

The Crystal Structure of the New REE–Te Oxychlorides: NdTe₂O₅Cl and GdTe₂O₅Cl

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The title compounds were synthesized and their crystal structures were determined by powder X-ray diffraction methods. Both phases are tetragonal and crystallize in space group *P4/mmm*, NdTe₂O₅Cl with cell constants $a = 4.0373(1)$, $c = 8.7912(3)$ Å, and GdTe₂O₅Cl $a = 3.9611(2)$, $c = 8.4043(8)$, $Z = 1$. These oxychlorides adopt layered structures belonging to the family of Sillen phases and are built of alternating [LnTe₂O₅⁺] and [Cl⁻] layers (*X*₁³ structure). Related structures and the nature of cation ordering in the metal–oxygen layers are discussed. © 1999 Academic Press

while the corresponding compounds LnTe₂O₅Cl described in (5) are centrosymmetric. An absence of a center of symmetry in a crystal structure is a prerequisite for the existence of pyro-, piezo-, and ferroelectric properties in materials. Thus the relationship between composition, structure, and physical properties of the LnTe₂O₅Hal compounds is of great interest.

The crystal structure of NdTe₂O₅Br is described in (4). In this paper the crystal structures of two representatives of the oxychloride group LnTe₂O₅Cl, NdTe₂O₅Cl, and GdTe₂O₅Cl are described.

INTRODUCTION

In our previous work (1–4), the synthesis and crystal structures of several new Bi–Te and REE–Te (REE = rare earth elements) oxybromides and oxyiodides were described. Some of them possess interesting nonlinear optical or pyroelectric properties which makes them promising new materials.

Most of these phases belong to a layered family known as Sillen phases, i.e., intergrowths of fluorite-like metal–oxygen layers [M₂O₂] or [M₃O_{4+y}] and single, double, or triple halogen sheets. However, little is known about the structure of the corresponding Bi–Te or REE–Te oxychlorides. The latter oxychlorides were found recently in LnOCl–TeO₂ systems with Ln = La, Nd, Sm, Gd, Er, Yb, Lu (5). They can be divided into three groups, according to their stoichiometry: Ln₂TeO₄Cl₂ (Ln = La, Nd, Sm, Gd, Er), LnTeO₃Cl (Ln = La, Nd, Sm, Gd, Er, Lu), and LnTe₂O₅Cl (Ln = La, Nd, Sm, Gd, Er, Lu). For most of them, cell parameters were found using their X-ray diffraction patterns.

It is interesting to note that the compounds LnTe₂O₅Br and LnTe₂O₅Cl are different from each other. According to second harmonic generation of laser light on powder samples all compounds LnTe₂O₅Br are noncentrosymmetric,

EXPERIMENTAL

LnTe₂O₅Cl were synthesized by heating stoichiometric mixtures of LnOCl and TeO₂ in evacuated quartz ampoules at 500°C for 720 h. LnOCl were prepared by heating LnCl₃·6H₂O (content of other REEs ≤ 0.01%) in a wet air stream at 550°C (6). TeO₂ was prepared by the usual technique (Te (99.9999%) was dissolved in *aqua regia* at 80°C and TeO₂ subsequently precipitated by addition of aqueous ammonia (7)).

Both compounds were obtained as fine, microcrystalline powders. No single crystals could be found in the bulk samples. The substances were identified by X-ray diffraction (Enraf–Nonius, FR-552, CuKα₁, Ge used as internal standard). Powder diagrams were indexed on the basis of a tetragonal unit cells with lattice parameters $a = 4.0373(1)$, $c = 8.7912(3)$ Å for NdTe₂O₅Cl, and $a = 3.9611(2)$, $c = 8.4043(8)$ Å GdTe₂O₅Cl.

The powders thus obtained were tested for second harmonic generation (SHG) of laser light ($\lambda = 1.064$ μm). No signals were observed.

X-ray intensity data for LnTe₂O₅Cl suitable for structure determination were collected with a Stoe STADI/P diffractometer, using a rotating sample mounted in symmetric transmission mode. Monochromatic CuKα₁ radiation was used. The step width was 0.02° 2θ. Data for NdTe₂O₅Cl were collected over the range of 3° < 2θ < 100°. Data for

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TABLE 1
Crystallographic Data for $LnTe_2O_5Cl$ ($Ln = Nd, Gd$)

	NdTe ₂ O ₅ Cl	GdTe ₂ O ₅ Cl
Crystal system	Tetragonal	Tetragonal
Space group	$P4/mmm$ (No. 123)	$P4/mmm$ (No. 123)
Cell constants		
a (Å)	4.0373(1)	3.9611(2)
b (Å)	8.7912(3)	8.4043(8)
Z	1	1
Calculated density (g/cm ³)	5.966	6.648
Color	creamy white	white
Diffractometer	Stoe STADI/P	Stoe STADI/P
Radiation	CuK α_1	CuK α_1
2θ range	3–100°	5–120°
$R_p\%$	4.40	4.66
w $R_p\%$	5.78	6.42

NdTe₂O₅Cl were collected over the range of $5^\circ < 2\theta < 120^\circ$. Both runs were approximately 15 h. Details of the X-ray diffraction experiments are given in Table 1.

STRUCTURE DETERMINATION

The structure model for NdTe₂O₅Cl (coordinates of the heavy atoms) was obtained in the space group $P4/m$ using direct methods by means of the program MULTAN from the CSD software package for PC (8). The choice of the space group was based on systematic absences. Also, a centrosymmetric space group was preferred due to the absence of a SHG signal. Coordinates of oxygen atoms were found in subsequent difference Fourier analyses. The model obtained permitted further refinement in more symmetrical space groups, of which $P4/mmm$ (No. 123) was finally chosen. The final structure refinement was carried out using a full-profile Rietveld method in the RIETAN (9) program. The experimental profile has several peaks of some impurity with $2\theta = 15.85, 26.74, 28.17, \text{ and } 39.42^\circ$, with the strongest intensity being less than 5% of that of the strongest NdTe₂O₅Cl peak. These reflections do not correspond to any known phase in the Nd–Te–O–Cl phase diagram. The reliability factors were $R_{wp} = 10.93$, $R_p = 7.32$, and $R_1 = 8.40\%$. After the removal from the Rietveld refinement of a range without reflections, from 3 to $8^\circ 2\theta$ and also exclusion of the impurity reflections mentioned above the reliability factors became $R_{wp} = 5.78$, $R_p = 4.40$, and $R_1 = 3.41\%$. The final positional and isotropic thermal parameters are presented in Table 2. Interatomic distances are given in Table 3. The final Rietveld refinement plot is given in Fig. 1.

The crystal structure of GdTe₂O₅Cl was determined using the model of NdTe₂O₅Cl. The GSAS program (10) was used for structure refinement, using a pseudo-Voigt peak

TABLE 2
Positional and Thermal Parameters for NdTe₂O₅Cl and GdTe₂O₅Cl

Atom	Site	x/a	y/b	z/c	U_{iso}
NdTe ₂ O ₅ Cl					
Nd	1a	0	0	0	0.033(3)
Te	2h	1/2	1/2	0.2753(4)	0.050(1)
Cl	1b	0	0	1/2	0.025(2)
O1	4i	1/2	0	0.182(1)	0.095(2)*
O2	1c	1/2	1/2	0	0.095(2)
GdTe ₂ O ₅ Cl					
Gd	1a	0	0	0	0.021(2)
Te	2h	1/2	1/2	0.2898(7)	0.030(1)
Cl	1b	0	0	1/2	0.038(2)
O1	4i	1/2	0	0.161(4)	0.147(2)
O2	1c	1/2	1/2	0	0.147(2)

Note. In both cases thermal parameters for oxygen atoms were refined as block parameters.

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DISCUSSION

As shown from our experiments (Tables 1–3) both compounds are isostructural. The structure of NdTe₂O₅Cl is depicted in Fig. 2. It can be seen that the compound belongs to the Sillen family as well as the corresponding oxybromides and oxyiodides.

$LnTe_2O_5Cl$ are built of $[LnTe_2O_5^+]$ triple fluorite-like layers separated by $[Cl^-]$ layers perpendicular to the c -axis (Fig. 2). From the Rietveld refinements, it appears that the cations (Ln and Te) in the metal–oxygen sheet are arranged

TABLE 3
Selected Interatomic Distances for $LnTe_2O_5Cl$ (Å)

Bond		Distance
NdTe ₂ O ₅ Cl		
Nd–O1	$\leftrightarrow 8$	2.576(11)
Te–Cl	$\leftrightarrow 4$	3.471(4)
Te–O1	$\leftrightarrow 4$	2.179(7)
Te–O2	$\leftrightarrow 1$	2.421(4)
GdTe ₂ O ₅ Cl		
Gd–O1	$\leftrightarrow 8$	2.398(21)
Te–Cl	$\leftrightarrow 4$	3.311(3)
Te–O1	$\leftrightarrow 4$	2.26(2)
Te–O2	$\leftrightarrow 1$	2.436(6)

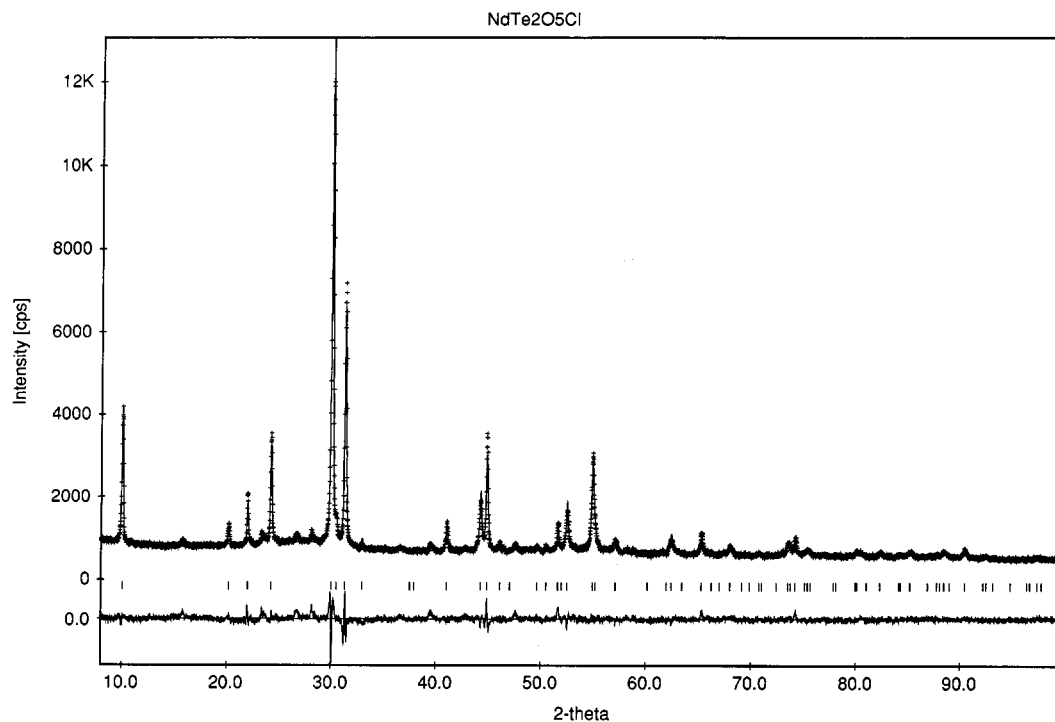


FIG. 1. Final Rietveld refinement plot for $\text{NdTe}_2\text{O}_5\text{Cl}$.

in stringent order. Tellurium atoms form the “outer” metal sublayer while Ln^{3+} constitute the “inner” sublayer. The coordination polyhedron of the Nd atom can be regarded as a four-capped cube (12 oxygen atoms = 8 + 4. Distances are 2.576 and 2.86 Å, respectively). The Gd atom in $\text{GdTe}_2\text{O}_5\text{Cl}$ has the same surrounding of oxygen atoms (2.398 and 2.800 Å), with the shortening of $\text{Ln}-\text{O}$ bonds in accordance with the reduction in ionic radii. The coordination polyhedron of Te atom consists of four oxygen O1 atoms (which form a square) and one O2 atom at a longer distance (below the square). Such “open” polyhedra are rather typical for cations having stereochemically active lone electron pairs. The distances $\text{Te}-\text{Cl}$ given in Table 3 show that the chlorine atoms form separate layers—they are not really connected to Te atoms in fluorite-like layers. Although the symmetries of the coordination environments around the two metal sites are entirely consistent with their occupation by a perfectly ordered Ln/Te distribution, the bond lengths around the Te site, in particular the relatively long $\text{Te}-\text{O}$ bonds, appear somewhat anomalous. This may be indicative of a slight degree of disorder of Ln/Te over the two sites. However, attempts to model this disorder in the Rietveld refinements did not give significantly modified site occupancies, nor did they produce significantly better fits. It seems likely that the coordination environment for Te in this family of phases is

inherently unusual, producing “long” $\text{Te}-\text{O}$ bonds—such behavior has also been noted in the case of $\text{Bi}_{0.97}\text{TeO}_3\text{Br}_{0.9}$, for example (3).

The compounds $\text{LnTe}_2\text{O}_5\text{Cl}$ belong to the $\text{Bi}_3\text{O}_4\text{Br}$ (X_1^3) structure type (11, 13). Its structure is built of “triple” (three metal sublayers) fluorite-like layers separated by single anion sheets. Other representatives of the structure type are $\text{Bi}_3\text{O}_4\text{Br}$, $\text{NdBi}_5\text{O}_8\text{Cl}_2$, $\text{Bi}_4\text{Te}_2\text{O}_9\text{Br}_2$, $\text{NdTe}_2\text{O}_5\text{Br}$, and $\text{LaBi}_2\text{O}_4\text{Cl}$ (1–4, 11–13). The optional occupancy of the O(2) site in the central metal layer gives rise to the possible flexibility in overall stoichiometry.

It is interesting to mention that $\text{NdTe}_2\text{O}_5\text{Br}$ and $\text{LnTe}_2\text{O}_5\text{Cl}$ ($\text{Ln} = \text{Nd}, \text{Gd}$) have related but slightly different structures. Contrary to the oxychloride, the corresponding bromide crystallizes in a noncentrosymmetric group, $F222$, and shows a superstructure ($a = 8.0148$, $b = 7.9766$, $c = 17.3334$ Å, $Z = 8$) (4). In the case of $\text{NdTe}_2\text{O}_5\text{Br}$, oxygen atoms are displaced from their ideal positions which they occupy in $\text{NdTe}_2\text{O}_5\text{Cl}$.

Upon comparison of all the known structures of Bi-Te and REE-Te oxyhalides, one can note a characteristic “behavior” of the Te atoms. On the one hand, these atoms are situated only in triple metal-oxygen layers $[\text{M}_3\text{O}_{4+y}]^+$, and, on the other hand, Te atoms form only the outer sublayers. The latter peculiarity occurs due to stereochemical activity of the lone pair of Te(IV) ions.

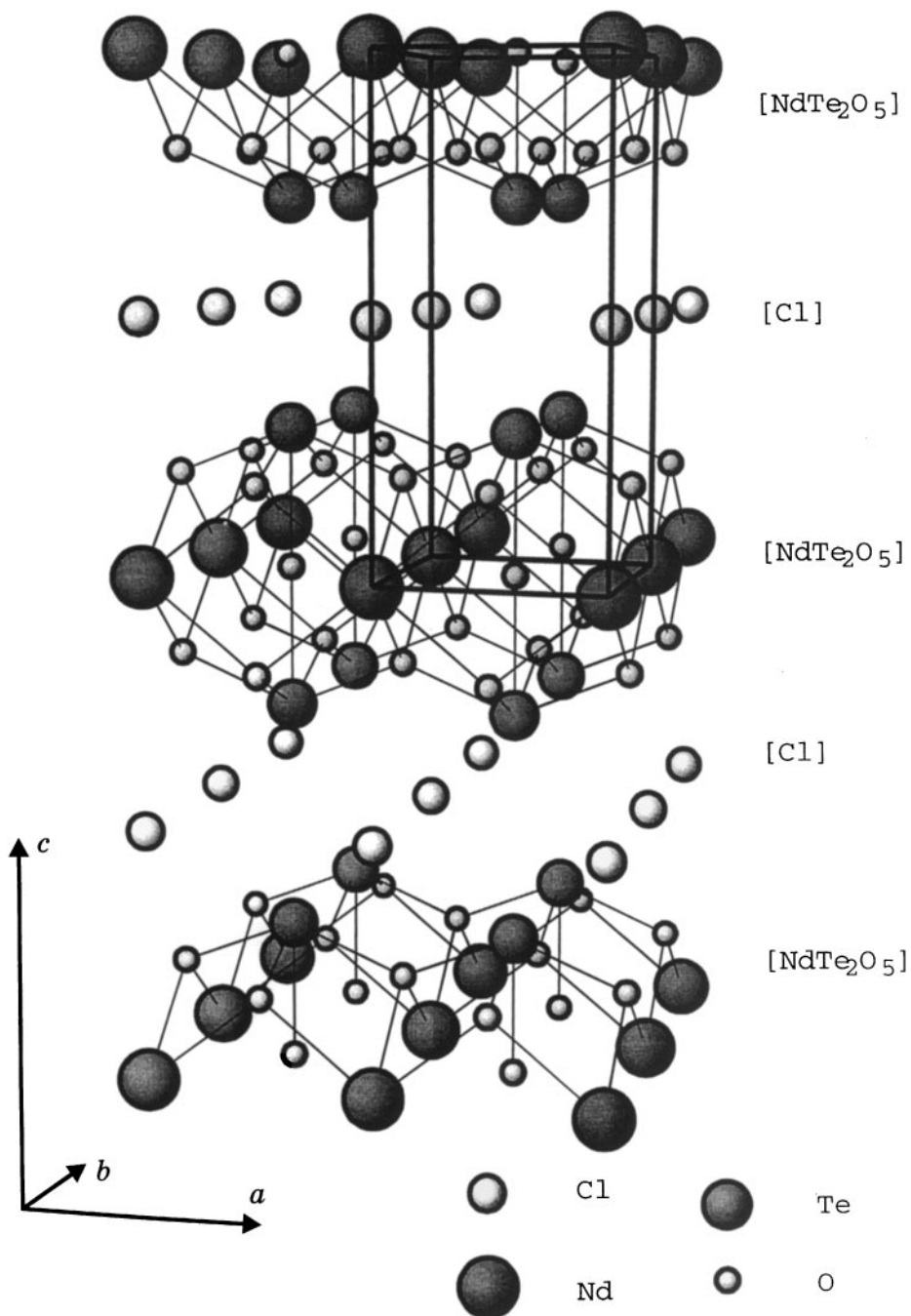


FIG. 2. A view of the crystal structure of NdTe₂O₅Cl (one unit cell is indicated). It can be seen that the structure consists of [NdTe₂O₅⁺] and [Cl⁻] layers.

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