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High-Pressure Synthesis of LaMS$_3$ (M = Ti, V, Cr)

S. Kikkawa,[1] Y. Fujii, Y. Miyamoto, and F. Kanamaru

The Institute of Scientific and Industrial Research, Osaka University, Osaka 567-0047, Japan

and

A. Meerschaut, A. Lafond, and J. Rouxel

Laboratoire de Chimie de Solides, Institut des Matériaux de Nantes, Nantes Cedex 03, France

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New compounds LaMS$_3$ with NH$_4$CdCl$_3$-type crystal structure could be prepared by high-pressure synthesis where M = Ti, V, Cr. The high-pressure compounds were obtained above 2.5 GPa at 1375 K for M = Cr, above 3.5 GPa at 1375 K for M = Ti, and above 5 GPa at 1475 K for M = V, respectively. The crystal structure of LaCrS$_3$ was refined as NH$_4$CdCl$_3$-type structure. It has an orthorhombic crystal lattice (*Pnma*) with $a = 0.787(1)$, $b = 0.3851(7)$, and $c = 1.334(2)$ nm. The polycrystalline product of LaCrS$_3$ was semiconducting and antiferromagnetic with $T_N = 195$ K and $\mu_{eff} = 3.83\mu_B$. © 1998 Academic Press

INTRODUCTION

Compounds containing more than two kinds of cation are interesting with respect to their crystal structures and properties. Misfit layered sulfides formulated as $(Ln\mathrm{S})_{1+x}M\mathrm{S}_2$ can be obtained by combination of rare earth metals (Ln) and 3d transition metals (M), where M = Ti, V, Cr (1). They have composite crystal lattice of both rocksalt-type LnS and CdI$_2$-type MS$_2$ stacking each other along their c axis. Their sublattice sizes are commensurate along the a axis but are incommensurate along the b axis in $(Ln\mathrm{S})_{1+x}M\mathrm{S}_2$, although the lengths are almost the same between $3b(Ln\mathrm{S})$ and $5b(M\mathrm{S}_2)$. There remains a slight difference in their length. The degree of incommensurability is related to the $1 + x$ value in the composition $(Ln\mathrm{S})_{1+x}M\mathrm{S}_2$. Either a cation or anion vacancy can be made in the LnS sublattice to reduce the interlayer stress induced by the size difference between sublattices (2, 3). M is always octahedrally coordinated in the CdI$_2$-type MS$_2$ layer, but Ln is surrounded by five neighboring sulfur atoms in the rocksalt-type LnS layer together with two or three sulfur atoms in the neighboring MS$_2$ layer depending on the relative position of these two sublattices.

The misfit layer structure is much more complicated in comparison both with LnMS$_3$ of hexagonal CsNiCl$_3$ type (M = Mn, Fe, Co, Ni) (4) and with LnCrSe$_3$ of orthorhombic NH$_4$CdCl$_3$ type (5). The crystal structure of CsNiCl$_3$ consists of the closest packing of Cs$^+$ and Cl$^-$ ions with Ni^{2+} in octahedral coordination. The coordination number around Cs is 12 in CsNiCl$_3$-type LnMS$_3$. The LaCrSe$_3$ structure of NH$_4$CdCl$_3$ type consists of distorted CrSe$_6$ octahedra forming their double chain with the edges sharing. Rare earth metals are surrounded by nine selenium atoms in the three double chains. Coordination numbers are always 6 around transition metal in these LaMX_3 (X = S, Se) but are variable around the rare-earth metal depending on the structure types including the above-mentioned misfit compounds. There has been no report on high-pressure synthesis of LnMS$_3$ where M = Ti, V, Cr. Effective ionic radii have been reported as 0.110 nm for La^{3+}(VII), 0.116 nm for La^{3+}(VIII), 0.122 nm for La^{3+}(IX), 0.136 nm for La^{3+}(XII), and 0.184 nm for S^{2-}(VI) (6). Coordination number around La may change by compressing the largest sulfur in ionic size in comparison to La atoms under high pressure.

In the present investigation high-pressure synthesis was used to study a structural change of the incommensurate $(\mathrm{LaS})_{1+x}M\mathrm{S}_2$ under high pressure. Crystal structure and electrical and magnetic properties were also investigated on the new LaCrS$_3$ compound obtained by high-pressure synthesis.

EXPERIMENTAL

Starting materials were La$_2$S$_3$ powder (Furuuchi Chemical Co. Ltd., 3N), crystalline S powder (Mitsuwa Chemical Co. Ltd., 5N) and Ti(2N) or V(2N) or Cr(3N) powder

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[1] To whom correspondence should be addressed.

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supplied by Nacalai Tesque Co. Ltd. They were mixed in the molar ratio 1 : 1 : 3 for La : M : S where M = Ti, V, Cr. Each mixture was respectively reacted at 1273 K for 100 h in a sealed silica tube prior to high-pressure and high-temperature reactions to accelerate the following reaction homogeneously. The high-pressure reaction was performed using cubic-type high-pressure equipment in a pressure range 2–5 GPa, changing reaction temperature in the range 1073–1473 K for 1–5 h. The sample was charged in an h-BN vessel installed in the high-pressure reaction cell assembly which has been described previously (7). The product was subjected to the same high-pressure and -temperature conditions again after it was well ground to increase its homogeneity.

Powder X-ray diffraction patterns were obtained using the Rigaku RAD-RB system with monochromatized Cu$K\alpha$ generated at 40 kV and 100 mA. The chemical composition of the product was analyzed using a Horiba X-ray microanalyzer EMAX 2770 installed on a Hitachi SEM S-2150. Rietveld structure refinement was performed on the X-ray diffraction data for the sample diluted with about nine times in weight of well-ground soda glass powder because of the small amount of single-batch product. The diffraction data were obtained in the 2θ range 20°–60° with a step scan mode of 0.02° interval and refined using the program RIETAN-94 (8, 9). Electrical resistivity was measured with the four-probe method in the temperature range 5.5–275 K using a Ag electrode. Magnetic susceptibility was measured using a vibrating sample magnetometer supplied by Riken Denshi Company Ltd. in the temperature range 80–475 K.

RESULTS AND DISCUSSION

The new Cr compound appeared in the product obtained by reacting a simple mixture of La_2S_3, Cr, and S under 3 GPa at 1373 K for 5 h, with slight contamination by Cr_2S_3 and La_4S_7 (JCPDS 16-689). The contamination could almost be removed using the reaction product in the silica tube as the starting material and subjecting the product to a second reaction under high pressure. Its powder X-ray diffraction pattern is quite different from that of the incommensurate $(LaS)_{1.2}CrS_2$ as shown in Fig. 1. It can be indexed with an orthorhombic lattice with $a = 0.787$, $b = 0.3851$, and $c = 1.334$ nm. The crystal structure was explicitly assumed to be isostructural to NH_4CdCl_3 (*Pnma*). The product was a mixture of incommensurate $(LaS)_{1+x}MS_2$ and MS_y for M = Ti below 3 GPa at 1373 K and also for M = V even under the high pressure of 4.5 GPa at 1473 K. The high-pressure Ti compound appeared in the product obtained under 3.5 GPa at 1373 K from the pretreated starting powder in the silica tube as a mixture with a small amount of TiS_2. It has lattice parameters of $a = 0.7945$, $b = 0.3813$, and $c = 1.324$ nm. A similar crystal structure could also be observed above 5 GPa at 1473 K in the V case as a component in a mixture with V_5S_8 and La_4S_7. The high-pressure $LaVS_3$ had an orthorhombic crystal lattice of $a = 0.785$, $b = 0.385$, and $c = 1.324$ nm. Reaction products in the vanadium case were mostly mixtures of V_5S_8 and $(LaS)_{1+x}VS_2$ in the region where no high-pressure compound was observed. The formation conditions can be summarized as shown in Fig. 2. The difference in reaction conditions needed to obtain the high-pressure compounds may be related to whether the transition metals (M) tend to form MS_y under the reaction conditions in the present investigation.

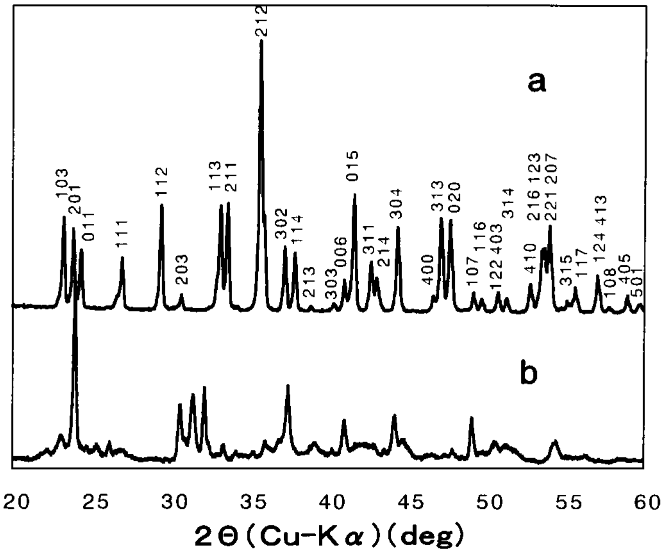

FIG. 1. Powder X-ray diffraction patterns of (a) high-pressure synthesized $LaCrS_3$ and (b) incommensurate $(LaS)_{1.2}CrS_2$.

The crystal structure was refined using the program RIETAN-94 for the Cr compound. The observed pattern fits very well with the calculated data assuming NH_4CdCl_3-type crystal structure as depicted in Fig. 3. Its refinement was performed as a two-phase mixture with a small amount of rhombohedral Cr_2S_3. The amount of Cr_2S_3 impurity was estimated to be 0.3% in weight from the refinement. The final parameters are summarized in Table 1. The CrS_3 structural unit is formed by double chains composed of edge-sharing CrS_6 octahedra as represented in Fig. 4. Lanthanum ion interleaved among the three double chains is surrounded by nine sulfur atoms in trigonal prismatic tricaped coordination. The coordination number is larger than the value of 7 or 8 in the misfit layered $(LaS)_{1+x}CrS_2$. Table 2 summarizes bond distances and angles in the high-pressure compound $LaCrS_3$. The distances between Cr–Cr along the b axis and Cr–Cr between single chains are 0.3851(7) and 0.3416(6) nm, respectively. The latter value is relatively short but it is longer than the interatomic distance in metallic chromium of 0.2498 nm. The bond distances for Cr–S(1), Cr–S(2), and Cr–S(3) are comparable to the

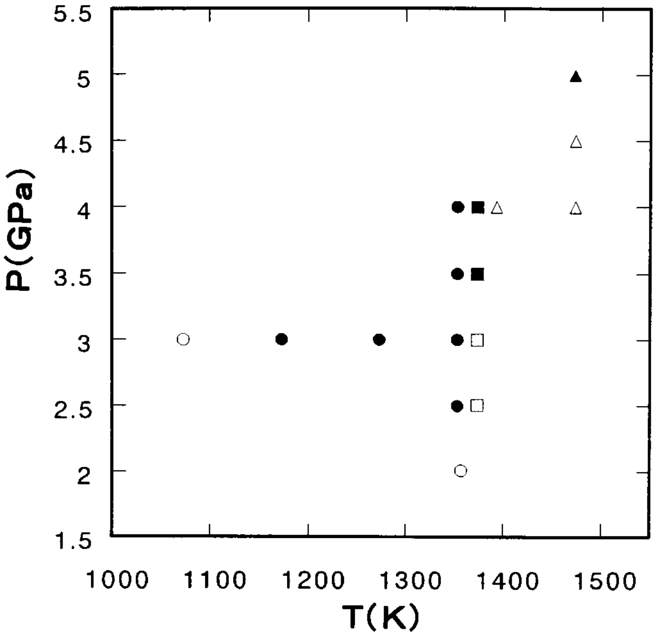

FIG. 2. Diagram of formation of high-pressure LaMS$_3$ compounds. Circles, squares, and triangles correspond to chromium, titanium, and vanadium. Filled and open symbols represent NH_4CdCl_3-type and incommensurate compounds observed in the high-pressure products, respectively.

generally reported Cr–S distance of 0.24 nm. La is isotropically coordinated with 9S in a range of bond distances between 0.30 and 0.32 nm.

$LaCrS_3$ was a semiconductor below 300 K as shown in Fig. 5, with $\rho_{275} = 15\,\Omega$-cm. $LaTiS_3$ showed similar semiconducting behavior. The magnetic property represented in Fig. 6 was observed for $LaCrS_3$. Its Neel and Weiss temperatures were $T_N = 195$ K and $\theta_a = -8.5$ K, respectively. Observed and calculated μ_{eff} values were $3.83\mu_B$ and $3.87\mu_B$ assuming La^{3+} and Cr^{3+}, respectively. Cr^{3+} ions directly couple each other antiferromagnetically, with a weaker ferromagnetic Cr^{3+}–S–Cr^{3+} superexchange. $LaCrSe_3$ had been reported to be antiferromagnetic with $T_N \approx 160$ K with a weak ferromagnetism below $T_C < 110$ K (10). The T_C value decreased to 77 K from sample to sample as a result of undetectable changes in stoichiometry or purity. The reported θ_a value was $+99$ K. The compound was an extrinsic semiconductor. Antiferromagnetic super-super-exchange interactions through the Cr–Se–Se–Cr path with secondary ferromagnetic interactions due to polarization of the ligands in cases of Cr–Se–Cr path with an angle of about $\pi/2$ have been proposed on the basis of its neutron diffraction patterns (11).

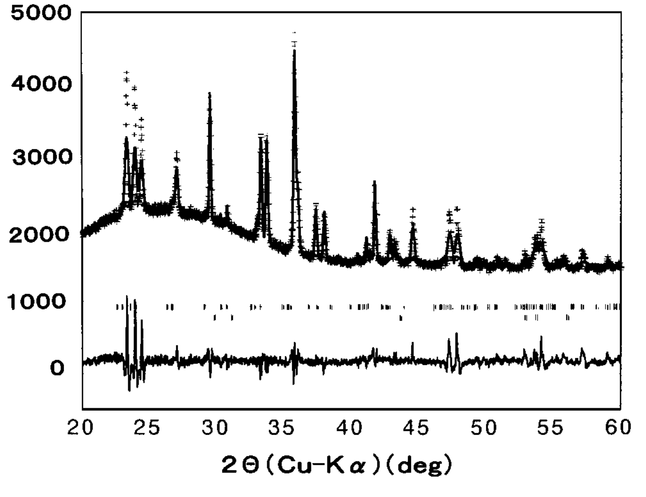

FIG. 3. Observed (crosses), calculated (solid line), and difference profiles for the high-pressure product $LaCrS_3$. Allowed reflection marks are for $LaCrS_3$ (top) and Cr_2S_3 (bottom).

TABLE 1
Final Parameters of $LaCrS_3$ Refined with RIETAN-94

System	orthorhombic		
Space group	*Pnma*		
Z	4	Wavelength (nm)	0.1540
a(nm)	0.787(1)	2θ range (deg)	20–60
b(nm)	0.3851(7)	R_F	0.040
c(nm)	1.334(2)	R_{wp}	0.079
V(nm^3)	0.405		

Positional parameters of $LaCrS_3$

	Wyckoff Position	x	y	z	B
La	4*c*	0.089(2)	1/4	0.171(1)	1.17(8)
Cr	4*c*	0.344(6)	1/4	0.947(2)	1.68(1)
S(1)	4*c*	0.191(6)	1/4	0.793(4)	1.43(5)
S(2)	4*c*	0.327(8)	1/4	0.510(5)	1.73(9)
S(3)	4*c*	0.486(7)	1/4	0.104(4)	1.92(7)

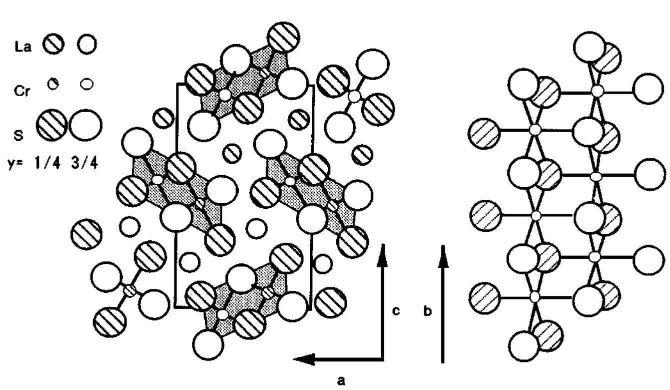

FIG. 4. Crystal structure of $LaCrS_3$ with NH_4CdCl_3 type projected along the b axis (left) and CrS_3 double chain (right).

TABLE 2
Bond Distances (nm) and Angles (degrees) in Polyhedra around Cr and La in $LaCrS_3$

Cr–S(1)	0.239(6)	Cr–Cr[a]	0.3851(7)
Cr–S(2) × 2	0.247(6)	Cr–Cr[b]	0.3416(6)
Cr–S(3)	0.236(6)	∠Cr–S(3)–Cr[a]	104(2)
Cr–S(3) × 2	0.245(5)	∠Cr–S(3)–Cr[b]	90.4(1)
La–S(1) × 2	0.300(4)	La–S(2)	0.324(8)
La–S(1) × 2	0.303(3)	La–S(3)	0.309(5)
La–S(2) × 2	0.298(7)	La–S(3)	0.324(8)

[a] Along *b* axis.
[b] Between single chains.

Transition metals beyond Mn in the 3*d* series form $LaMS_3$ with $CsNiCl_3$-type crystal structure. The structure consists of the closest packing of La^{3+} and S^{2-} ions with M^{3+} in their octahedral sites. La^{3+} ions are surrounded by 12 sulfur ions. The electron cloud around S^{2-} may slightly shrink to form the closest packing with La^{3+} ions due to a polarizing effect of M^{3+}. Polarizing power decreases with an increase in ionic radius among ions with the same valence. It becomes weaker in the series from Ni^{3+} to Ti^{3+}. The crystal structures of $(LaS)_{1+x}MS_2$ are the incommensurate layered type in the cases of Ti, V, and Cr, where the coordination numbers around the lanthanum ions are 7 or 8 depending on the position of La^{3+} in the incommensurate lattice. Nine coordination of sulfur could be attained around La^{3+} in the present high-pressure products $LaMS_3$ (M = Ti, V, Cr). It is worth noting that in the Sn–Ti–S system $Sn_{2-x}Ti_xS_3$ ($0 < x < 0.8$), which can be formulated as $Sn_{1.2}Ti_{0.8}S_3$ when the upper limit is reached (12), is also of the NH_4CdCl_3 type, whereas $(SnS)_{1.2}TiS_2$ (13) belongs to the group of misfit compounds. That $LaCrSe_3$ is of the NH_4CdCl_3 type, a structure that is obtained for $LaCrSe_3$ when treated under pressure, sheds some light on the tendency for a given compound to adopt NH_4CdCl_3 or misfit structure types.

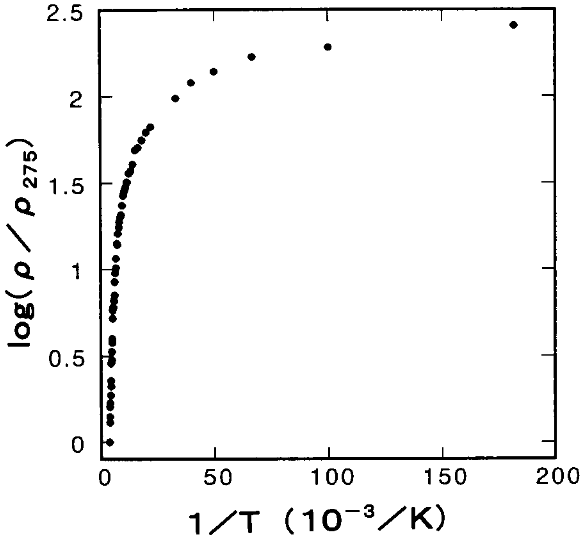

FIG. 5. Variation of electrical resistivity against reciprocal temperature on $LaCrS_3$.

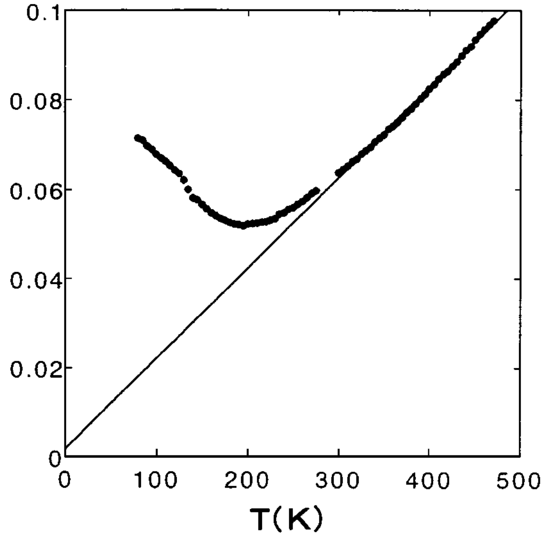

FIG. 6. Inverse magnetic susceptibility against temperature on $LaCrS_3$.

In summary, new compounds $LaMS_3$ (M = Ti, V, Cr) with NH_4CdCl_3-type crystal structure were obtained by high-pressure synthesis. The coordination number around La with sulfur increased to 9 in the high-pressure products from a value of 7 or 8 in the incommensurate $(LaS)_{1+x}MS_2$. The new compound appeared at the lowest pressure–temperature conditions in chromium among them.

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