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New Series $\mathrm{CrLn_8Te_{13}Cl}$ (Ln = Sm, Gd, Tb): Pseudo-Misfit-Layer Compounds

Olivier Tougait and James A. Ibers*

Department of Chemistry, Northwestern University, 2145
Sheridan Road, Evanston, Illinois 60208-3113

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Introduction

Materials containing a 3d metal and a 4f element are of a great interest. Among these, oxides have been of particular interest because of their spectroscopic properties, and intermetallic compounds have been heavily studied because of their magnetic properties.[1,2] However, studies of other 3d/4f materials have revealed extraordinary structural and bonding features.[3−5]

Among the solid-state 3d/4f chalcogenides, the number of ternary compounds decreases dramatically as we move from the sulfides to the tellurides. Ternary 4f sulfides are known for all 3d metals. A few selenides are reported, usually as the sulfide analogues,[6] and tellurides are only known for $\mathrm{LnCu_xTe_2}$, $0.28 \le x \le 0.5$, (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho).[7−9] The ternary 3d/4f tellurides are virtually unexplored. In the course of our studies, we synthesized and report here an unexpected new series of compounds, $\mathrm{CrLn_8Te_{13}Cl}$ (Ln =Sm, Gd, Tb). Their crystal structures bear some resemblances to the framework of certain misfit layer compounds.[10]

Experimental Section

Syntheses. Sm (Alfa, 40 mesh 99.9%), Gd (Alfa, 40 mesh 99.9%), Tb (Alfa, 40 mesh 99.9%), Cr (Alfa, 325 mesh, 99.99%), Te (Aldrich, 200 mesh, 99.8%), and $\mathrm{CrCl_3}$ (Alfa 99.9%) were stored as received in an Ar-filled glovebox. Single crystals of $\mathrm{CrLn_8Te_{13}Cl}$ (Ln = Sm, Gd, Tb) were obtained from the reaction of 1.25 mmol Ln, 0.25 mmol Cr, 2.125 mmol Te, and 0.25 mmol $\mathrm{CrCl_3}$. The materials were loaded into fused-silica tubes that were then flame-sealed under a vacuum of 10^{-4} Torr, heated to 850 °C over a 48 h period, maintained at 850 °C for 96 h, cooled to 600 °C at 2.5 °C/h, at which temperature the furnace was turned off. The final products appear as black lustrous needles mixed with an unidentified light-gray powder. Neither needles nor powder is hydrolytically stable. These needles, about 0.30 mm × 0.015 mm × 0.010 mm in size, are suitable for further characterization. Semiquantitative energy dispersive X-ray analyses were carried out on several single crystals from each preparation with the use of a 3500N Hitachi scanning electron microscope. The atomic ratios of Cr (3(2)), Ln (40(3)), Te (53(3)), and Cl (3(2)) may be compared with the calculated values for a composition $\mathrm{CrLn_8Te_{13}Cl}$ of Cr (4.3), Ln (34.8), Te (56.5), and Cl (4.3) (Ln = Sm, Gd, Tb).

Table 1. X-ray Crystallographic Details

formula	$\mathrm{CrSm_8Te_{13}Cl}$	$\mathrm{CrGd_8Te_{13}Cl}$	$\mathrm{CrTb_8Te_{13}Cl}$
fw	2949.05	3004.25	3017.61
space group	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$
a (Å)	4.2281(7)	4.1923(5)	4.1700(3)
b (Å)	26.575(4)	26.464(3)	26.3485(17)
c (Å)	23.829(4)	23.730(3)	23.6092(15)
V (Å^3)	2677.4(8)	2632.8(5)	2594.0(3)
temp (°C)	−120	−120	−120
Z	4	4	4
ρ_{calc} (g cm^{-3})	7.32	7.58	7.73
λ (Å)	0.710 73	0.710 73	0.710 73
μ (cm^{-1})	316.0	344.5	363.2
$R(F)^a$	0.0260	0.0237	0.0261
$R_w(F_o^2)^b$	0.0599	0.0588	0.0641

^{a} $R(F) = \sum||F_o| - |F_c|/\sum|F_o|$. ^{b} $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$ for $F_o^2 > 0$ and $w = 1/\sigma^2(F_o^2)$ for $F_o^2 \le 0$.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker Smart 1000 CCD diffractometer at −120 °C with the use of monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The diffracted intensities generated by a scan of 0.3° in ω were recorded on four sets of 606 frames covering more than a hemisphere of the Ewald sphere, with an exposure time of 20 s/frame. For each compound, cell refinement and data reduction were carried out with the use of the program SAINT[11] and a face-indexed absorption correction was made with the use of the program XPREP.[12] Then the program SADABS[11] was employed to make incident beam and decay corrections. The crystal structures were solved in the noncentrosymmetric space group $Cmc2_1$. The positions of Ln and Te were located with the direct methods program SHELXS of the SHELXTL-PC suite of programs,[12] and the positions of the Cr and Cl atoms were located from successive difference electron density syntheses. The structures were refined by full-matrix least-squares techniques with the program SHELXL of the SHELXTL-PC suite of programs.[12] Final refinements included anisotropic displacement parameters and a secondary extinction correction. $\mathrm{CrGd_8Te_{13}Cl}$ and $\mathrm{CrTb_8Te_{13}Cl}$ appear to be racemically twinned, whereas $\mathrm{CrSm_8Te_{13}Cl}$ is not. Examination of the resultant structures with the program MISSYM[13] did not reveal additional symmetry. Some crystallographic details are presented in Table 1. Others may be found in Supporting Information. Selected bond distances for $\mathrm{CrLn_8Te_{13}Cl}$ (Ln = Sm, Gd, Tb) are given in Table 2.

Results

Metal halides are good reaction media for crystal growth, but on occasion incorporation of anions or cations from the flux or transporting agent occurs.[14−16] Incorporation occurred in the present instance when single crystals of $\mathrm{CrTb_8Te_{13}Cl}$ resulted from a preparation that involved $\mathrm{CrCl_3}$ as a flux. The synthesis is reproducible; moreover, single crystals of $\mathrm{CrLn_8Te_{13}Cl}$ (Ln = Sm, Gd) have been obtained in a similar manner.

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[1] Helszan, J. *YIG Resonators and Filters*; John Wiley & Sons: New York, 1985.

[2] Herbst, J. F. *Rev. Mod. Phys.* **1991**, *63*, 819−898.

[3] Ruck, M.; Simon, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 327−336.

[4] Ebihara, M.; Martin, J. D.; Corbett, J. D. *Inorg. Chem.* **1994**, *33*, 2079−2084.

[5] Cody, J. A.; Ibers, J. A. *J. Solid State Chem.* **1995**, *114*, 406−412.

[6] Flahaut, J. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L. R., Eds.; North-Holland: New York, 1979; Vol. 4, pp 1−88.

[7] Pardo, M.-P.; Dung, N. H. *C. R. Acad. Sci., Paris* **1987**, *12*, 637−639.

[8] Dung, N.-H.; Pardo, M.-P.; Boy, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 668−670.

[9] Huang, F. Q.; Brazis, P.; Kannewurf, C. R.; Ibers, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 80−86.

[10] Rouxel, J.; Meerschaut, A.; Wiegers, G. A. *J. Alloys Compd.* **1995**, *229*, 144−157.

[11] SMART Version 5.054 Data Collection and SAINT-Plus Version 6.02A Data Processing Software for the SMART System; Bruker Analytical X-Ray Instruments, Inc., Madison, WI, 2000.

[12] Sheldrick, G. M. *SHELXTL*, DOS/Windows/NT version 5.10; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 1997.

[13] Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264−269.

[14] Meerschaut, A.; Gressier, P.; Guemas, L.; Rouxel, J. *J. Solid State Chem.* **1984**, *51*, 307−314.

[15] Brennan, T. D.; Mansuetto, M. F.; Ibers, J. A. *J. Solid State Chem.* **1993**, *107*, 547−553.

[16] Tranchitella, L. J.; Fettinger, J. C.; Eichhorn, B. W. *J. Solid State Chem.* **1999**, *147*, 592−600.

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Table 2. Selected Interatomic Distances (Å)

		Ln = Sm	Ln = Gd	Ln = Tb			Ln = Sm	Ln = Gd	Ln = Tb
Ln(1)	Cl(1)	3.122(4)	3.128(3)	3.108(3)	Ln(2)	Te(11) × 2	3.1359(9)	3.1194(7)	3.1029(8)
Ln(1)	Te(12) × 2	3.1512(9)	3.1369(7)	3.1225(8)	Ln(2)	Te(8) × 2	3.2091(9)	3.1891(7)	3.1708(8)
Ln(1)	Te(10) × 2	3.203(1)	3.1828(8)	3.1657(8)	Ln(2)	Te(10) × 2	3.2284(9)	3.2083(7)	3.1898(8)
Ln(1)	Te(9) × 2	3.205(1)	3.1831(7)	3.1690(8)	Ln(2)	Te(1)	3.333(1)	3.3112(9)	3.284(1)
Ln(1)	Te(2)	3.312(1)	3.294(1)	3.280(1)	Ln(2)	Te(4)	3.511(1)	3.5010(10)	3.499(1)
Ln(3)	Cl(1)	2.956(3)	2.950(3)	2.923(3)	Ln(4)	Te(7) × 2	3.1608(9)	3.1452(7)	3.1280(8)
Ln(3)	Te(11) × 2	3.1413(9)	3.1274(7)	3.1123(8)	Ln(4)	Te(9) × 2	3.189(1)	3.1731(7)	3.1550(8)
Ln(3)	Te(4)	3.1861(9)	3.159(1)	3.137(1)	Ln(4)	Te(8) × 2	3.219(1)	3.2000(8)	3.1861(9)
Ln(3)	Te(13) × 2	3.1861(9)	3.1704(8)	3.1600(8)	Ln(4)	Te(3)	3.360(1)	3.3422(10)	3.319(1)
Ln(3)	Te(12) × 2	3.216(1)	3.2027(7)	3.1884(8)	Ln(4)	Te(6)	3.414(1)	3.3961(10)	3.376(1)
Ln(5)	Te(13) × 2	3.1287(9)	3.1168(7)	3.1029(8)	Ln(6)	Cl(1) × 2	2.854(2)	2.8285(18)	2.824(2)
Ln(5)	Te(5) × 2	3.193(1)	3.1734(8)	3.1596(8)	Ln(6)	Te(3) × 2	3.216(1)	3.1947(7)	3.1804(8)
Ln(5)	Te(3) × 2	3.2159(9)	3.1923(7)	3.1744(8)	Ln(6)	Te(1) × 2	3.229(1)	3.2099(8)	3.1916(8)
Ln(5)	Te(7)	3.335(1)	3.311(1)	3.290(1)	Ln(6)	Te(11)	3.284(1)	3.2601(10)	3.244(1)
Ln(5)	Te(4)	3.463(1)	3.455(1)	3.443(1)	Ln(6)	Te(9)	3.293(1)	3.2717(10)	3.257(1)
Ln(7)	Te(2) × 2	3.1493(9)	3.1343(7)	3.1171(8)	Ln(8)	Te(6)	3.106(1)	3.0776(10)	3.055(1)
Ln(7)	Te(5) × 2	3.2031(9)	3.1806(7)	3.1649(8)	Ln(8)	Te(12)	3.119(1)	3.1028(10)	3.084(1)
Ln(7)	Te(1) × 2	3.2171(9)	3.1970(8)	3.1799(8)	Ln(8)	Te(7) × 2	3.1244(9)	3.1094(7)	3.0952(8)
Ln(7)	Te(10)	3.317(1)	3.295(1)	3.271(1)	Ln(8)	Te(2) × 2	3.1470(9)	3.1270(7)	3.1131(8)
Ln(7)	Te(6)	3.557(1)	3.550(1)	3.548(1)	Ln(8)	Te(13)	3.171(1)	3.1517(10)	3.128(1)
Cr(1)	Te(8)	2.699(3)	2.692(2)	2.684(2)	Cr(1)	Te(6) × 2	2.764(2)	2.751(2)	2.740(2)
Cr(1)	Te(5)	2.714(3)	2.705(2)	2.701(2)	Cr(1)	Te(4) × 2	2.764(2)	2.752(2)	2.743(2)

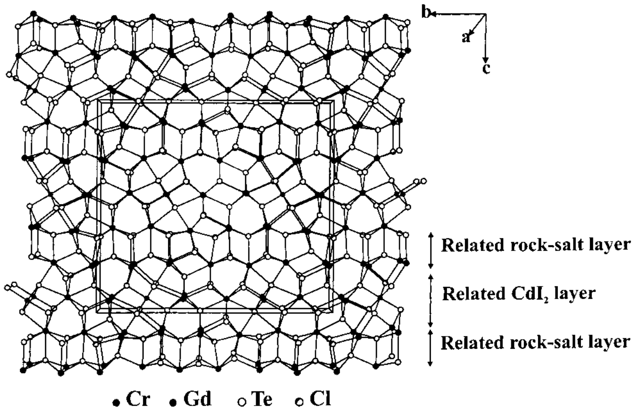

Figure 1. Projection of the unit cell of $CrGd_8Te_{13}Cl$ onto the *bc* plane.

Crystal Structure Description. The new compounds $CrLn_8Te_{13}Cl$ (Ln = Sm, Gd, Tb) are isostructural and crystallize in a new structure type. A projection on the *bc* plane of the three-dimensional structure of $CrGd_8Te_{13}Cl$ is displayed in Figure 1. The eight independent Ln atoms per asymmetric unit are found in two different coordination polyhedra. The first one is derived from an octahedron with one apex split into two positions. It is adopted by atoms Ln(1), Ln(3), and Ln(8). The centered Ln^{3+} cations are coordinated approximately quadratically by four Te atoms, forming the pseudoequatorial plane, and triangularly in a perpendicular plane by three other atoms. Atoms Ln(1) and Ln(3) adopt a mixed environment of one Cl and six Te atoms, the Cl atom being located in a terminal position of the axial plane. Atom Ln(8) is surrounded by seven Te atoms. The second polyhedron is a bicapped trigonal prism. The trigonal prisms centered by atoms Ln(2), Ln(4), Ln(5), and Ln(7) consist of six Te atoms, whereas the trigonal prism centered by atom Ln(6) consists of four Te and two Cl atoms. Two of the rectangular faces are capped by additional Te atoms at longer distances. The Cr atom is surrounded by six Te atoms in a slightly distorted octahedral arrangement with four long Cr−Te equatorial bonds and two short Cr−Te axial bonds.

The main building units of the structure are motifs derived from trigonal prisms and octahedra. The heights of these moieties correspond to the length of the *a* axis, and thus, interconnection in the [100] direction occurs by the face sharing of trigonal prisms and Te−Te edge sharing of octahedra. Therefore, the crystal structure can be described by the orientation and the linkage of the basic units in the *bc* plane. The polyhedra join by face sharing, and the resulting arrangement can be viewed as an alternation along the *c* axis of a distorted double rock-salt type of layer with a related CdI_2-type layer. The rock-salt layer of composition $[Ln_6Te_5Cl]$ results from the close packing of the individual motifs centered by atoms Ln(1), Ln(2), Ln(3), Ln(4), Ln(6), and Ln(7), whereas the CdI_2-type layer of composition $[Ln_2CrTe_6]$ is formed by the close packing of $[Cr(1)Te_6]$, $[Ln(5)Te_7]$, and $[Ln(8)Te_8]$ polyhedra. The “tetrahedral” sites defined at the junction of the rock-salt and CdI_2 layers are filled by two extra Te atoms, which complete the coordination around the two Ln^{3+} cations of the CdI_2 layer. Such a description of the crystal structure of $CrLn_8Te_{13}Cl$ (Ln = Sm, Gd, Tb) emphasizes the structural resemblance to that of the misfit layer class of compounds. Among such compounds, the monolayer derivatives of stoichiometry $[MQ][TQ_2]$ (M = Ln, Sn, Pb, Bi; T = 3d metal; Q = S, Se) consist of an [MQ] layer with a rock-salt-related structure that alternates with one CdI_2-related $[TQ_2]$ layer. Structural cohesion results from indirect interactions between the two layers. The stacking periodicity does not coincide perfectly, giving rise to a modulated composite structure.[17]

Despite the very different chemical formulas of the present compounds and that of a single slab misfit layer chalcogenide, the structural framework comprises an identical intergowth of two sublattices. For $CrLn_8Te_{13}Cl$ (Ln = Sm, Gd, Tb) the packing mode within the rock-salt layer is not really affected by the substitution of one Te by a Cl atom. The main differences occur in the joining of the two types of layers and in the CdI_2 slab. Indeed, the junction results from the formation of Ln−Te bonds between the two types of layered lattices. These bonds, which consolidate the packing between the two types of layers, range in length from approximately 3.30 to 3.55 Å, significantly longer than a typical Ln−Te bond distance of 3.25 (Tb) to 3.29 Å (Sm).[18] In the CdI_2-type structure, the layer results from a

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(17) Kato, K. *Acta Crystallogr., Sect. B: Struct. Sci.* **1990**, *46*, 39−44.

(18) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751−767.

hexagonal close-packed sheet of metal atoms sandwiched between two hexagonal close-packed sheets of anions; the metal is octahedrally coordinated. In the present structures the deviation from an ideal CdI_2 layer comes from the substitution of two Cr atoms by two Ln atoms. Consequently, the hexagonal packing of Te atoms is distorted to accommodate the Ln atoms because these require a prismatic site and a larger coordination number.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $CrSm_8Te_{13}Cl$, $CrGd_8Te_{13}Cl$, and $CrTb_8Te_{13}Cl$. This material is available free of charge via the Internet at http://pubs.acs.org.

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