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Crystal structure of the high-pressure modification of $NdTaO_4$

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Abstract

The crystal structure of the metastable $NdTaO_4$ high-pressure modification (HPM) has been studied by X-ray powder diffraction. It was found that the crystal structure of HPM $NdTaO_4$ belongs to the monoclinic $LaTaO_4$-type structure (space group $P2_1/c$, $a=7.5920(7)$ Å, $b=5.4673(5)$ Å, $c=7.7022(7)$ Å, $\beta=100.032(6)°$, $Z=4$). The difference in structure between $LnTaO_4$ with Ln=Nd–Lu (fergusonite-type structure) and that with Ln=La–Pr (monoclinic $LaTaO_4$-type structure) is most likely due to the difference in size of the rare-earth cations. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polymorphism; Crystal structure; X-ray powder diffraction

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1. Introduction

The tantalates $LnTaO_4$ (Ln=La–Pr), in which the ionic radius of Ln exceeds that of Nd, have two perovskite-like layered polymorphic modifications with monoclinic $LaTaO_4$-type structure [1–3] and $BaMnF_4$-type structure [3–6]. The other rare-earth orthotantalates (Ln=Nd–Lu) crystallise in M- and M^I-fergusonite structures [7]. The expected possibility of polymorphic transformation of $LnTaO_4$ (Ln=Nd–Lu) from the M-fergusonite type structure into a modification of the monoclinic $LaTaO_4$-type structure, reasoning from the principle of the highest atomic packing in the latter one, was realized in practice under high pressure conditions on an example of $NdTaO_4$ [8]. The purpose of the present work is the crystal structure determination of the metastable high-pressure modification (HPM) of $NdTaO_4$.

Table 1
Crystallographic data for HPM $NdTaO_4$ (monoclinic $LaTaO_4$-type structure)

Atom	Site	*x*	*y*	*z*	Occupancy
Nd	4*e*	0.3462(3)	0.7746(11)	0.1010(4)	1.00
Ta	4*e*	0.1677(3)	0.2665(11)	0.3081(3)	1.00
O(1)	4*e*	0.1525(44)	0.1093(62)	0.0644(39)	1.00
O(2)	4*e*	0.0743(41)	0.6305(48)	0.2177(30)	1.00
O(3)	4*e*	0.3971(41)	0.4334(48)	0.2880(39)	1.00
O(4)	4*e*	0.3558(40)	$-0.0063(62)$	0.3789(36)	1.00
Space group			$P2_1/c$ (no. 14)		
Lattice constants (Å)			$a=7.5920(7)$		
			$b=5.4673(5)$		
			$c=7.7022(7)$		
			$\beta=100.032°(6)$		
Density for $Z=4$ (g/cm^3)			$d_{cal}=8.211$		
			$d_{obs}=8.20$		
Independent reflections			289		
Total isotropic *B* factor (Å^2)			0.17(2)		
Reliability factors			$R_{IO}=0.0419$		
			$R_W=0.0550$		

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Table 2
Part of the X-ray powder diffraction data for HPM $NdTaO_4$ (Cu Kα radiation)

d_{cal} (Å)	$d_{obs.}$ (Å)	I_{cal}	I_{obs}	*hkl*	d_{cal} (Å)	d_{obs} (Å)	I_{cal}	I_{obs}	*hkl*
4.435	4.465	21	90	0 1 1	1.869	1.869	85	90	4 0 0
4.413	4.423	58		1 1 0	1.858		6		−1 2 3
3.997	–	0	–	−1 1 1	1.856	–	1	–	0 2 3
3.792	3.792	127	121	0 0 2	1.845	–	0	–	−3 2 1
3.738	3.741	193	186	2 0 0	1.842	1.841	10	18	3 2 0
3.655	–	2	–	1 1 1	1.839		5		−3 1 3
3.648	3.651	59	63	−1 0 2	1.831	–	2	–	2 1 3
3.167	3.169	61	63	1 02	1.827	1.827	250	283	2 2 2
3.116	3.118	853	847	0 1 2	1.824		18		−2 0 4
3.086	3.088	1000	993	2 1 0	1.823	–	3	–	3 1 2
3.035	3.036	331	343	−1 1 2	1.811	–	2	–	−1 1 4
3.013	3.012	19		−2 1 1	1.806	1.806	70	70	−4 0 2
2.929	2.932	135	130	−2 0 2	1.791	1.791	37	34	0 1 4
2.740	2.737	128	497	1 1 2	1.789		0		−4 1 1
2.734		361		0 2 0	1.772		19		0 3 1
2.725	–	3	–	2 1 1	1.771	–	2	–	1 3 0
2.582	2.582	178	207	−2 1 2	1.768	1.768	184	241	4 1 0
2.572		19		0 2 1	1.766		26		1 0 4
2.567		7		1 2 0	1.754	–	3	–	−2 2 3
2.492	–	4	–	3 0 0	1.750	–	0	–	1 2 3
2.477	2.481	6	8	−1 2 1	1.747	1.748	115	123	−3 2 2
2.457	2.457	171	173	2 0 2	1.740	–	5		−1 3 1
2.389	–	5	–	1 2 1	1.739	–	0	–	3 2 1
2.298	2.297	23	22	−1 1 3	1.730	–	6	–	−2 1 4
2.295		1		0 1 3	1.715	1.715	9	9	−4 1 2
2.274	2.272	4	116	−3 1 1	1.709	–	0	–	1 3 1
2.272		95		−3 0 2	1.681	1.681	138	148	1 1 4
2.268		9		3 1 0	1.663	1.663	3	7	4 1 1
2.241	2.244	15	10	2 1 2	1.654	1.655	15	10	−3 0 4
2.218	2.218	34	31	0 2 2	1.643	1.642	111	272	0 3 2
2.207	2.207	91	95	2 2 0	1.638	1.639	146		2 3 0
2.188	2.188	27	20	−1 2 2	1.630	1.630	45	77	−1 3 2
2.180		3		−2 2 1	1.627		25		−2 3 1
2.110	–	0	–	−2 1 3	1.589	1.588	6	8	−3 2 3
2.102	2.103	11	14	1 1 3	1.584		3		2 2 3
2.098		4		−3 1 2	1.583	1.583	1	148	2 0 4
2.084	–	0	–	3 1 1	1.583		140		−3 1 4
2.069	2.070	61	99	1 2 2	1.580		32		1 3 2
2.063	2.062	32		2 2 1	1.579	1.579	29	67	3 2 2
1.999	1.999	137	145	−2 2 2	1.577		4		2 3 1
1.934	1.933	26	24	3 0 2	1.576		0		−4 1 3
1.919	1.919	173	179	−1 0 4	1.571		20		4 0 2
1.896	1.896	15	14	0 0 4	1.571	1.571	131	151	−1 2 4

2. Experimental

HPM $NdTaO_4$ was obtained in a high pressure apparatus of the anvil type with recess in toroidal form (cell from lithographic stone with graphite heater) by exposing the M-fergusonite modification $NdTaO_4$ to high pressure (8×10^9 Pa) and temperature (1500°C) within 1 min. The samples were quenched at a cooling rate of 500°C/s under pressure, ground into a powder and then annealed in air (600°C, 3 h).

The crystal structure of HPM $NdTaO_4$ has been studied by X-ray powder diffraction. The diffraction diagram was detected in a discrete regime (step scan 0.03°, counting time per step 8 s) with filtered copper radiation. Process control of shooting, data collection, primary processing of the diffraction pattern and the structural calculations were carried out using a hardware–software complex [9].

3. Results

The indexing of the powder diffraction pattern of HPM $NdTaO_4$ led to monoclinic symmetry. The monoclinic unit cell parameters of HPM $NdTaO_4$ were found to be slightly different from those listed in Ref. [8]. Taking into account the systematic extinctions, the space group of HPM $NdTaO_4$ was determined as $P2_1/c$.

The initial position parameters of each atom in HPM

Table 3
Selected interatomic distances (not exceeding 3.0 Å) in the crystal structures of $LaTaO_4$, $CeTaO_4$ monoclinic modifications and HPM $NdTaO_4$

Polyhedron	Atom–Atom	*d*, Å		
		$LaTaO_4$ [1]	$CeTaO_4$ [2]	HPM $NdTaO_4$
TaO_6	Ta–O(1)	2.05(3)	2.032(5)	2.049(31)
	Ta–O(1)	2.00(3)	1.980(5)	2.110(32)
	Ta–O(2)	2.07(3)	2.041(4)	2.185(26)
	Ta–O(2)	1.94(3)	1.960(5)	1.960(30)
	Ta–O(3)	2.01(3)	2.013(4)	1.996(31)
	Ta–O(4)	1.91(3)	1.914(5)	2.071(32)
	$(Ta–O)_{av}$	2.00	1.990	2.062
	$(Ta–O)_{max}-(Ta–O)_{min}$	0.16	0.13	0.23
LnO_8	Ln–O(1)	2.49(3)	2.518(5)	2.334(34)
	Ln–O(2)	2.74(3)	2.688(6)	2.517(31)
	Ln–O(3)	2.43(3)	2.380(5)	2.347(28)
	Ln–O(3)[a]	2.40(3)	2.361(5)	2.168(29)
	Ln–O(3)	2.52(3)	2.545(6)	2.972(30)
	Ln–O(4)	2.47(3)	2.464(5)	2.443(29)
	Ln–O(4)[a]	2.84(3)	2.826(6)	2.717(32)
	Ln–O(4)	2.41(3)	2.375(5)	2.264(31)
	$(Ln–O)_{av}$	2.54	2.52	2.47
	$(Ln–O)_{max}-(Ln–O)_{min}$	0.44	0.465	0.80

[a] These are the interblock Ln–O distances.

$NdTaO_4$ were estimated from those in the monoclinic modification of $LaTaO_4$ (space group $P2_1/c$ [1]). A comparison of the observed and the calculated intensities shows a good agreement for this structure model. The results of the refinement procedure and diffraction data are reported in Tables 1–3, and are shown in Figs. 1 and 2.

The crystal structure of HPM $NdTaO_4$ is formed by two-dimensional perovskite-like blocks, each of them consisting of two goffered slabs of deformed TaO_6 octahedrons (Ta–O distances ranging from 1.960(30) to 2.185(26) Å). Each TaO_6 octahedron has four common vertices with adjacent octahedrons within the same block (Fig. 2). The difference in TaO_6 octahedron distortion between the HPM $NdTaO_4$ structure and monoclinic $LaTaO_4$ and $CeTaO_4$ consists mainly in the increasing (0.27 Å in comparison with $LaTaO_4$) length of the octahedron diagonal O(2)–Ta–O(4) and height (0.11 Å).

The direct connection between TaO_6 octahedrons with neighbouring perovskite-like blocks is absent. They are linked by means of interblock bonds –O–Nd–O–. The necessity of such bond formation is caused by Nd atom displacements from cubooctahedral type holes almost to the boundary of the perovskite-like block. Therefore their coordination number is reduced to 8. The Nd atom is

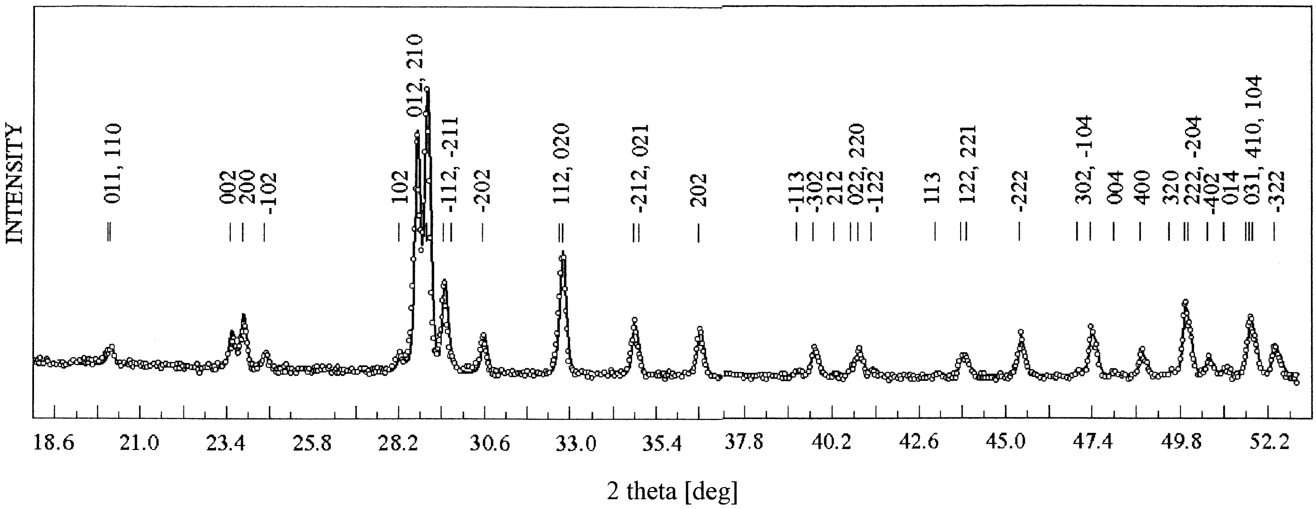

Fig. 1. Part of the X-ray diffraction powder pattern (points) and calculated pattern (solid line) for HPM $NdTaO_4$ (Cu Kα radiation).

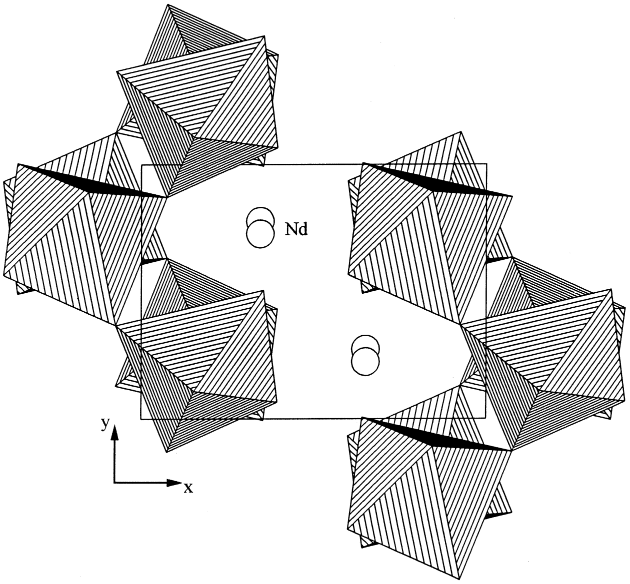

Fig. 2. Projection of the HPM $NdTaO_4$ structure on the XY plane.

surrounded by six oxygen atoms (one O(1), one O(2), two O(3) and two O(4)) in the same block and two oxygen atoms (O(3), O(4)) in the neighbouring block at distances ranging from 2.168(29) to 2.972(30) Å (Table 3). The next ninth oxygen atom is separated from Nd by 3.34 Å.

The coordination number of the oxygen atoms is 3 for O(1), O(2) and 4 for O(3), O(4). The first two are bonded to two Ta atoms and one Nd atom, whereas the other two are bonded to one Ta and three Nd atoms.

According to Refs. [1,2] the formal balance of valencies for the representatives of monoclinic $LaTaO_4$ structural type is almost ideal. The deviations of valency from the valency of oxygen is 2%. Such values indicate that only a small part of the distortion is needed to balance the electrostatic charge.

At the same time, the degree of distortion (the range of interatomic Me–O distances) of the TaO_6 and especially the LnO_8 polyhedrons in the structure of HPM $NdTaO_4$ appeared to be much greater than those in the compounds $LnTaO_4$. The latter are formed under conditions of ambient pressure and containing atoms larger than Nd in the A-position ($LaTaO_4$, $CeTaO_4$).

From the above, it follows that the change in structural type of $LnTaO_4$, which takes place while passing from $PrTaO_4$ (monoclinic $LaTaO_4$-type structure) to $NdTaO_4$ (M-fergusonite type structure) is caused mainly by the size of the Ln cations. Their mismatch with the sizes of the holes in the monoclinic $LaTaO_4$-type structure, that increase with R_{Ln} decreasing, leads to the necessity of the enormous distortion of the LnO_8 and TaO_6 polyhedrons. That is why the formation of $LnTaO_4$ with the monoclinic $LaTaO_4$-type structure, beginning from Ln=Nd, became possible only under conditions of high pressure.

4. Conclusion

The novel HPM $NdTaO_4$ was characterised by X-ray powder diffraction. It was found that the crystal structure of HPM $NdTaO_4$ belongs to the monoclinic $LaTaO_4$-type structure. The degree of distortion of LnO_8 and TaO_6 polyhedrons in the structure of HPM $NdTaO_4$ is higher than in the monoclinic $LaTaO_4$ and $CeTaO_4$.

References

[1] T.A. Kurova, V.B. Aleksandrov, Dokl. Akad. Nauk SSSR 201 (1971) 1095.

[2] A. Santoro, M. Marezio, R.S. Roth, D. Minor, J. Solid State Chem. 35 (1980) 167.

[3] R.S. Roth, T. Negas, H.S. Parker, D. Minor, C. Jones, Mater. Res. Bull. 12 (1977) 1173.

[4] R.J. Cava, R.S. Roth, J. Solid State Chem. 36 (1981) 139.

[5] Yu.A. Titov, A.M. Sych, A.A. Kapshuk, Neorganicheskie Materialy 34 (1998) 608.

[6] Yu.A. Titov, Dop. Nat. Akad. Nauk Ukrainy 11 (1999) 140.

[7] H.P. Rooksby, E.A.D. White, Acta Crystallogr. 16 (1963) 888.

[8] Yu.A. Titov, A.M. Sych, A.N. Sokolov, A.A. Kapshuk, V.P. Yashchuk, Neorganicheskie Materialy 33 (1997) 67.

[9] V. Markiv, N. Belyavina, in: Proceedings of the Second International Scientific Conference of Engineering and Functional Materials, EFM-97, Lviv, 14–16 October, 1997, p. 260.