (6). Because of the great peak width difference between main and superstructure reflections, it is

TABLE 1
X-Ray Diffraction Data for $Na_{2/3}Th_{1/3}TiO_3$

h	k	l	d_{obs} (Å)	I_{obs}	I_{cal}
0	0	½	7.6931	(14)	
1	0	0	3.8472	4	4
1	0	½	3.4413	(26)	
1	1	0	2.7204	100	100
1	1	½	2.5648	(7)	
0	0	½	2.5648		
1	1	1	2.2212	17	19
1	0	½	2.1343	(3)	
2	0	0	1.9237	46	42
1	1	½	1.8668	(10)	
2	0	½	1.8668		
2	1	0	1.7210	5	4
2	1	½	1.6802	(4)	
2	1	1	1.5712	48	44
2	0	½	1.5398	(1)	
0	0	½	1.5398		
1	0	½	1.4292	(3)	
2	1	½	1.4292		
2	2	0	1.3608	23	23
2	2	1	1.2830	1	2
3	1	0	1.2172	21	20
3	1	1	1.1608	6	5
2	2	2	1.1110	9	8
3	2	0	1.0673	2	1
3	2	1	1.0285	27	28
4	0	0	0.9620	4	4
4	1	0	0.9335	1	1
3	2	2	0.9335	1	1
4	1	1	0.9072	7	7
3	3	0	0.9072	15	14

Note. Intensity was calculated on the average structure.

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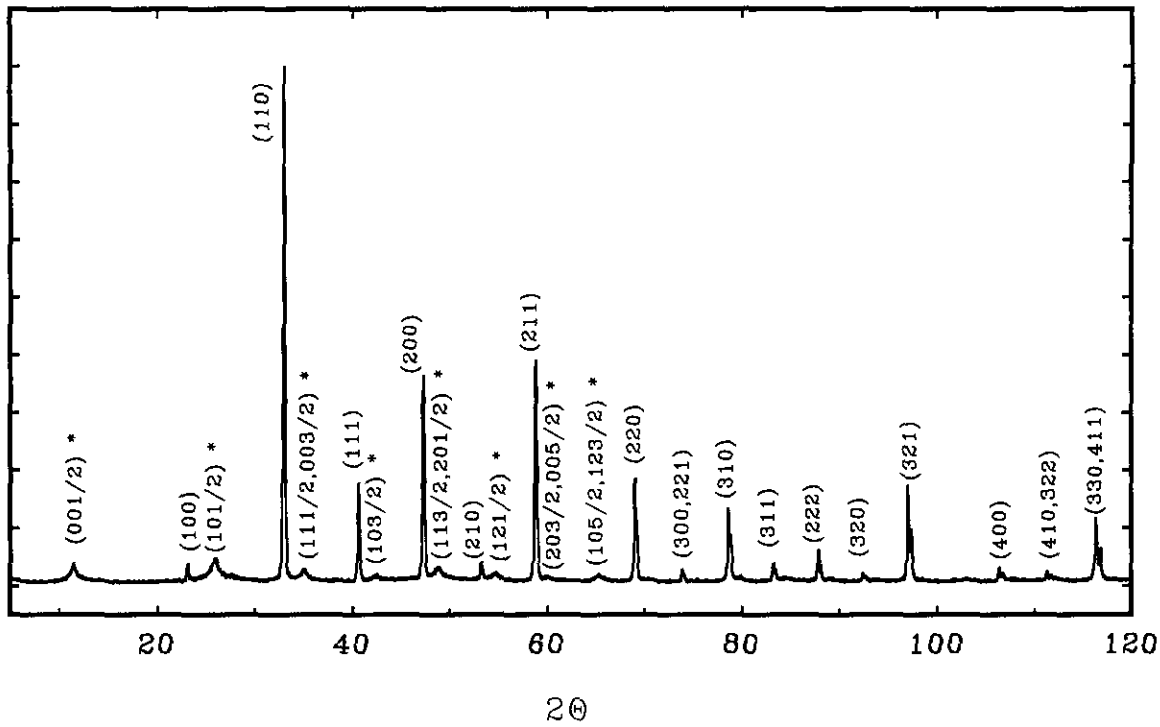

FIG. 1. X-ray diffraction pattern for $Na_{2/3}Th_{1/3}TiO_3$ (where a = 3.8477 Å). Peaks indicated by asterisks were due to a $2a_p$ cubic superstructure.

difficult to deduce the reliable ordering parameters of Na^+ and Th^{4+} from profile refinement. The severe broadening of superstructure reflections was considered to be related to a disordered microstructure. Small domains with the supercell $2a_p$ intergrown with a minority of the basic structure a_p can give the rather diffuse superstructure reflections, whereas the main reflections are still sharp. These characteristics bear much resemblance to those of its analogue $Li_{1/2}La_{1/2}TiO_3$ (6).

We are unable to prepare the Ce^{4+}-containing analogue $Na_{2/3}Ce_{1/3}TiO_3$. It has the small ion Ce^{4+} and the lower tolerance factor (r_{Ce} = 0.92 Å, t = 0.80), as compared with that for $Na_{2/3}Th_{1/3}TiO_3$ (r_{Th} = 1.02 Å, t = 0.82). The present phase is the first example of titanium perovskite oxides with a tetravalent cation at the A site.

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