single-crystal samples of the BCT form suggested a slight deficiency in the boron content from the stoichiometry, but the poor accuracy of the analysis (owing to the small quantity of the sample) did not permit measurement of the degree of the deficiency. However, the closeness of the cell volume (per chemical formula) of the two forms, 103·0 Å^3 for the BCT and 103·3 Å^3 for the PT, indicates that the deficiency, if any, is small. Further study will be necessary to elucidate the relation between the boron content and the relative stability.

X-ray diffraction measurements were carried out using the diffractometer at the Department of Applied Physics, Faculty of Engineering, Tohoku University. We express thanks to Professors T. Ikeda and N. Yamada for providing an opportunity to use the apparatus and Dr S. Kawano for his technical assistance in the diffraction experiments.

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Dineodymium Magnesium Titanate(IV). A Rietveld Refinement of Neutron Powder Diffraction Data

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(*Received* 22 *November* 1985; *accepted* 9 *July* 1986)

Abstract. Nd_2MgTiO_6, $M_r = 456·69$, monoclinic, $P2_1/n$, $a = 5·4661$ (2), $b = 5·5905$ (2), $c = 7·7768$ (3) Å, $\beta = 90·010$ (9)°, $V = 237·65$ (2) Å^3, $Z = 2$, $D_x = 6·382$ (2) Mg m^{-3}, $\mu R = 0·59$. The structure has been refined by Rietveld analysis of neutron powder diffraction data recorded at room temperature [$\lambda = 2·5790$ (3) Å, $R_I = 2·02$, $R_p = 6·30$, $R_{wp} = 6·93\%$]. The structure is of a monoclinic $GdFeO_3$-type perovskite with a high degree of order between Mg and Ti. The mean Nd—O, Mg—O and Ti—O distances are 2·552 (7), 2·068 (6) and 1·961 (6) Å, respectively. An analysis of octahedra tilting is given.

Introduction. In a research program covering the suitability of oxides as a host lattice for nuclear waste, we have investigated compounds with the general formula $Ln_2M_1M_2O_6$ (M_1 = Mg, Ni; M_2 = Ti, Ru; Ln = lanthanide ion). These compounds have a perovskite-type structure with a high degree of order for M_1 and M_2. Raman spectra (Macke, 1977) indicate that the order is not complete. The same conclusion can be drawn from luminescence experiments on Ti perovskites (Macke & Blasse, 1976). Nd_2MgTiO_6, with Nd as an average lanthanide ion, deserves special attention because Nd constitutes a substantial part of nuclear waste. Nd_2MgTiO_6 has been mentioned already by German & Kovba (1983), but they did not describe the structure. Calculations of the rotation of octahedra are given, based on the work of Megaw (1972), Glazer (1972), O'Keeffe & Hyde (1977) and Lelieveld & IJdo (1980).

Experimental. AR starting materials Nd_2O_3, MgO, TiO_2 thoroughly mixed in an agate mortar in the appropriate ratio; mixture heated to 1673 K for a total of 50 d in air, followed by repeated grindings at 295 K.

X-ray powder diffraction patterns obtained with a Philips PW 1050 diffractometer. No other phases observed in the diffraction pattern. Systematic absences $h0l$ $h + l = 2n + 1$ and $0k0$ $k = 2n + 1$ indicating the space group $P2_1/n$. Since no single crystals were available, Rietveld's (1969) method was used for refinement of neutron powder diffraction data on the powder diffractometer at the Petten High-Flux Reactor;

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$5 < 2\theta < 163°$ in steps of 0·1°; neutrons at 295 K from the (111) planes of a Cu crystal; pyrolytic graphite with a total thickness of 120 mm as a second-order filter; Soller slits, horizontal divergence 0·5°, placed between the reactor and the monochromator and in front of the four ^{3}He counters; sample holder ($\varnothing = 14·46$ mm) consisted of a V tube, closed with Cu plugs fitted with O rings. No precautions to avoid preferred orientation. Maximum absorption correction 5%, $\mu R = 0·59$ (Weber, 1967). Background determined by extrapolation between those parts in the diagram containing no contribution or, for high values of 2θ, only a small contribution, from reflections. Statistically expected value of R_{wp} 4·87%.

The structure of $CaTiO_3$ (modified for the lower symmetry) was used as a trial model (Kay & Bailey, 1957) with allowance for a translation $(-\frac{1}{4},\frac{1}{2},-\frac{1}{2})$ of the atomic parameters. Nd, O(1), O(2) and O(3) at (x,y,z), Mg at $(\frac{1}{2},0,0)$ and Ti at $(0,\frac{1}{2},0)$.

29 parameters in the refinement: a scale factor, three half-width parameters defining the Gaussian line shape of the reflections, the counter zero error, an asymmetry parameter, the unit-cell parameters, the atomic positional parameters, the isotropic thermal parameters and the occupation rate of Mg and Ti.

Coherent scattering lengths: Nd 7·69, Mg 5·38, Ti −3·44, O 5·81 fm (Koester, Rauch, Herkens & Schroeder, 1981). The Rietveld program minimizes the function $\chi^2 = \sum_i w_i[y_i(\text{obs.}) - (1/c)y_i(\text{calc.})]^2$, where $y_i(\text{obs.})$ and $y_i(\text{calc.})$ are the observed and the calculated data points, w_i is the statistical weight $[1/y_i(\text{obs.})]$ allotted to each data point and c is the scale factor. The R factors $R_I = 100\sum|I_i(\text{obs.}) - (1/c)I_i(\text{calc.})|/\sum I_i(\text{obs})$, $R_p = 100\sum|y_i(\text{obs.}) - (1/c)y_i(\text{calc.})|/\sum y_i(\text{obs.})$ and $R_{wp} = 100[\sum w_i|y_i(\text{obs.}) - (1/c)y_i(\text{calc.})|^2/\sum w_i|I_i(\text{obs.})|^2]^{1/2}$ were calculated, where $I_i(\text{obs.})$ and $I_i(\text{calc.})$ are the observed and calculated integrated intensities of each reflection. $\Delta/\sigma = 0·3$ in final cycle. Largest correlation matrix element for structural parameters 0·83.

Discussion. Atomic parameters are given in Table 1 and selected atomic distances in Table 2. The agreement between the observed and calculated profile is shown in Fig. 1.* Figs. 2 and 3 show the structure of Nd_2MgTiO_6.

The structure can be described as a perovskite with almost regular MgO_6 and TiO_6 octahedra. These octahedra are rotated around a twofold axis parallel to [110] and a fourfold axis parallel to [001] of the aristotype. As a consequence of these rotations the coordination number of Nd has changed from 12 to 8. The geometry can be described as that of a bicapped prism or of a distorted Archimedes antiprism. The mean Nd—O, Mg—O and Ti—O distances are 2·552 (7), 2·068 (6) and 1·961 (6) Å, respectively, in rough agreement with the distances from the ionic radii: 2·48, 2·09, 1·98 Å (Shannon, 1976). The order between Mg and Ti is not complete (there is 4% disorder in their positions). This may be caused by twinning (White & Segall, 1985).

Table 1. *Fractional atomic coordinates, thermal parameters* (Å^2) *and occupation number* (%) *of* Nd_2MgTiO_6 *at* 295 K

	x	y	z	B	n
Nd	0·5103 (7)	0·5472 (4)	0·2503 (6)	0·24 (6)	100
Mg(1)	0·5	0	0	0·8 (2)	96·0 (6)
Mg(2)*	0	0·5	0	0·5 (3)	4·0 (6)
Ti(1)	0	0·5	0	0·5 (3)	96·0 (6)
Ti(2)*	0·5	0	0	0·8 (2)	4·0 (6)
O(1)	0·196 (1)	0·210 (1)	−0·0494 (9)	0·9 (2)	100
O(2)	0·2852 (9)	0·698 (1)	−0·042 (1)	0·6 (2)	100
O(3)	0·4130 (6)	0·9746 (4)	0·2559 (9)	0·52 (9)	100

* 4% of the Mg and Ti ions are disordered, and are indicated as Mg(2) and Ti(2).

Table 2. *Atomic distances* (Å) *at* 295 K (*mean values and values of the atomic distances using the Shannon radii.are included*)

MgO_6 octahedra					
Mg—O(1)	2·071 (6)	2×	Mean	2·068 (6)	
Mg—O(2)	2·083 (6)	2×	Shannon	2·09	
Mg—O(3)	2·051 (7)	2×			
TiO_6 octahedra					
Ti—O(1)	1·981 (6)	2×	Mean	1·961 (6)	
Ti—O(2)	1·939 (5)	2×	Shannon	1·98	
Ti—O(3)	1·962 (7)	2×			
NdO_8 bicapped prism					
Nd—O(1)	2·619 (7)	1×	Nd—O(3)	2·448 (3)	1×
	2·351 (7)	1×		2·350 (5)	1×
	2·742 (8)	1×	Mean	2·552 (7)	
Nd—O(2)	2·718 (8)	1×	Shannon	2·48	
	2·627 (8)	1×			
	2·397 (8)	1×			

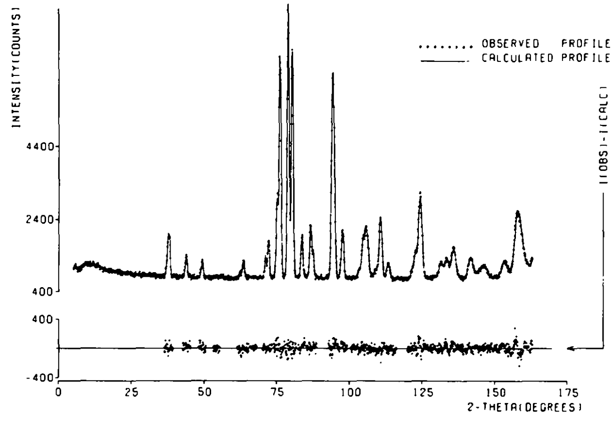

Fig. 1. The observed and calculated profiles of Nd_2MgTiO_6.

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* A list of numerical values corresponding to the data in Fig. 1 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43107 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure can be derived from the well known perovskite $NdFeO_3$ (Marezio, Remeika & Dernier, 1970), which has a $CaTiO_3$-type structure. Because the Nd ion is smaller than an O ion all FeO_6 octahedra are tilted to reduce the void for the Nd ion. In Nd_2MgTiO_6 the Fe is replaced by Mg and Ti in an ordered way so that each MgO_6 octahedron shares corners with six TiO_6 octahedra and *vice versa* as can be seen in Fig. 2. This lowers the space group from $P2_1/b2_1/n2_1/m$ for $NdFeO_3$ to $P2_1/n$ for Nd_2MgTiO_6. The order is not complete, as was also found by Macke (1977) and Macke & Blasse (1976) for La_2MgTiO_6. Megaw (1972), Glazer (1972), O'Keeffe & Hyde (1977) and Lelieveld & IJdo (1980) analysed the tilt of the octahedra for perovskites ABO_3 in terms of regular octahedra; w denotes a rotation about (001) of the aristotype (a fourfold axis) and j denotes a rotation about (110) of the aristotype (a twofold axis), interactions between the two being neglected.

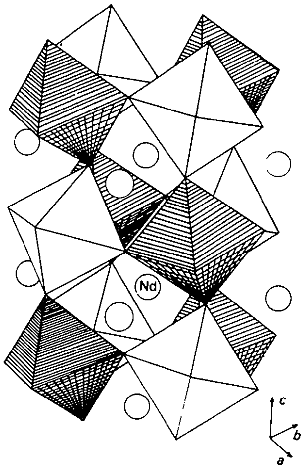

Fig. 2 An impression of the structure of Nd_2MgTiO_6.

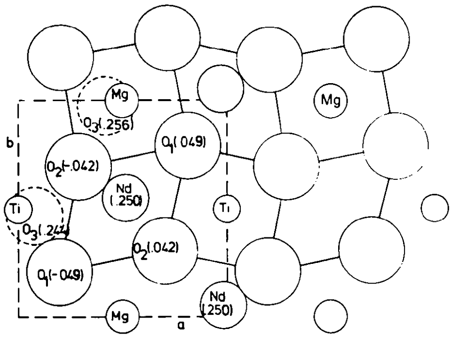

Fig. 3. The structure of Nd_2MgTiO_6 projected along the c axis. Fractional heights are indicated.

Table 3. *Tilt angles* (°) *for the* Mg *and* Ti *octahedra in* Nd_2MgTiO_6 [$w(B)$, $j(B)$ *and* $J(B)$ *are defined in the text*]

Calculated from the lattice parameters and the Shannon radii [Mg–O = 2·09, Ti–O = 1·98 Å]			
$w(\mathrm{Mg})_l$	13·4	$j(\mathrm{Ti})_l$	12·5
$w(\mathrm{Ti})_l$	14·2	$J(\mathrm{Mg})_l$	16·7
$j(\mathrm{Mg})_l$	11·8	$J(\mathrm{Ti})_l$	17·7
Calculated from the lattice parameters and the mean observed radii [Mg–O = 2·068 (6), Ti–O = 1·961 (6) Å]			
$w(\mathrm{Mg})_l$	10·8	$j(\mathrm{Ti})_l$	12·4
$w(\mathrm{Ti})_l$	11·4	$J(\mathrm{Mg})_l$	14·8
$j(\mathrm{Mg})_l$	11·8	$J(\mathrm{Ti})_l$	15·6
Calculated from the atomic position parameters			
$w(\mathrm{Mg})_c$	10·0	$j(\mathrm{Mg})_c$	14·0
$w(\mathrm{Ti})_c$	10·6	$j(\mathrm{Ti})_c$	14·7

For perovskites of general formula $A_2BB'O_6$, w and j must be replaced by $w(B)$, $w(B')$, $j(B)$ and $j(B')$ because the octahedra are not the same size. The parameters w and j for BO_6 $B'O_6$ can be derived in two ways: (1) from the lattice parameters (a,b,c) and the B—O and the B'—O distances calculated from the Shannon radii (assuming regular octahedra), and (2) from the atomic positions without any assumptions at all.

For calculations from the lattice parameters the rotation around the fourfold axis (parallel to [001]) is given by:

$$w(B)_l = \arccos\{[b^2 + 2(B\text{—O})^2 - 2(B'\text{—O})^2]/2b\sqrt{2}(B\text{—O})\}$$

$$w(B')_l = \arccos\{[b^2 + 2(B'\text{—O})^2 - 2(B\text{—O})^2]/2b\sqrt{2}(B'\text{—O})\}.$$

The rotation around the fourfold axis is obtained from the value of the b axis, which is only affected by this rotation.

The rotation around the twofold axis (parallel to [010]) can be obtained in two different ways. The first method uses a contraction of the a axis compared with the b axis. The expressions are:

$$\begin{aligned} j(B)_l = {} & \arccos[(-2a\cos w(B) + \{4a^2\cos^2 w(B) \\ & - 4[\cos^2 w(B') - \cos^2 w(B)]X\}^{1/2}) \\ & \times \{2\sqrt{2}(B - \mathrm{O})[\cos^2 w(B') - \cos^2 w(B)]\}^{-1}] \\ X = {} & [2(B'\text{—O})^2\cos^2 w(B') - 2(B\text{—O})^2\cos^2 w(B') - a^2] \end{aligned}$$

$$j(B')_l = \arccos\left\{1 - \frac{2(B\text{—O})^2}{2(B'\text{—O})^2}[1 - \cos^2 j(B)]\right\}^{1/2}.$$

The calculations are based on geometrical considerations. The formulae are obtained from a second-order relation, which implies that these formulae cannot be used for structures with only one type of octahedron. The formula for structures with one type of octahedron is:

$$j(B)_l = \arccos[a/2\sqrt{2}(B\text{—O})\cos w(B)].$$

The second method takes account of the value of the c axis with the assumption $\beta = 90°$. The formulae are as follows:

$$J(B)_l = \arccos\{[-4(B'\text{—O})^2 + 4(B\text{—O})^2 + c^2]/4(B\text{—O})c\}$$

$$J(B')_l = \arccos\{[-4(B\text{—O})^2 + 4(B'\text{—O})^2 + c^2]/4(B'\text{—O})c\}.$$

The latter method is probably the best because only the *c* axis is affected by the rotation around the twofold axis. This implies that a difference between the values obtained from the two methods (*j* and *J*) is a degree of the nonideality of the octahedra, or a measure of the relevance of the method used.

For the calculation of the tilt angles from the atomic positional parameters we have:

$$w(B)_c = \tfrac{1}{2}\text{arctg}\left[\frac{x(\text{O}2)-x(\text{O}1)}{y(\text{O}2)-y(\text{O}1)}\cdot\frac{a}{b}\right] + \tfrac{1}{2}\text{arctg}\left[\frac{1-y(\text{O}1)-y(\text{O}2)}{x(\text{O}1)+x(\text{O}2)}\cdot\frac{b}{a}\right]$$

$$w(B')_c = \tfrac{1}{2}\text{arctg}\left[\frac{x(\text{O}2)-x(\text{O}1)}{1+y(\text{O}1)-y(\text{O}2)}\cdot\frac{a}{b}\right] + \tfrac{1}{2}\text{arctg}\left[\frac{1-y(\text{O}2)-y(\text{O}1)}{1-x(\text{O}2)-x(\text{O}1)}\cdot\frac{b}{a}\right]$$

$$j(B)_c = \text{arctg}\,[(\{[\tfrac{1}{2}-x(\text{O}3)]a\}^2 + \{[1-y(\text{O}3)]b\}^2)^{1/2}/[z(\text{O}3)]c]$$

$$j(B')_c = \text{arctg}[(\{[\tfrac{1}{2}-x(\text{O}3)]a\}^2 + \{[1-y(\text{O}3)]b\}^2)^{1/2}/[\tfrac{1}{2}-z(\text{O}3)]c].$$

In Table 3 the calculated rotation angles for the MgO_6 and TiO_6 octahedra are given. These were calculated from the Shannon radii and from the mean observed radii; angles calculated from the atomic positional parameters are also included. From this table it can be seen that the rotation angles $J(B)_l$ and $j(B)_l$, calculated from the mean observed radii, are closer to the real rotation angles $j(B)_c$ than those calculated from the Shannon radii. The same conclusion can be drawn for the rotation angles $J(B')_l$, $j(B')_l$, $w(B)_l$ and $w(B')_l$. This is in agreement with the result that the mean observed radii are about 2% smaller than the Shannon radii.

This research project was partly financed by the Commission of the European Communities. The authors are indebted to Mr J. F. Strang and Dr R. B. Helmholdt of the Energie-onderzoek Centrum Nederland, Petten, for collection of the neutron diffraction data.

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Acta Cryst. (1986). C**42**, 1475–1477

Structure du Séléniate(IV) de Cérium

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(*Reçu le* 9 *mai* 1986, *accepté le* 24 *juin* 1986)

Abstract. CeSe_2O_6, $M_r = 349{\cdot}03$, synthesized by solid-state reaction, monoclinic, $P2_1/n$, $a = 7{\cdot}008\,(1)$, $b = 10{\cdot}587\,(2)$, $c = 7{\cdot}262\,(1)$ Å, $\beta = 107{\cdot}00\,(1)°$, $V = 515{\cdot}27\,(2)$ Å^3, $Z = 4$, $D_x = 5{\cdot}08$ Mg m^{-3}, $\lambda(\text{Mo}\ K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 24{\cdot}1$ mm^{-1}, $F(000) = 696$, room temperature, final $R = 0{\cdot}032$ for 1242 significant

0108-2701/86/111475-03$01.50