

# Synthesis and Characterization of the New Rare-Earth/Transition-Metal Oxysulfides $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ and $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$

Jason A. Cody and James A. Ibers

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received December 1, 1993; in revised form May 10, 1994; accepted May 18, 1994

The new compounds  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  have been prepared from the reaction of  $\text{La}_2\text{S}_3$  with  $\text{TiO}_2$ . Both phases are highly resistive and weakly paramagnetic. Single-crystal X-ray diffraction measurements show that  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  crystallizes in space group  $C_{2h}^2-P2_1/m$  of the monoclinic system with two formula units in a cell of dimensions  $a = 12.572(10)$ ,  $b = 4.053(2)$ ,  $c = 16.289(14)$  Å,  $\beta = 96.79(1)^\circ$  ( $T = 113$  K). The structure contains six crystallographically independent La atoms with four different coordination geometries, and Ti atoms in octahedral coordination. The Ti octahedra form an infinite, corner-sharing dimeric chain in the  $b$  direction.  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  crystallizes in the monoclinic space group  $C_{2h}^3-C2/m$  with four formula units in a cell with dimensions  $a = 18.363(9)$ ,  $b = 3.886(2)$ ,  $c = 17.911(9)$  Å,  $\beta = 109.83(2)^\circ$  ( $T = 113$  K). The structure is composed of La atoms in tricapped trigonal prisms and Ti atoms in octahedra and highly distorted tetrahedra. There are four distinct linkages between these octahedra that include edge- and corner-shared O and S atoms. © 1995 Academic Press, Inc.

## INTRODUCTION

Compared to the large number of oxides and sulfides that are known, there are very few oxysulfides. The only two naturally occurring oxysulfides known are kermesite,  $\text{Sb}_2\text{S}_2\text{O}$  (1), and sarabaute,  $\text{CaSb}_{10}\text{S}_6\text{O}_{10}$  (2). This paper is concerned with synthetic quaternary oxysulfides that contain both a rare earth and an early transition metal. Some of the relatively few examples of such compounds display interesting magnetic properties. The compounds  $\text{LaCrQ}_2\text{O}$  ( $Q = \text{S}, \text{Se}$ ) (3) are ferromagnetic, a property attributed to superexchange interactions (4), while  $\text{NdCrS}_2\text{O}$  is antiferromagnetic and undergoes a spin-flop transition (5). The compounds  $\text{La}_5\text{V}_3\text{S}_6\text{O}_7$  (6) and  $\text{Ln}_2\text{M}_3\text{Q}_2\text{O}_8$  ( $\text{Ln} = \text{La}, \dots, \text{Nd}$ ;  $\text{M} = \text{Nb}, \text{Ta}$ ;  $\text{Q} = \text{S}, \text{Se}$ ) (7) contain mixed-valent transition metals with formal oxidation states of +3 to +5. The  $\text{MO}_2$  units in these oxysulfides consist of chains of edge-sharing metal-centered octahedra of oxygen atoms similar to those of the  $\text{TiO}_2$  groups in rutile.

Here we present the synthesis, structures, and some physical properties of  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ .

## EXPERIMENTAL

**Syntheses.** Single crystals of  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  were prepared from the reaction of  $\text{La}_2\text{S}_3$  (Alfa, 99%) with  $\text{TiO}_2$  (Anatase, Aldrich, 99.9+%) in ratios of 2:1 and 2:5, respectively. A KBr flux was used to promote crystal growth. The reaction mixtures were ground together and loaded into quartz tubes that were evacuated to approximately  $10^{-4}$  Torr and sealed. The tubes were kept at  $650^\circ\text{C}$  for 12 hr, were kept at  $950^\circ\text{C}$  for 4 days, and were then cooled at  $3^\circ\text{C}/\text{hr}$  to room temperature. Plate-like needles suitable for X-ray structure determination were produced. When the proportions of the starting materials were varied, different ratios of  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  (red) and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  (black) were obtained. Both phases are stable in air and water. Analysis of several crystals from each phase with the microprobe of an EDAX-equipped Hitachi S-570 scanning electron microscope revealed the presence of La, Ti, and S in the approximate ratios 6:2:7 for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and 4:3:3 for  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ . Powder samples were prepared by the reaction of  $\text{La}_2\text{S}_3$ ,  $\text{La}_2\text{O}_3$  (Aldrich, 99.999%), and  $\text{TiO}_2$  in the ratios 2.76:0.33:2 for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and 1.33:0.67:3 for  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ . These mixtures were loaded into quartz tubes, were kept at  $1000^\circ\text{C}$  for 4 days, and were then cooled at a rate of  $20^\circ\text{C}/\text{hr}$  to room temperature. The samples were reground and then heated a second time in the same manner.

**Electrical conductivities.** Single crystals of  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  ranging in length from 0.4 to 0.6 mm were mounted with Ag paint on Au wires with graphite extensions. Four-probe ac resistivity measurements along the needle axes ( $b$ ) were made at room temperature.

**Magnetic susceptibilities.** Measurements of powder samples of  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  (24.7 mg) and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  (27.9 mg) were made at 5 kG over the temperature ranges of 5–200 and 5–300 K, respectively, with the use of a Quantum Design MPMS variable temperature SQUID magnetic susceptometer. Gelatin capsules were used as sample holders. At each temperature the data points from three

measurements were averaged. The data were corrected for ion-core diamagnetism (8).

**Structure determinations.** For both compounds initial cell parameters and Laue symmetry  $2/m$  were determined from the analysis of Weissenberg photographs taken at room temperature. Final cell parameters were determined from reflections automatically centered at 113 K on a Picker diffractometer (9) in the range  $14 < 2\theta$  ( $\text{MoK}\alpha_1$ )  $< 42^\circ$  (20 reflections) for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and in the range  $30 < 2\theta$  ( $\text{MoK}\alpha_1$ )  $< 39^\circ$  (22 reflections) for  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ . During data collection 6 standard reflections measured after every 100 reflections showed no significant variations in intensity. The data were processed and corrected for absorption effects with methods and programs standard for this laboratory (10). Additional experimental details are given in Table 1.

The systematic absences ( $0k0$ ,  $k = 2n + 1$ ) for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  are consistent with the space groups  $C_{2h}^2-P2_1$  and  $C_{2h}^3-P2_1/m$ . The excellent agreement among Friedel pairs strongly suggests that the centrosymmetric space group  $C_{2h}^3-P2_1/m$  is correct. For  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  the systematic absences ( $hkl$ ,  $h + k = 2n + 1$ ) are consistent with space groups  $C_3^3-Cm$ ,  $C_2^3-C2$ , and  $C_{2h}^3-C2/m$ . Intensity statistics and agreement among Friedel pairs favored the centrosymmetric space group  $C2/m$ .

The positions of the La atoms in  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  were determined by direct methods with the program SHELXS (11). The positions of the Ti, O, and S atoms were determined from subsequent electron density maps. The structures were refined by full-matrix least-squares techniques with the use of the program SHELXL = 92 (12), which minimizes the function  $\sum w(F_o^2 - F_c^2)^2$ . Isotropic thermal parameters were refined for all atoms. The program STRUCTURE TIDY (13) was used to standardize the positional parameters. Final refinements resulted in values of  $R_w(F_o^2)$  of 0.147 for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and 0.115 for  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ . For reflections having  $F_o^2 > 2\sigma(F_o^2)$  the conventional  $R$  index  $R(F)$  is 0.064 and 0.051 for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ , respectively. The final difference electron density maps show no features with heights greater than 4.3% and 1.8% that of a La atom in  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ , respectively.

Final values of atomic parameters and isotropic thermal parameters are given in Table 2 for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and in Table 3 for  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ . Final structure amplitudes are available as supplementary material.<sup>1</sup>

<sup>1</sup> See NAPS Document No. 05123 for 13 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge of \$15 for this service. Foreign orders add \$4.50 for postage and handling. Add \$1.75 for postage of any microfiche orders.

TABLE 1  
Crystal Data and Intensity Collection for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$   
and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$

Formula	$\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$	$\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$
Formula mass (amu)	1265.74	955.58
Space group	$P2_1/m$	$C2/m$
$a$ (Å)	12.572(10) <sup>a</sup>	18.363(9) <sup>a</sup>
$b$ (Å)	4.053(2)	3.886(2)
$c$ (Å)	16.289(14)	17.911(9)
$\beta$ (°)	96.79(1)	109.83(2)
$V$ (Å <sup>3</sup> )	824.2(10)	1202.3(10)
$Z$	2	4
$\rho_c$ (g cm <sup>-3</sup> )	5.100	5.279
$T$ of data collection (K) <sup>b</sup>	113	113
Crystal shape	Rectangular needle (0.32 × 0.025 × 0.008 mm) bounded by {100}, {010}, {001}	Needle (0.15 × 0.022 × 0.013 mm) bounded by {100}, {010}, {001}
Crystal volume (mm <sup>3</sup> )	$6.4 \times 10^{-5}$	$4.3 \times 10^{-5}$
Radiation	$\lambda(\text{MoK}\alpha_1) = 0.7093$ Å	$\lambda(\text{MoK}\alpha_1) = 0.7093$ Å
Linear absorption coefficient (cm <sup>-1</sup> )	171.17	164.91
Transmission factors <sup>c</sup>	0.657 to 0.871	0.659 to 0.827
Detector aperture (mm)	6.5 × 6.5, 32 cm from crystal	6.5 × 6.5, 32 cm from crystal
Scan type	$\theta-2\theta$	$\theta-2\theta$
Scan speed (deg min <sup>-1</sup> )	3	2
Scan range (deg)	-0.7 to +0.8	-0.6 to +0.7
Takeoff angle (deg)	2.5	2.5
$\theta$ limits (deg)	$1.63 \leq \theta \leq 30.57$	$2.26 \leq \theta \leq 31.07$
Background counts <sup>d</sup>	10 sec at each end of scan	10 sec at each end of scan
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) +$ $(0.04 \times F_o^2)^2$	$w^{-1} = \sigma^2(F_o^2) +$ $(0.04 \times F_o^2)^2$
Data collected	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
No. of data collected	8964	4314
No. of unique data, including $\theta \geq F_o^2 \geq$ $-3\sigma(F_o^2)$	2703	2156
$R_{\text{average}}$	0.102	0.060
No. of variables	64	58
$R_w(F^2)$	0.147	0.115
$R$ (on $F$ for $F_o^2 >$ $2\sigma(F_o^2)$ )	0.064	0.051
Error in observation of unit weight ( $e^2$ )	1.44	1.13

<sup>a</sup> Obtained from a refinement with the constraints  $\alpha = \gamma = 90^\circ$ .

<sup>b</sup> The low-temperature system is based on a design by Huffman (9).

<sup>c</sup> The analytical method, as employed in the Northwestern absorption program AGNOST, was used for the absorption correction (21).

<sup>d</sup> The diffractometer was operated with the use of the Indiana University PCPS system (22).

## RESULTS AND DISCUSSION

**Structure of  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ .** The crystal structure viewed down the unique axis ( $b$ ) is shown in Fig. 1. The

TABLE 2  
Positional Parameters and Equivalent Isotropic Thermal  
Parameters for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$

Atom	x	y	z	$U_{eq} (\text{\AA}^2)^a$
La(1)	0.00203(9)	$\frac{1}{4}$	0.61957(8)	0.0095(3)
La(2)	0.06888(9)	$\frac{1}{4}$	0.88183(8)	0.0076(2)
La(3)	0.39605(9)	$\frac{1}{4}$	0.87348(8)	0.0070(2)
La(4)	0.61678(9)	$\frac{1}{4}$	0.60210(8)	0.0111(3)
La(5)	0.67897(9)	$\frac{1}{4}$	0.35162(8)	0.0082(2)
La(6)	0.72961(9)	$\frac{1}{4}$	0.89916(8)	0.0074(2)
Ti(1)	0.1533(4)	$\frac{1}{4}$	0.2324(3)	0.0287(11)
Ti(2)	0.4406(3)	$\frac{1}{4}$	0.2268(3)	0.0117(8)
S(1)	0.0878(4)	$\frac{1}{4}$	0.0682(3)	0.0082(9)
S(2)	0.1962(5)	$\frac{1}{4}$	0.3737(4)	0.0225(13)
S(3)	0.2252(4)	$\frac{1}{4}$	0.7313(3)	0.0076(9)
S(4)	0.3916(4)	$\frac{1}{4}$	0.5359(3)	0.0100(10)
S(5)	0.4303(4)	$\frac{1}{4}$	0.0611(3)	0.0082(9)
S(6)	0.7632(4)	$\frac{1}{4}$	0.0768(3)	0.0073(9)
S(7)	0.8855(4)	$\frac{1}{4}$	0.4550(3)	0.0096(10)
S(8)	0.9697(4)	$\frac{1}{4}$	0.2458(3)	0.0102(10)
O(1)	0.2877(11)	$\frac{1}{4}$	0.1938(10)	0.013(3)
O(2)	0.4538(12)	$\frac{1}{4}$	0.3383(10)	0.014(3)
O(3)	0.5660(11)	$\frac{1}{4}$	0.7828(9)	0.010(3)
O(4)	0.5827(10)	$\frac{1}{4}$	0.2123(9)	0.006(3)
O(5)	0.8511(12)	$\frac{1}{4}$	0.7818(10)	0.016(3)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_j.$$

unique metal-atom environments and labeling scheme are shown in Fig. 2. Selected bond distances and angles are presented in Table 4. The La-S and La-O bond distances

TABLE 3  
Positional Parameters and Equivalent Isotropic Thermal  
Parameters for  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$

Atom	x	y	z	$U_{eq} (\text{\AA}^2)$
La(1)	0.19999(5)	0	0.56913(5)	0.0048(2)
La(2)	0.36624(5)	0	0.06357(5)	0.0066(2)
La(3)	0.45059(5)	0	0.31728(5)	0.0043(2)
La(4)	0.69131(5)	0	0.17980(6)	0.0070(2)
Ti(1)	0.0102(2)	0	0.1896(2)	0.0093(6)
Ti(2)	0.1509(2)	0	0.3296(2)	0.0071(6)
Ti(3)	0	0	0.5000	0.0102(8)
Ti(4)	0	0.1558(20)	0	0.027(2)
S(1)	0.1332(2)	0	0.8096(2)	0.0058(7)
S(2)	0.2095(2)	0	0.0641(2)	0.0091(8)
S(3)	0.2834(2)	0	0.3021(2)	0.0057(7)
S(4)	0.4213(2)	0	0.5288(2)	0.0066(7)
O(1)	0.0427(6)	0	0.3063(6)	0.006(2)
O(2)	0.0429(6)	0	0.9235(7)	0.011(2)
O(3)	0.0679(6)	0	0.6059(6)	0.004(2)
O(4)	0.1144(6)	0	0.2019(7)	0.007(2)
O(5)	0.2145(6)	0	0.4350(6)	0.004(2)
O(6)	0.4941(6)	0	0.1906(7)	0.007(2)
O(7)	0.5690(8)	0	0.0497(9)	0.029(3)
O(8)	0.6635(6)	0	0.3210(7)	0.008(2)

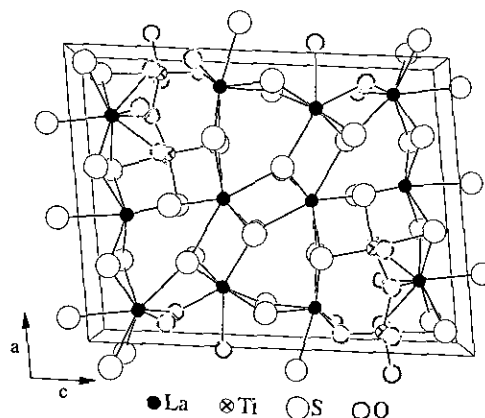


FIG. 1. Unit cell of  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ . Here and in succeeding figures the atoms are drawn with arbitrary sizes.

found in  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  fall within the range of distances found in  $\text{La}_2\text{O}_3$  (2.39 to 2.78  $\text{\AA}$ ) (14) and  $\text{La}_2\text{S}_3$  (2.90 to 3.16  $\text{\AA}$ ) (15). Similarly, the Ti-O bond distances are comparable to those found in  $\text{TiO}_2$  (rutile; 1.944(4) to 1.988(6)  $\text{\AA}$ ) (16). The Ti-S bonds in  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  are similar to those found in  $\text{TiS}_3$  (2.358(4) to 2.855(6)  $\text{\AA}$ ) (17). The La atoms in  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  are seven-, eight-, and nine-coordinated. Atom La(1) is coordinated to eight S atoms in a bicapped trigonal prism; atom La(2) is coordinated to seven S atoms in a monocapped trigonal prism. Atoms La(3) and La(4) are in trigonal prisms of four S atoms and two O atoms; the trigonal prism surrounding atom La(4) is capped with one S atom, whereas the trigonal prism about atom La(3) is capped with two S atoms and with one O atom, if atom O(3) is included. Atom La(5) is seven-coordinated with four S atoms in an equatorial

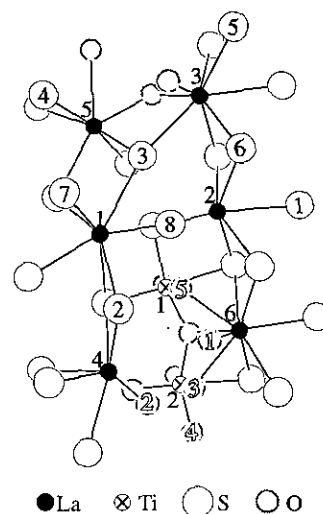


FIG. 2. Unique metal-atom environments in  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ .

TABLE 4  
Bond Distances (Å) and Angles (°) for La<sub>6</sub>Ti<sub>2</sub>S<sub>8</sub>O<sub>5</sub>

La(1)–S(7)	2×	2.826(4)	La(4)–S(2)	2×	3.094(5)
La(1)–S(7)		2.898(6)	La(5)–O(4)		2.442(14)
La(1)–S(8)	2×	2.976(4)	La(5)–S(3)	2×	2.787(4)
La(1)–S(3)		3.159(5)	La(5)–O(2)		2.814(15)
La(1)–S(2)	2×	3.224(5)	La(5)–S(7)		2.924(5)
La(2)–S(8)	2×	2.903(4)	La(5)–S(4)	2×	2.939(4)
La(2)–S(6)	2×	2.947(4)	La(6)–O(1)	2×	2.524(9)
La(2)–S(1)	2×	3.005(4)	La(6)–O(5)		2.58(2)
La(2)–S(1)		3.016(6)	La(6)–O(3)		2.628(14)
La(3)–O(4)	2×	2.494(9)	La(6)–S(6)		2.875(6)
La(3)–O(3)		2.737(15)	La(6)–S(5)	2×	2.979(4)
La(3)–S(3)		2.967(5)	La(6)–S(1)	2×	3.061(4)
La(3)–S(6)	2×	3.025(4)	Ti(1)–O(1)		1.87(2)
La(3)–S(5)		3.035(6)	Ti(1)–O(5)	2×	2.040(2)
La(3)–S(5)	2×	3.075(4)	Ti(1)–S(2)		2.300(9)
La(4)–O(2)	2×	2.458(9)	Ti(1)–S(8)		2.344(7)
La(4)–S(4)		2.907(6)	Ti(1)–S(1)		2.705(8)
La(4)–S(4)	2×	3.019(5)	Ti(2)–O(2)		1.80(2)
			Ti(2)–O(4)		1.830(14)
			Ti(2)–O(1)		1.934(14)
			Ti(2)–O(3)	2×	2.033(2)
			Ti(2)–S(5)		2.687(7)
S(7)–La(1)–S(7)		91.6(2)	S(8)–La(2)–S(1)		70.36(13)
S(7)–La(1)–S(7)		79.99(14)	S(8)–La(2)–S(1)		127.26(13)
S(7)–La(1)–S(8)		78.84(14)	S(6)–La(2)–S(1)		151.3(2)
S(7)–La(1)–S(8)		141.53(14)	S(6)–La(2)–S(1)		87.09(11)
S(7)–La(1)–S(8)		133.20(9)	S(1)–La(2)–S(1)		84.81(14)
S(8)–La(1)–S(8)		85.8(2)	S(8)–La(2)–S(1)		135.02(9)
S(7)–La(1)–S(3)		78.02(13)	S(6)–La(2)–S(1)		78.51(13)
S(7)–La(1)–S(3)		148.24(15)	S(1)–La(2)–S(1)		72.76(13)
S(8)–La(1)–S(3)		63.57(11)	O(4)–La(3)–O(4)		108.7(5)
S(7)–La(1)–S(2)		153.3(2)	O(4)–La(3)–O(3)		63.6(3)
S(7)–La(1)–S(2)		89.53(13)	O(4)–La(3)–S(3)		71.2(3)
S(7)–La(1)–S(2)		73.94(15)	O(3)–La(3)–S(3)		96.8(3)
S(8)–La(1)–S(2)		115.4(2)	O(2)–La(4)–S(2)		142.6(4)
S(8)–La(1)–S(2)		64.67(14)	S(4)–La(4)–S(2)		137.67(9)
S(3)–La(1)–S(2)		128.16(13)	S(4)–La(4)–S(2)		119.6(2)
S(2)–La(1)–S(2)		77.9(2)	S(4)–La(4)–S(2)		67.33(14)
S(8)–La(2)–S(8)		88.6(2)	S(2)–La(4)–S(2)		81.8(2)
S(8)–La(2)–S(6)		134.31(15)	O(4)–La(5)–S(3)		75.2(2)
S(8)–La(2)–S(6)		74.82(12)	S(3)–La(5)–S(3)		93.3(2)
S(8)–La(2)–S(6)		134.31(15)	O(4)–La(5)–O(2)		62.9(5)
S(6)–La(2)–S(6)		86.91(14)	S(3)–La(5)–O(2)		116.8(2)
O(4)–La(3)–S(6)		74.0(3)	O(4)–La(5)–S(7)		147.6(3)
O(4)–La(3)–S(6)		144.3(3)	S(3)–La(5)–S(7)		82.75(13)
O(3)–La(3)–S(6)		136.70(10)	O(2)–La(5)–S(7)		149.5(4)
S(3)–La(3)–S(6)		76.58(13)	O(4)–La(5)–S(4)		115.2(2)
S(6)–La(3)–S(6)		84.11(14)	S(3)–La(5)–S(4)		169.52(15)
O(4)–La(3)–S(5)		123.5(3)	S(3)–La(5)–S(4)		88.88(12)
O(3)–La(3)–S(5)		121.1(3)	O(2)–La(5)–S(4)		70.9(2)
S(3)–La(3)–S(5)		142.13(15)	S(7)–La(5)–S(4)		87.36(13)
S(6)–La(3)–S(5)		75.54(12)	S(4)–La(5)–S(4)		87.2(2)
O(4)–La(3)–S(5)		127.7(2)	O(1)–La(6)–O(1)		106.8(6)
O(4)–La(3)–S(5)		62.6(3)	O(1)–La(6)–O(5)		64.7(4)
O(3)–La(3)–S(5)		67.7(2)	O(1)–La(6)–O(3)		64.1(3)
S(3)–La(3)–S(5)		133.58(9)	O(5)–La(6)–O(3)		87.0(5)
S(6)–La(3)–S(5)		144.46(15)	O(1)–La(6)–S(6)		126.6(3)
S(6)–La(3)–S(5)		86.03(11)	O(5)–La(6)–S(6)		135.7(4)
S(5)–La(3)–S(5)		68.94(13)	S(2)–Ti(1)–S(1)		175.9(3)

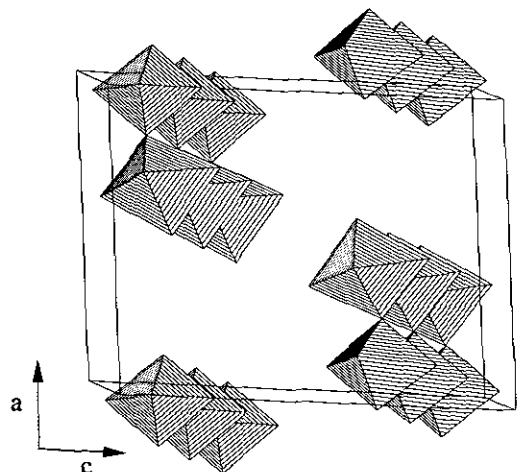
TABLE 4—Continued

S(5)–La(3)–S(5)	82.44(13)	S(8)–Ti(1)–S(1)	84.5(2)
O(2)–La(4)–O(2)	111.1(6)	O(1)–Ti(1)–O(5)	88.6(5)
O(2)–La(4)–S(4)	76.4(3)	O(5)–Ti(1)–S(5)	167.0(10)
O(2)–La(4)–S(4)	149.9(4)	O(1)–Ti(1)–S(2)	102.8(5)
O(2)–La(4)–S(4)	76.0(3)	O(5)–Ti(1)–S(2)	96.5(5)
S(4)–La(4)–S(4)	77.11(14)	O(1)–Ti(1)–S(8)	165.8(6)
S(4)–La(4)–S(4)	84.3(2)	O(5)–Ti(1)–S(8)	89.8(5)
O(2)–La(4)–S(2)	73.4(3)	S(2)–Ti(1)–S(8)	91.4(3)
O(3)–La(6)–S(6)	137.4(3)	O(1)–Ti(1)–S(1)	81.3(5)
O(1)–La(6)–S(5)	64.6(3)	O(5)–Ti(1)–S(1)	83.5(5)
O(1)–La(6)–S(5)	131.6(3)	O(2)–Ti(2)–O(4)	98.9(7)
O(5)–La(6)–S(5)	129.3(2)	O(2)–Ti(2)–O(1)	104.5(7)
O(3)–La(6)–S(5)	70.5(3)	O(4)–Ti(2)–O(1)	156.6(7)
S(6)–La(6)–S(5)	78.68(12)	O(2)–Ti(2)–O(3)	94.3(4)
S(5)–La(6)–S(5)	85.71(14)	O(4)–Ti(2)–O(3)	91.2(4)
O(1)–La(6)–S(1)	130.2(3)	O(1)–Ti(2)–O(3)	87.1(4)
O(1)–La(6)–S(1)	65.3(3)	O(3)–Ti(2)–O(3)	170.5(9)
O(5)–La(6)–S(1)	68.4(3)	O(2)–Ti(2)–S(5)	177.5(5)
O(3)–La(6)–S(1)	129.2(2)	O(4)–Ti(2)–S(5)	78.6(5)
S(6)–La(6)–S(1)	78.88(13)	O(1)–Ti(2)–S(5)	78.0(5)
S(5)–La(6)–S(1)	157.52(15)	O(3)–Ti(2)–S(5)	85.8(4)
S(5)–La(6)–S(1)	91.34(11)		
S(1)–La(6)–S(1)	82.92(13)		

plane and one S and two O atoms in a perpendicular plane. This polyhedral environment is similar to that found in La<sub>2</sub>S<sub>3</sub> (15). The La(5)–O(2) distance of 2.81 Å is long but agrees well with a long La–O distance found in La<sub>2</sub>O<sub>3</sub> (2.78 Å) (14). Atom La(6) is in a tricapped trigonal prism comprising a trigonal prism of four S atoms and two O atoms with one S atom and two O atoms as caps.

There are two unique Ti atoms in La<sub>6</sub>Ti<sub>2</sub>S<sub>8</sub>O<sub>5</sub>. The Ti(1) atom is in a distorted octahedron of three S atoms and three O atoms. Atom Ti(2) is in a distorted octahedron of one S atom and five O atoms; an O(1) atom bridges atoms Ti(1) and Ti(2). These two octahedra form an oxygen-bridged, corner-sharing, dimeric chain,  $\frac{1}{2}[\text{Ti}_2\text{S}_4\text{O}_7]^{-14}$ , linked through atoms O(5) and O(3), that extends along the *b* axis. A polyhedral representation of this chain is shown in Fig. 3.

*Structure of La<sub>4</sub>Ti<sub>3</sub>S<sub>4</sub>O<sub>8</sub>.* The unit cell viewed down the unique axis (*b*) is shown in Fig. 4. Selected bond distances and angles are given in Table 5. The metal-atom environments and labeling scheme are given in Fig. 5. The four crystallographically unique La atoms have tricapped trigonal prismatic coordination. Atom La(1) is in a trigonal prism of four S atoms and two O atoms with three capping O atoms. Atoms La(2) and La(4) are both in trigonal prisms of four S atoms and two O atoms, and each have one S atom and two O atoms that cap the faces. Atom La(3) is coordinated to two S atoms and four O atoms with the capping atoms being two S atoms and one O atom. Three of the four unique Ti atoms are octa-

FIG. 3. Polyhedral network of corner-sharing "Ti<sub>5</sub>O<sub>8</sub>" octahedra.

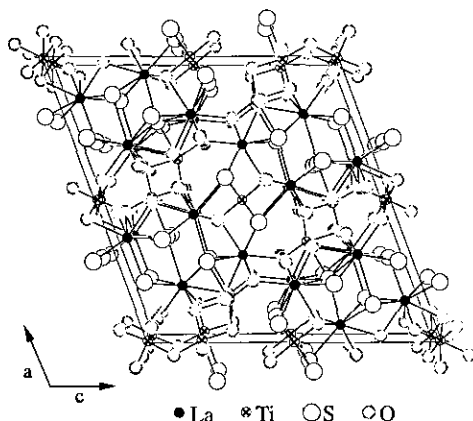
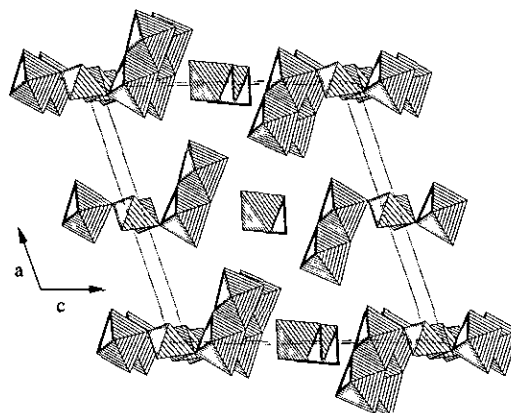
hedrally coordinated. Atoms Ti(1) and Ti(2) are each coordinated by five O atoms and one S atom while atom Ti(3) is coordinated by four S atoms and two O atoms. While atom Ti(4) is in an octahedron of six O atoms, it is disordered over two sites in such a way as to achieve

TABLE 5  
Bond Distances (Å) and Angles (°) for La<sub>4</sub>Ti<sub>3</sub>S<sub>4</sub>O<sub>8</sub>

La(1)-O(5)	2.506(11)	La(4)-O(8)	2.744(11)
La(1)-O(5)	2× 2.514(6)	La(4)-S(2)	2× 2.941(3)
La(1)-O(8)	2.609(11)	La(4)-S(3)	2× 2.987(3)
La(1)-O(3)	2.721(10)	La(4)-S(1)	3.163(4)
La(1)-S(3)	2× 2.951(3)	Ti(1)-O(4)	1.850(11)
La(1)-S(4)	2× 3.027(3)	Ti(1)-O(2)	1.927(12)
La(2)-O(2)	2× 2.520(7)	Ti(1)-O(6)	2× 1.966(2)
La(2)-O(6)	2.658(11)	Ti(1)-O(1)	1.970(11)
La(2)-O(7)	2.677(14)	Ti(1)-S(1)	2.638(5)
La(2)-S(2)	2.881(4)	Ti(2)-O(5)	1.852(11)
La(2)-S(2)	2× 2.964(3)	Ti(2)-O(1)	1.887(10)
La(2)-S(1)	2× 2.987(3)	Ti(2)-O(8)	2× 1.969(2)
La(3)-O(3)	2× 2.470(6)	Ti(2)-O(4)	2.155(12)
La(3)-O(1)	2× 2.627(7)	Ti(2)-S(3)	2.639(5)
La(3)-O(6)	2.649(11)	Ti(3)-O(3)	2× 1.883(10)
La(3)-S(4)	2.955(4)	Ti(3)-S(4)	4× 2.576(3)
La(3)-S(3)	2.990(4)	Ti(4)-O(7)	2× 1.850(12)
La(3)-S(1)	2× 2.989(3)	Ti(4)-O(2)	2× 1.897(11)
La(4)-O(4)	2× 2.511(7)	Ti(4)-Ti(4)	2.68(2)
La(4)-O(7)	2.631(15)		
O(5)-La(1)-O(5)	72.6(3)	O(6)-La(2)-O(7)	99.1(4)
O(5)-La(1)-O(8)	101.2(3)	O(2)-La(2)-S(2)	129.1(2)
O(5)-La(1)-O(8)	109.6(3)	O(6)-La(2)-S(2)	126.2(2)
O(5)-La(1)-O(8)	64.7(3)	O(7)-La(2)-S(2)	134.7(3)
O(5)-La(1)-O(3)	128.7(3)	O(2)-La(2)-S(2)	71.8(2)
O(5)-La(1)-O(3)	128.6(2)	O(6)-La(2)-S(2)	135.05(10)
O(8)-La(1)-O(3)	121.7(3)	O(7)-La(2)-S(2)	68.2(2)
O(5)-La(1)-S(3)	137.12(8)	S(2)-La(2)-S(2)	78.16(11)
O(5)-La(1)-S(3)	67.3(2)	O(2)-La(2)-S(2)	134.4(3)

TABLE 5—Continued

O(5)-La(1)-S(3)	129.2(2)	S(2)-La(2)-S(2)	81.93(11)
O(8)-La(1)-S(3)	65.9(2)	O(2)-La(2)-S(1)	66.2(2)
O(3)-La(1)-S(3)	71.1(2)	O(2)-La(2)-S(1)	126.9(3)
S(3)-La(1)-S(3)	82.37(11)	O(6)-La(2)-S(1)	64.8(2)
O(5)-La(1)-S(4)	75.0(2)	O(7)-La(2)-S(1)	133.52(15)
O(5)-La(1)-S(4)	145.4(3)	S(2)-La(2)-S(1)	75.11(9)
O(5)-La(1)-S(4)	80.3(2)	S(2)-La(2)-S(1)	153.28(11)
O(8)-La(1)-S(4)	140.07(5)	S(2)-La(2)-S(1)	92.30(9)
O(3)-La(1)-S(4)	66.4(2)	S(1)-La(2)-S(1)	81.17(11)
S(3)-La(1)-S(4)	137.42(10)	O(3)-La(3)-O(3)	103.7(4)
S(3)-La(1)-S(4)	83.75(9)	O(3)-La(3)-O(1)	70.9(3)
S(4)-La(1)-S(4)	79.86(10)	O(3)-La(3)-O(1)	146.8(3)
O(2)-La(2)-O(2)	100.9(4)	O(1)-La(3)-O(1)	95.4(3)
O(2)-La(2)-O(6)	63.6(3)	O(3)-La(3)-O(6)	128.0(2)
O(2)-La(2)-O(7)	67.6(3)	O(1)-La(3)-O(6)	63.1(2)
O(3)-La(3)-S(4)	72.3(2)	O(8)-La(4)-S(2)	138.61(6)
O(1)-La(3)-S(4)	75.0(2)	S(2)-La(4)-S(2)	82.71(11)
O(6)-La(3)-S(4)	115.0(2)	O(4)-La(4)-S(3)	126.6(3)
O(3)-La(3)-S(3)	73.7(2)	O(4)-La(4)-S(3)	65.8(2)
O(1)-La(3)-S(3)	131.4(2)	O(7)-La(4)-S(3)	138.62(8)
O(6)-La(3)-S(3)	121.4(2)	O(8)-La(4)-S(3)	63.9(2)
S(4)-La(3)-S(3)	123.55(11)	S(2)-La(4)-S(3)	140.83(11)
O(3)-La(3)-S(1)	143.4(2)	S(2)-La(4)-S(3)	85.16(10)
O(3)-La(3)-S(1)	77.3(2)	O(4)-La(4)-S(3)	126.6(3)
O(1)-La(3)-S(1)	127.0(2)	S(3)-La(4)-S(3)	81.17(11)
O(1)-La(3)-S(1)	68.9(2)	O(4)-La(4)-S(1)	127.3(2)
O(6)-La(3)-S(1)	64.9(2)	O(7)-La(4)-S(1)	126.8(3)
S(4)-La(3)-S(1)	138.65(6)	O(8)-La(4)-S(1)	116.7(2)
S(3)-La(3)-S(1)	71.53(9)	S(2)-La(4)-S(1)	71.66(9)
S(1)-La(3)-S(1)	81.09(11)	S(3)-La(4)-S(1)	69.17(9)
O(4)-La(4)-O(4)	101.4(4)	O(4)-Ti(1)-O(2)	105.0(5)
O(4)-La(4)-O(7)	77.5(3)	O(4)-Ti(1)-O(6)	98.7(3)
O(4)-La(4)-O(8)	64.2(3)	O(2)-Ti(1)-O(6)	89.2(3)
O(7)-La(4)-O(8)	116.5(4)	O(6)-Ti(1)-O(6)	162.3(6)
O(4)-La(4)-S(2)	78.7(2)	O(4)-Ti(1)-O(1)	86.9(5)
O(4)-La(4)-S(2)	145.8(3)	O(2)-Ti(1)-O(1)	168.1(5)
O(7)-La(4)-S(2)	69.1(2)	O(6)-Ti(1)-O(1)	89.0(3)
O(8)-La(4)-S(2)	138.61(6)	O(4)-Ti(1)-S(1)	173.3(4)
O(7)-La(4)-S(2)	69.1(2)	O(2)-Ti(1)-S(1)	81.7(3)
O(6)-Ti(1)-S(1)	81.2(3)		
O(1)-Ti(1)-S(1)	86.4(3)		
O(5)-Ti(2)-O(1)	118.5(5)		
O(5)-Ti(2)-O(8)	91.7(3)		
O(1)-Ti(2)-O(8)	97.2(3)		
O(8)-Ti(2)-O(8)	161.4(6)		
O(5)-Ti(2)-O(4)	160.7(4)		
O(1)-Ti(2)-O(4)	80.8(4)		
O(8)-Ti(2)-O(4)	85.4(3)		
O(5)-Ti(2)-S(3)	83.6(3)		
O(1)-Ti(2)-S(3)	157.9(4)		
O(8)-Ti(2)-S(3)	81.1(3)		
O(4)-Ti(2)-S(3)	77.1(3)		
O(3)-Ti(3)-O(3)	180.0		
O(3)-Ti(3)-S(4)	91.3(2)		
O(3)-Ti(3)-S(4)	88.7(2)		
S(4)-Ti(3)-S(4)	180.0		
S(4)-Ti(3)-S(4)	97.92(13)		
S(4)-Ti(3)-S(4)	82.08(13)		
O(7)-Ti(4)-O(7)	87.4(7)		
O(7)-Ti(4)-O(2)	101.2(5)		
O(7)-Ti(4)-O(2)	105.5(5)		
O(2)-Ti(4)-O(2)	142.8(5)		

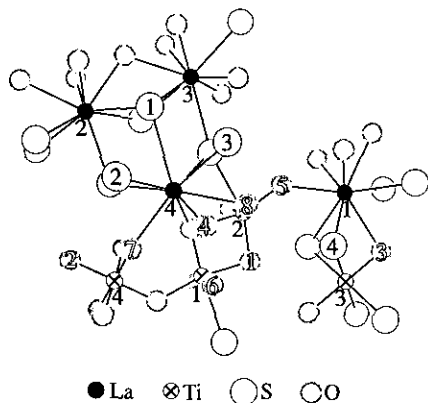
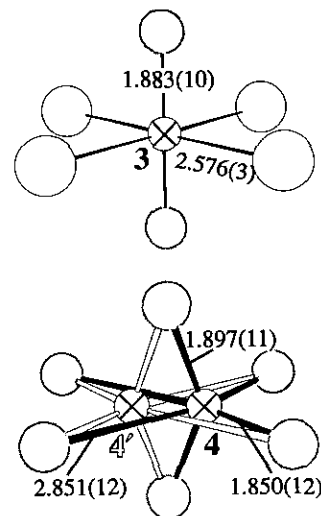
FIG. 4. Unit cell of  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ .FIG. 6. Polyhedral network of edge- and corner-sharing  $\text{TiS}_4\text{O}_6$  octahedra.

tetrahedral coordination (*vide infra*). The octahedron about atom Ti(3) shares an edge of two S(4) atoms in the  $b$  direction to form a  $\frac{1}{2}[\text{TiS}_2\text{O}_2^{-2}]$  chain. The octahedra containing atoms Ti(1) and Ti(2) edge-share through oxygen atoms O(1) and O(4), and atom Ti(1) further shares atom O(2) with the octahedron surrounding atom Ti(4), as illustrated in Fig. 6. This octahedron is linked through a second O(2) atom to another dimeric chain that contains atoms Ti(1) and Ti(2). An isolated slab of these five octahedra extends infinitely in the  $b$  direction through Ti(1)–O(6)–Ti(1) and Ti(2)–O(8)–Ti(2) linkages and the edge sharing of atoms O(7) between the octahedra surrounding atom Ti(4). The resultant cation–anion bond distances are normal (Table 5), being similar to those found in  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and in simple binary compounds.

The six O atoms of the octahedron surrounding atom Ti(4) are positioned so that the center-to-vertex distances range from 1.798 Å for the axial O(2) atom to 2.326 Å for the equatorial O(7) atom with angles in the equatorial

plane of 113.3 and 66.7°; if atom Ti(4) were in the center of this octahedron, unreasonably long Ti–O distances would result. Rather atom Ti(4) shifts along the  $b$  direction toward one edge of the octahedron to achieve severely distorted tetrahedral coordination with normal Ti–O distances of 1.891(11) and 1.849(12) Å and O–Ti–O angles of 87.4(7) to 142.8(5)°. This shift along  $b$  is random, resulting in a disorder of atom Ti(4) equally over two sites, which seems reasonable structurally (Fig. 7).<sup>2</sup>

<sup>2</sup> This disorder is required in space group  $C2/m$ . While in polar space group  $C2$  this shift would be in one direction only, the good agreement among Friedel pairs does not support the choice of this space group. But we cannot eliminate a model in space group  $C2$  in which atom Ti(4) is ordered *and* all other atoms lie very close to the  $y = 0$  plane.

FIG. 5. Unique metal-atom environments in  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ .FIG. 7. The parallel  $\text{TiS}_4\text{O}_2$  and  $\text{TiO}_6$  octahedra in  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ , showing the split position for atom Ti(4).

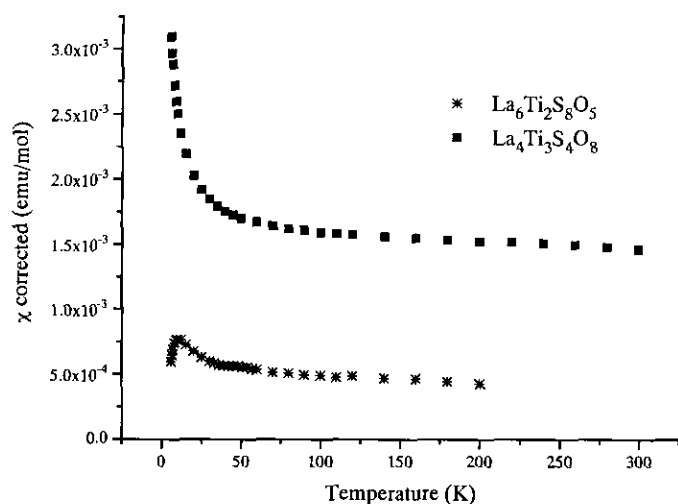


FIG. 8. Plot of magnetic susceptibility versus temperature for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ .

The three oxysulfides (18)  $(\text{LaO})_4\text{Ga}_{1.33}\text{S}_4$ ,  $(\text{CeO})_4\text{Ga}_2\text{S}_5$ , and  $(\text{LaO})_4\text{Sn}_2\text{S}_6$  each have split, multiple positions for a Ga or Sn atom in a "tetrahedral" hole inside an octahedron of S atoms. These three structures contain similar "LaSO" frameworks and are distinguished solely by the occupancies of the Ga and Sn atoms in these sites.

**Physical measurements.** Room-temperature four-probe electrical conductivity measurements (19) show that  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  are highly resistive. The conductivity is below  $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ , the minimum detection limit of our instrument. The high electrical resistivity is consistent with the closed-shell formalism of  $\text{Ti}^{\text{IV}}$  and  $\text{La}^{\text{III}}$  that can be assigned to these compounds in view of the absence of close anion-anion interactions.

Plots of the temperature dependence of the magnetic susceptibility ( $\chi$ ) at 5 kG are given for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  and  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  in Fig. 8. The data for  $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$  show weak temperature-independent paramagnetism to 30 K. The susceptibility increases to a maximum at 12 K and then decreases. The data for  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  were fit by a least-squares procedure to the equation  $\chi = C/(T + \theta) + \chi_0$ . The values obtained for  $\theta$ ,  $C$ , and  $\chi_0$  are 1.5(2) K, 0.0120(3) emu K/mole, and  $1.47(1) \times 10^{-3}$  emu/mole,

respectively. The effective magnetic moment from the formula (20)  $\mu_{\text{eff}} = (8C)^{1/2}$  is 0.30 BM per  $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$  unit.

#### ACKNOWLEDGMENTS

This research was supported by NSF Grant DMR 91-14934. This work made use of the MRL Central Facilities supported by the National Science Foundation at the Materials Research Center of Northwestern University under Grant DMR91-20521. We thank Dr. Theodore D. Brennan for the initial observation of this reaction.

#### REFERENCES

1. V. Kupčík, *Naturwissenschaften* **54**, 114 (1967).
2. I. Nakai, K. Nagashima, K. Koto, and N. Morimoto, *Acta Crystallogr., Sect. B Struct. Crystallogr. Cryst. Chem.* **34**, 3569 (1978).
3. J. Dugué, T. Vovan, and J. Villers, *Acta Crystallogr., Sect. B Struct. Crystallogr. Cryst. Chem.* **36**, 1291 (1980).
4. M. Wintenberger, T. Vovan, and M. Guittard, *Solid State Commun.* **53**, 227 (1985).
5. M. Wintenberger, J. Dugue, M. Guittard, N. H. Dung, and V. V. Tien, *J. Solid State Chem.* **70**, 295 (1987).
6. J. Dugué, T. Vovan, and P. Laruelle, *Acta Crystallogr., Sect. C Cryst. Struct. Commun.* **41**, 1146 (1985).
7. T. D. Brennan, L. E. Aleandri, and J. A. Ibers, *J. Solid State Chem.* **91**, 312 (1991).
8. L. N. Mulay and E. A. Boudreaux, Eds., "Theory and Applications of Molecular Diamagnetism," Wiley-Interscience, New York (1976).
9. J. C. Huffman, Ph.D. Thesis, Indiana University (1974).
10. J. M. Waters and J. A. Ibers, *Inorg. Chem.* **16**, 3273 (1977).
11. G. M. Sheldrick, "SHELXTL PC Version 4.1 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data," Siemens Analytical X-Ray Instruments, Inc. Madison, WI.
12. G. M. Sheldrick, "SHELXL-92," Unix Beta-test Version.
13. L. M. Gelato and E. Parthé, *J. Appl. Crystallogr.* **20**, 139 (1987).
14. H. Müller-Buschbaum and H. G. von Schnering, *Z. Anorg. Allg. Chem.* **340**, 232 (1965).
15. P. Basançon, C. Adolphe, J. Flahaut, and P. Laruelle, *Mater. Res. Bull.* **4**, 227 (1969).
16. W. H. Baur, *Acta Crystallogr.* **9**, 515 (1956).
17. S. Furuseth, L. Brattås, and A. Kjekshus, *Acta Chem. Scand., Ser. A* **29**, 623 (1975).
18. M. Guittard, S. Benazeth, J. Dugué, S. Jaulmes, M. Palazzi, P. Laruelle, and J. Flahaut, *J. Solid State Chem.* **51**, 227 (1984).
19. T. E. Phillips, J. R. Anderson, C. J. Schramm, and B. M. Hoffman, *Rev. Sci. Instrum.* **50**, 263 (1979).
20. J. M. van den Berg and P. Cossee, *Inorg. Chim. Acta* **2**, 143 (1968).
21. J. de Meulenaer and H. Tompa, *Acta Crystallogr.* **19**, 1014 (1965).
22. J. C. Huffman, Unpublished work.