

Synthesis, Crystal Structure, and Electrical Properties of a New Quaternary Manganese Mixed Sulfide, BaLa₂MnS₅

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A new quaternary sulfide, BaLa₂MnS₅, was prepared by the reaction of CS₂ with a mixture of BaCO₃, La₂O₃, and MnO₂ at 1323 K. The crystal structure of this compound is tetragonal with space group *I4/mcm*. The lattice parameters are $a = 8.014(2)$ and $c = 13.867(3)$ Å. The refinement of the diffraction data was carried out by the Rietveld method yielding (Ba_{1/3},La_{2/3}) in *4a* (0, 0, 1/4) and *8h* (0.1620, 0.6620, 0), Mn in *4b* (0, 1/2, 1/4), S(1) in *4c* (0, 0, 0), and S(2) in *16l* (0.1514, 0.6514, 0.6352). The final reliability factors were $R_{wp} = 13.22$, $R_p = 9.91$, $R_1 = 2.94$, and $R_F = 1.82\%$. The interatomic distance showed a deviation according to the bonds giving distances longer or shorter than the crystal radius sums, which suggests the existence of some covalency in the crystal. The electrical conductivity and Hall coefficient were measured using the van der Pauw method in a temperature range from 18 to 300 K. The electrical conductivity was on the order of 10^2 S m⁻¹, and it increased with increasing temperature showing that BaLa₂MnS₅ is semiconductive. The negative Hall coefficient indicated that the conduction is *n*-type. The activation energy of conduction was 16 meV above 200 K.

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INTRODUCTION

Barium lanthanum manganese oxide with perovskite structure, Ba_xLa_{1-x}MnO₃, is known to exhibit extraordinary magnetic and electrical properties (1,2). However, the sulfide counterpart of this oxide with perovskite structure has not been found to exist. Murugesan *et al.* (3) obtained a mixed sulfide LaMnS₃ by repeated heating of LaMnO₃ in a stream of CS₂/N₂ gas at 1373 K for a total period of ~150 h. The compound was assigned to the hexagonal *2H* type CsNiCl₃ structure. Collin and Laruelle (4) reported the formation of another lanthanum and manganese sulfide which contains a hexagonal subcell with the approximate formula La₆Mn₂S₁₀. The compound has a complicated monoclinic structure (space group *Bm*) comprising 12 equivalent La sites, in which four are partially occupied. In

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addition, there are six Mn sites, and two of these sites are half occupied. The strict composition of the compound was shown to be La_{32.66}Mn₁₁S₆₀. As for barium manganese sulfides, two compounds, Ba₂MnS₃ (5) and BaMnS₂ (6), are known to exist. Ba₂MnS₃ was prepared by heating a mixture of BaS, Mn, and S in a calculated ratio in a sealed evacuated quartz ampoule at 1323 K. BaMnS₂ was prepared by heating the mixture of BaCO₃ and Mn, in a stream of H₂S at 1273 K. Ba₂MnS₃ contains the linear chains of MnS₄ tetrahedra. The structure is isotypic with K₂AgI₃. BaMnS₂ has a layer structure isotypic with SrZnO₂.

In this work, a new quaternary barium lanthanum manganese sulfide, BaLa₂MnS₅, was prepared by heating a mixture of BaCO₃, La₂O₃, and MnO₂ in a calculated metal ratio in a CS₂/N₂ gas stream. The composition of the compound was analyzed by electron probe microanalysis (EPMA), and the crystal structure was determined by X-ray powder diffractometry. The electrical conductivity and Hall coefficient were measured by the van der Pauw method (7) in a temperature range of 18–300 K.

EXPERIMENTAL

The BaCO₃, MnO₂, and CS₂ used were analytical grade obtained from Wako Pure Chemicals Industries, Ltd. La₂O₃ of 99.9% purity was obtained from Nihon Yttrium Co., Ltd. BaCO₃, La₂O₃, and MnO₂ were weighed in the intended ratio and wet mixed with ethyl alcohol for half an hour in an agate mortar. The mixture in a graphite boat was placed in a vertical type Keramax furnace. After evacuation, a CS₂/N₂ mixed gas, which was obtained by bubbling N₂ gas through liquid CS₂ at room temperature, was introduced into the system. Subsequently, the furnace temperature was raised to 1323 K in 5 h and kept at this temperature for 12 h.

Phase analysis and determination of the elements in the product were carried out by using a Hitachi X-560 electron probe microanalyzer. The standard deviations of the determined values for barium, lanthanum, manganese, and sulfur were 2.9, 6.5, 1.4, and 2.4 wt%, respectively.

X-ray powder diffraction measurements were carried out with a Rigaku RAD-IC diffractometer using CuK α radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. The slit system was 0.5°–0.5°–0.05 mm–0.6 mm. The measurement was performed from $2\theta = 10$ to 110° by step scanning with an interval of 0.02° . The measurement time was 10 s for one point. The determination of crystal system and indexing of the reflections were made with the aid of the ITO (8) and TREOR (9) programs. The lattice parameters and peak intensities were calculated with the LCR2 (10) and LAZY-PULVERIX (11) programs, respectively. The program RIETAN (12) was used for refinement through peak profile analysis by the Rietveld method.

The density of BaLa₂MnS₅ was measured by the toluene displacement method at 298 K with a sample powder of about 0.5 g using a glass bulb of 7.423 g weight and 2.863 mL inner volume.

The electrical conductivity and the Hall effect were measured by the four-probe van der Pauw method for a pelletized sample of 10 mm diameter and about 1 mm thick. The pellet was obtained by sintering the compound at 1323 K for 12 h in a flow of CS₂/N₂ gas. At four diagonal points on the side of the sintered pellet, fine copper wires were connected by indium contacts. After the pellet was placed in the measuring device, it was cooled to 18 K in vacuum by a Daikin UV202CL helium refrigerator. Then, the temperature of the pellet was raised to 300 K with a tape heater at a rate of 0.5 K min⁻¹ under the control of a Chino KP-1000 digital programmer. During the above heating process, the electrical resistivity data were automatically collected at 1 min intervals. A constant current of 30 mA (Advantest TR-6143) was applied to the sample, and the potential drop was measured by a Keithley Model 182 voltmeter of which the input impedance was > 10 G Ω . The hysteresis of electrical resistivity was checked by lowering the sample temperature from room temperature to 18 K at the same rate. The Hall coefficient was measured for the same pellet every 10 K between 18 K and room temperature, during which a constant current of 30 mA and a magnetic field of 0.58 T were applied to the sample. Measurements were made by reversing the magnetic field and current to eliminate misalignment and thermal voltage effects.

RESULTS AND DISCUSSION

After heating the mixture of BaCO₃, La₂O₃, and MnO₂ (Ba:La:Mn metal ratio 1:2:1) in a stream of CS₂/N₂ at 1323 K, a light brown compound was obtained. The X-ray powder diffraction pattern suggested that the compound was a new sulfide. The X-ray diffraction lines were all indexed on the basis of a tetragonal cell with lattice parameters of $a = 8.014(2)$ and $c = 13.867(3)$ Å. The reflection conditions were seen to be $h + k + l = 2n$ for general hkl and $h, l = 2n$ for $h0l$. This compound was obtained as

a mixture with BaMnS₂ and MnS if the the mixture of BaCO₃, La₂O₃, and MnO₂ (Ba:La:Mn metal ratio 1:1:2) was heated under the same conditions as above. The metal ratio of 1:1:2 was that of a hypothetical perovskite, BaLaMn₂S₆.

The phase analysis was carried out by EPMA for the compound of Ba:La:Mn = 1:2:1. The result was consistent with X-ray diffraction analysis that the quaternary sulfide was obtained in a single phase. The EPMA data for the elemental analysis of barium, lanthanum, manganese, and sulfur are listed in Table 1. Although the standard deviations are relatively large, these values are close to the theoretical wt% of Ba:La:Mn:S = 21.78:44.07:8.71:25.43 for BaLa₂MnS₅. For this formula, the formal valence of manganese is +2 if those of barium, lanthanum, and sulfur are +2, +3, and -2, respectively.

The measured density of the compound was 4.5(3) g cm⁻³. Since the theoretical density for BaLa₂MnS₅ was 4.70 g cm⁻³ ($Z = 4$), the measured density is in agreement with the theoretical density taking into account the experimental error.

The crystal structure of this compound was thought to be isostructural with tetragonal Cs₃CoCl₅ having space group $I4/mcm$, $Z = 4$ (13). In this crystal, cesium atoms are located in two different sites, Cs(1) and Cs(2) in $4a$ (0, 0, 1/4) and $8h$ ($x, x + 1/2, 0$) with $x = 0.167$, respectively. Cobalt atoms are in $4b$ (0, 1/2, 1/4). Chlorine atoms also occupy two different sites, Cl(1) and Cl(2) in $4c$ (0, 0, 0) and $16l$ ($x, x + 1/2, z$) with $x = 0.155$ and $z = 0.67$, respectively. Since barium and lanthanum ions in the present compound cannot be distinguished by X-ray diffraction because their electron numbers are the same, the crystal structure was refined assuming that the barium and lanthanum atoms are distributed statistically in the $4a$ and $8h$ positions. The manganese atoms are in $4b$, and the sulfur atoms are in the $4c$ and $16l$ positions, respectively. Profile fitting was performed using the program RIETAN based on the Rietveld method with the pseudo-Voigt fitting function in a 2θ range from 10 to 110° . Correction of 2θ (obs) was made. Three positional parameters, five isotropic temperature factors, and one scaling factor were calculated. As the temperature factor for barium and lanthanum in the same positional site, one value with

TABLE 1
Composition of Barium Lanthanum Manganese Sulfide (Atom Ratio Ba:La:Mn = 1:2:1) Determined by EPMA (Wt%)

Element	Ba	La	Mn	S
Measured	23.7(2.9) ^a	39.1(6.5) ^a	8.7(1.4) ^a	23.8(2.4) ^a
Theoretical (BaLa ₂ MnS ₅)	21.78	44.07	8.71	25.43

^a Values in parentheses are standard deviations.

an average character was used. The calculated pattern was in good agreement with that observed one ($R_{wp} = 13.22$, $R_p = 9.91$, $R_1 = 2.94$, and $R_F = 1.82\%$). It was concluded that the compound obtained has the formula $BaLa_2MnS_5$ and is isostructural with Cs_3CoCl_5 . The observed X-ray diffraction pattern of $BaLa_2MnS_5$ is shown in Fig. 1 as a dotted line. The refined peak profile by the Rietveld method is also shown as a solid line. The final refined structural parameters are listed in Table 2. The definitions of the reliability factors R_{wp} , R_p , R_1 , and R_F are given as footnotes to Table 2. Table 3 compares the intensities I_{calc} calculated by using the refined crystal data and atomic parameters with the observed integrated intensities I_{obs} obtained from the X-ray diffraction pattern. The interatomic distances are listed in Table 4.

As described above, it was not clear whether barium and lanthanum (1:2 atom ratio) were located in the $4a$ and $8h$ sites statistically or in an ordered manner. Attempts to prepare similar compounds, BaY_2MnS_5 , $SrLa_2MnS_5$, and $SrTb_2MnS_5$, resulted in formation of the products which were composed of a mixture of a few phases. The diffraction patterns of these mixtures gave no evidence that the desired compounds had the same crystal structure as the present compound. Under these circumstances, the Madelung energies, E_M , were calculated with the program MADEL (12) using the crystal data and atomic parameters obtained for the following three structure models by assuming that $BaLa_2MnS_5$ is ionic and that Ba, La, Mn, and S take on

+2, +3, +2 and -2 valencies, respectively. Model (1): The barium atoms are located in the $4a$ site and the lanthanum atoms in the $8h$ site in an ordered manner. Model (2): The barium and lanthanum atoms are randomly located in the $4a$ and $8h$ sites, similar to Cs_3CoCl_5 . Model (3): The lanthanum atoms occupy the $4a$ site and half of the $8h$ sites (occupancy factor 1/2). The barium atoms occupy the remaining half of the $8h$ site, as found for strontium in Sr_2EuMeO_5 ($Me = Fe$ and Al) (14). The results are shown in Table 5. As seen in this table, E_M has the lowest value for the disordered Model (2), although the E_M difference is small in the three models.

The structure of $BaLa_2MnS_5$ illustrated in Fig. 2 is based on stacking of the $MMnS_4$ ($M = Ba_{1/3}, La_{2/3}$) layer (A) and SM_4 layer (B), with the sequence ABAB... The coordination of atoms around S(1), M(1) in $4a$, and M(2) in $8h$ are shown in Figs. 3a, 3b, and 3c, respectively. The coordination numbers are 6 for sulfur, 10 for M(1), 8 for M(2), and 4 for manganese. As shown in Table 4, both the M(1)-2S(1) and M(1)-8S(2) distances (3.44-3.47 Å) are longer than the average ionic radius sum, 3.19 Å, obtained from Shannon's crystal radii (15) (1.66 Å for Ba^{2+} , 1.41 Å for La^{3+} with CN = 10, and 1.70 Å for S^{2-} with CN = 6). On the other hand, the M(2)-2S(1) and M(2)-2S(2) distances in Table 4 are shorter than the average ionic radius sum 3.09 Å (1.56 Å for Ba^{2+} and 1.30 Å for La^{3+} with CN = 8), although the M(2)-4S(2) distance 3.13 Å is slightly longer. The above variation suggests a significant effect of covalency in

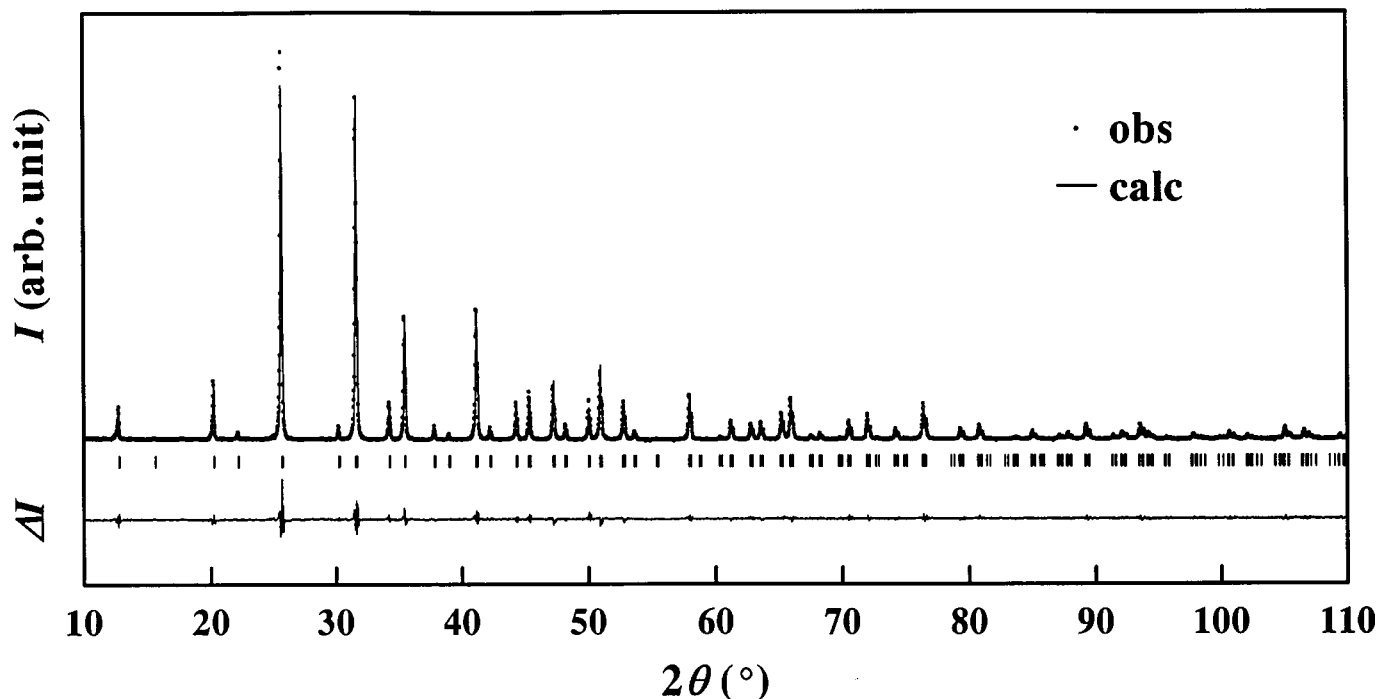


FIG. 1. X-ray powder diffraction profile of $BaLa_2MnS_5$ together with the final Rietveld refinement profile. ΔI is the difference in the intensities.

TABLE 2
Crystal Data and Atomic Parameters of BaLa₂MnS₅

Atom	Site	Atomic parameters				
		g^a	x	y	z	B (Å ²)
Ba(1)	4a	1/3	0	0	1/4	1.10(5)
Ba(2)	8h	1/3	0.1620(1)	0.6620	0	0.59(4)
La(1)	4a	2/3	0	0	1/4	1.10(5)
La(2)	8h	2/3	0.1620(1)	0.6620	0	0.59(4)
Mn	4b	1.0	0	1/2	1/4	1.01(11)
S(1)	4c	1.0	0	0	0	0.82(19)
S(2)	16l	1.0	0.1514(4)	0.6514	0.6352(2)	0.83(10)

Note. Crystal data (tetragonal, space group *I4/mcm* (No. 140)) $a = 8.014(2)$, $c = 13.867(3)$ Å, $V = 890.7$ Å³, $Z = 4$ (formula BaLa₂MnS₅), R values (17):

$$R_{wp} = \left\{ \frac{\sum w_i [y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2}{\sum w_i [y_i(\text{obs})]^2} \right\}^{1/2}$$

$$R_p = \frac{\sum |y_i(\text{obs}) - (1/c)y_i(\text{calc})|}{\sum y_i(\text{obs})}$$

$$R_I = \frac{\sum |I_K(\text{obs}) - I_K(\text{calc})|}{\sum I_K(\text{obs})}$$

$$R_F = \frac{\sum |[I_K(\text{obs})]^{1/2} - [I_K(\text{calc})]^{1/2}|}{\sum [I_K(\text{obs})]^{1/2}}$$

where $1/c$ is the scaling factor, w_i is the weight, y_i is the intensity at the i th step and I_K is the K th integrated intensity. $I_K(\text{obs})$ means calculated "observed" intensity.

^a g : occupancy factor.

BaLa₂MnS₅. It might also suggest some ordering of barium and lanthanum. The ionic radius sums become 3.36 and 3.00 Å if the 4a and 8h sites are exclusively occupied by Ba²⁺ and La³⁺, respectively.

The crystal structure of BaLa₂MnS₅ consists of MnS₄ tetrahedra in the plane perpendicular to the c -axis. These tetrahedra are linked via 4a M ($=1/3\text{Ba} + 2/3\text{La}$) atoms. The two planes of the tetrahedra are separated by a sheet composed of an infinite two-dimensional network of planar SM_4 groups, of which the M atoms are those in the 8h site. The variation in the distance of M -S described above is therefore considered to be linked to the form of the MnS₄ tetrahedra in the *I4/mcm* space group. The distance 2.34 Å for Mn-S is a little shorter than that calculated from the crystal radii 2.50 Å (0.80 Å for Mn²⁺, CN = 4). Here, the Madelung energy E_M was calculated as a function of atomic parameter x of S(2), which relates to the deformation of the MnS₄ tetrahedra. In the calculation, the atomic parameter z was constrained by fixing the distance of Mn-S(2) as 2.34 Å, i.e., the MnS₄ tetrahedra would be lengthened along the c -axis by decreasing the x value. The result is shown in

TABLE 3
Observed and Calculated Peak Positions and Intensities for BaLa₂MnS₅

h	k	l	d_{obs}	d_{calc}	I_{obs}	I_{calc}
0	0	2	6.954	6.933	8	8
1	1	2	4.392	4.388	13	15
2	0	0	4.012	4.007	2	2
2	1	1		3.470		26
2	0	2	3.471	3.469	100	52
0	0	4		3.467		22
1	1	4	2.959	2.957	3	3
2	2	0	2.832	2.834	91	18
2	1	3		2.832		73
2	2	2	2.623	2.623	11	4
2	0	4		2.622		7
3	1	0	2.535	2.534	34	33
3	1	2	2.380	2.380	4	4
0	0	6	2.311	2.311	2	2
2	2	4	2.193	2.194	39	14
2	1	5		2.193		25
1	1	6	2.139	2.140	3	3
3	1	4	2.046	2.046	11	10
3	2	3	2.001	2.003	14	1
2	0	6		2.002		12
4	1	1		1.925	17	5
4	0	2	1.924	1.925		12
3	3	0	1.889	1.889	5	5
3	3	2	1.822	1.823	11	10
4	2	0		1.792		11
4	1	3	1.791	1.792	24	12
2	2	6		1.791		1
4	2	2		1.735		1
4	0	4		1.735		2
2	1	7	1.733	1.734	13	2
0	0	8		1.733		8
3	1	6	1.707	1.708	3	3
4	2	4	1.591	1.592	16	9
4	1	5		1.592		6
5	1	2	1.532	1.533	1	1
4	0	6	1.513	1.514	7	7
5	2	1	1.478	1.480	6	2
2	2	8		1.479		4
3	3	6	1.461	1.463	7	7
3	1	8	1.430	1.431	9	9
4	4	0		1.417		3
5	2	3	1.415	1.417	17	10
2	1	9		1.416		3
4	1	7	1.386	1.387	2	1
5	3	0	1.374	1.374	2	2
6	0	0	1.335	1.336	7	6
4	4	4		1.311		2
5	2	5	1.310	1.311	10	6
2	0	10		1.310		2
5	1	6	1.300	1.300	1	1
5	3	4	1.276	1.278	5	3
3	3	8		1.277		2
5	4	1		1.247		1
6	2	2	1.245	1.247	15	4
6	0	4		1.246		4
4	2	8		1.246		6
5	4	3	1.207	1.208	6	4
4	1	9		1.207		2

TABLE 4
Interatomic Distances in BaLa₂MnS₅

	Distance (Å)
M(1) ^a -2 S(1)	3.467(1)
-8 S(2)	3.437(1)
M(2) ^b -2 S(1)	3.004(1)
-2 S(2)	2.826(1)
-4 S(2)	3.135(1)
Mn-4 S(2)	2.341(1)

^a M(1): (Ba_{1/3},La_{2/3}) in 4a.

^b M(2): (Ba_{1/3},La_{2/3}) in 8h.

TABLE 5
Madelung Energies E_M for the Three Models of BaLa₂MnS₅

Model number	Structure type	Site				E_M (10 ³ kJmol ⁻¹)
		4a	g^a	8h	g^a	
Model (1)	Ordered Cs ₃ CoCl ₅	Ba	1.0	La	1.0	-75.01
Model (2)	Cs ₃ CoCl ₅	Ba	1/3	Ba	1/3	-75.81
Model (3)	Sr ₂ EuMeO ₅ (Me = Fe, Al)	La	2/3	La	2/3	-75.07
		La	1.0	Ba	1/2	
				La	1/2	

^a g : occupancy factor.

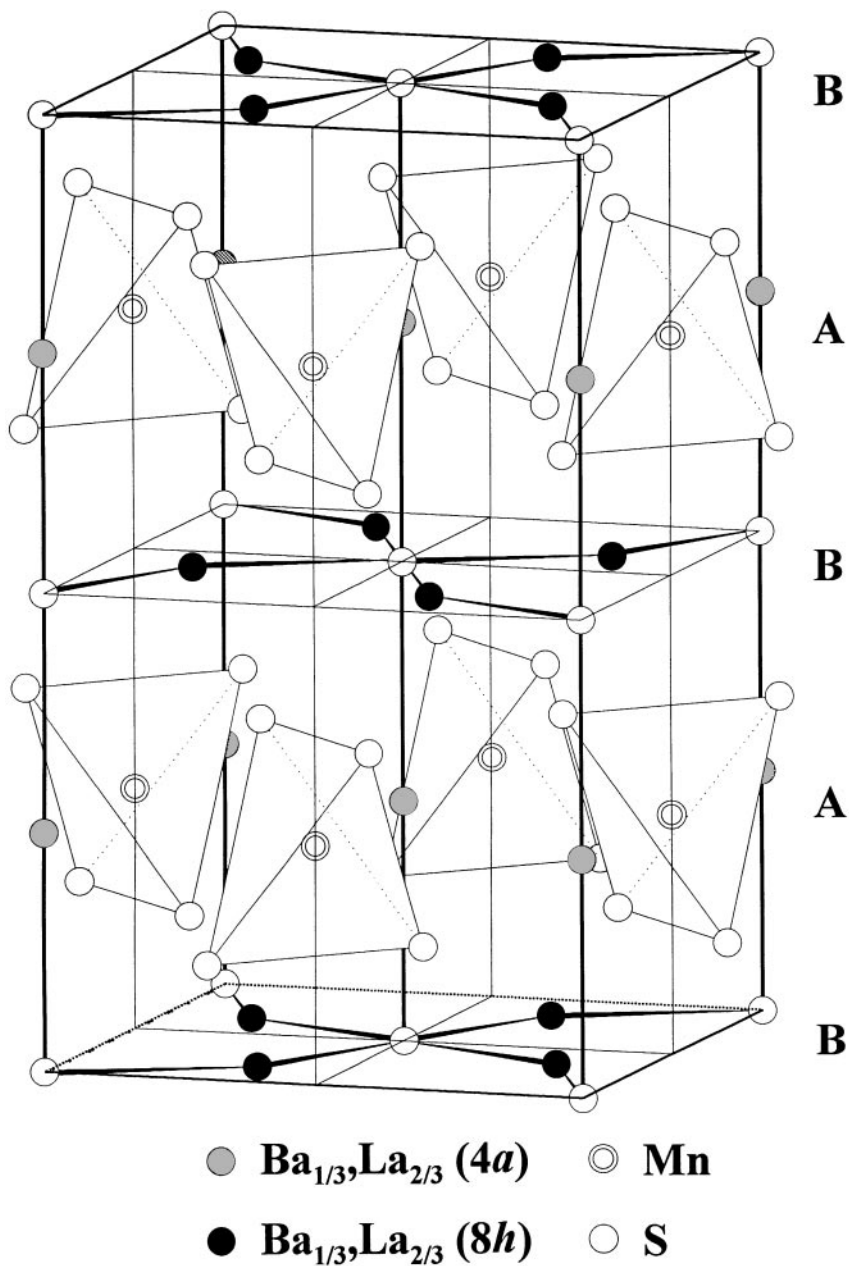


FIG. 2. Crystal structure of BaLa₂MnS₅.

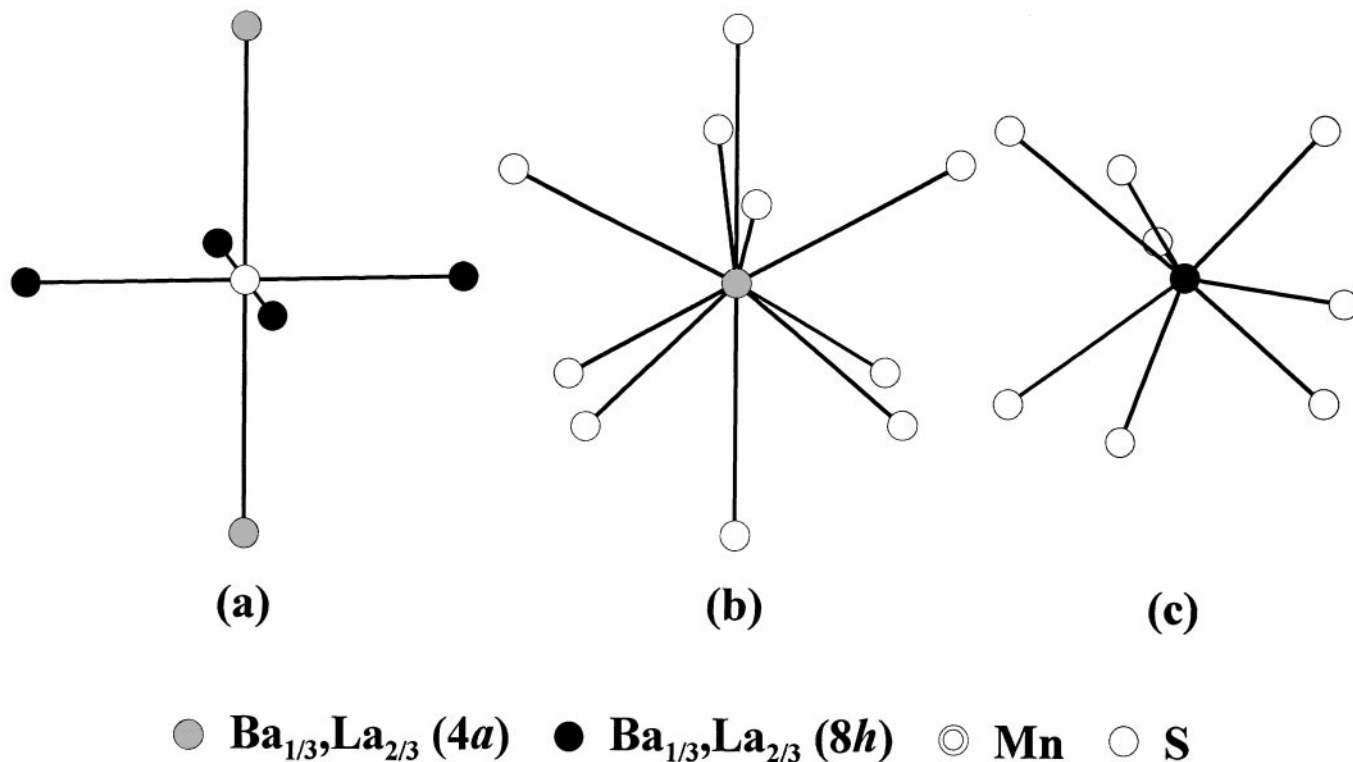


FIG. 3. Coordination of atoms. (a): $M(1)$ and $M(2)$ atoms around $S(1)$; (b) and (c): sulfur atoms around $M(1)$ and $M(2)$, respectively.

Fig. 4. The lowest E_M was obtained at $x = 0.14$; a slight deviation from the experimentally determined value of $x = 0.151$ (Rietveld result). With $x = 0.14$, the distances of

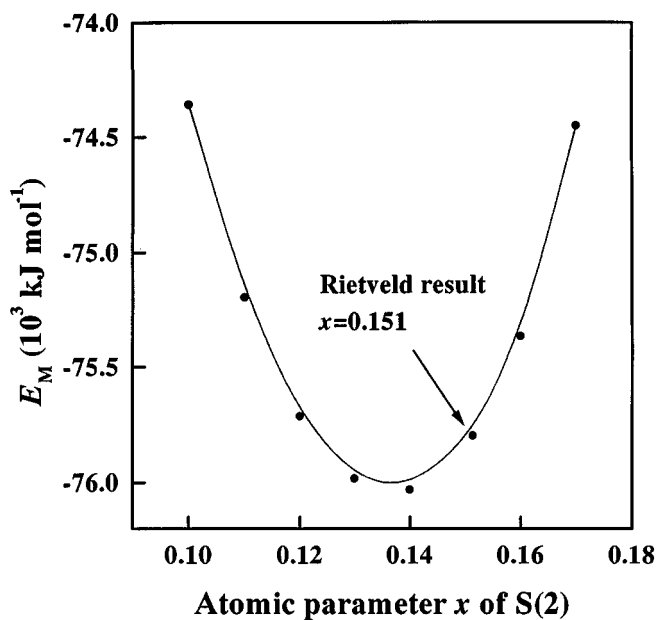


FIG. 4. Madelung energy, E_M , as a function of atomic parameter x of $S(2)$ in $\text{BaLa}_2\text{MnS}_5$.

$M(1)-8S(2)$, $M(2)-2S(2)$, and $M(2)-4S(2)$ are given as 3.54, 2.84, and 2.99 Å, respectively, which deviate more from the ionic radius sum than the actual crystal.

The temperature dependence of the specific resistivity ρ for a sintered pellet of $\text{BaLa}_2\text{MnS}_5$ is shown in Fig. 5. The measured densities of the pellet were $\sim 85\%$ of theoretical as calculated from the dimensions of the pellet. Correction for porosity was not made to the resistivity data. The small peak around 50 K is ascribed to the noise in measurement. Since no significant hysteresis was observed in the measured specific resistivities in the heating and cooling processes, only the heating curve is depicted in the figure. The magnitude of the resistivity is on the order of $10^{-2} \Omega \text{ m}$. The negative temperature dependence and the relatively high resistivity value suggest that this compound is a semiconductor. The resistance was unaffected by a magnetic field (0.58 T) applied perpendicular to the pellet.

Figure 6 shows the Hall coefficient, R_H , as a function of temperature. Since the Hall coefficients are negative, this compound is basically n -type. The carrier concentration, n , and the Hall mobility, μ , were calculated on the basis of the single-carrier model. The carrier density at 300 K was estimated to be as low as 6.84×10^{-6} per molecule of $\text{BaLa}_2\text{MnS}_5$. Figure 7 shows a plot of $\ln(n)$ versus $1/T$. As seen in this figure, two temperature ranges can be distinguished. At low temperatures below 100 K, $\ln(n)$ is almost

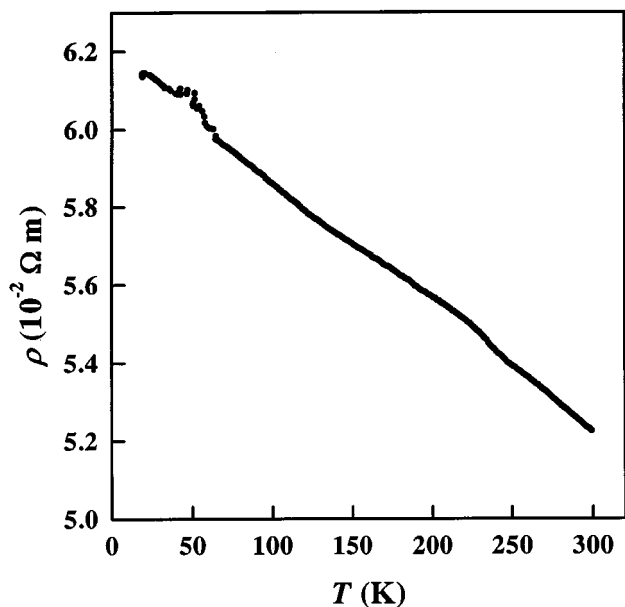


FIG. 5. Specific resistivity, ρ , as a function of temperature for $\text{BaLa}_2\text{MnS}_5$.

independent of temperature. The carriers of lower concentrations in this temperature range are considered to be formed either by slight nonstoichiometry or by the increased covalency of the compound. At high temperatures above 200 K, $\ln(n)$ increases linearly with increasing temperature. The activation energy was calculated in the range above 200 K by using the equation

$$n(T) = A \exp[-E_a/2k_B T],$$

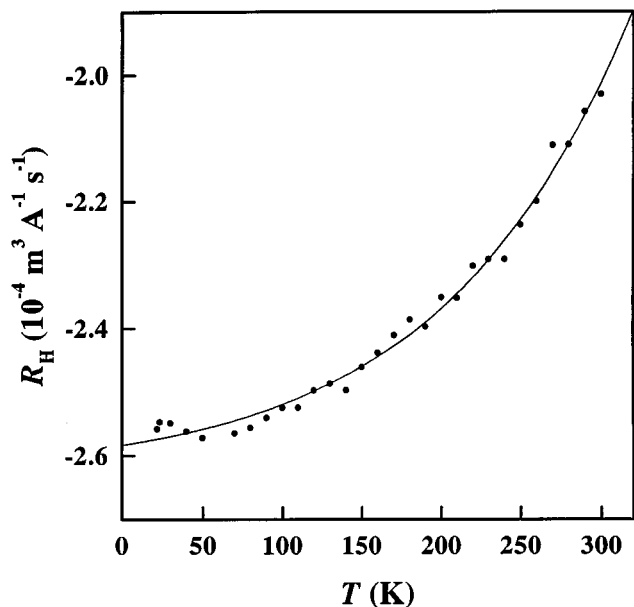


FIG. 6. Hall coefficient, R_H , as a function of temperature for $\text{BaLa}_2\text{MnS}_5$.

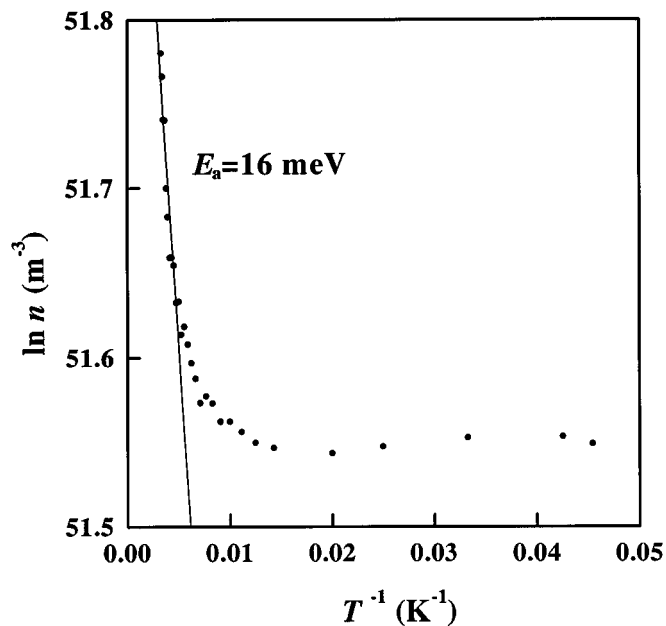


FIG. 7. Plot of $\ln n$ vs $1/T$ for $\text{BaLa}_2\text{MnS}_5$.

where A is the temperature-independent constant and k_B is the Boltzmann constant. The activation energy, E_a , was obtained as 16 meV. This small E_a value can be explained by the impurity donor level present just below the bottom of the conduction band. Figure 8 shows the temperature dependence of the Hall mobility on a logarithmic scale. At temperatures below 150 K, the temperature dependence of the Hall mobility is very weak ($\sim T^{0.03}$ slope) suggesting that the dominant scattering mechanism is neutral impurity scattering (16). At temperatures higher than 240 K, the Hall

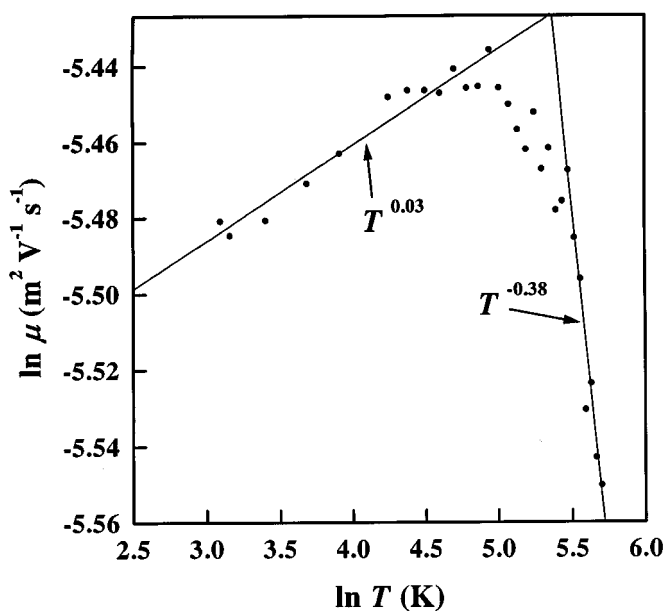


FIG. 8. Plot of $\ln \mu$ vs $\ln T$ for $\text{BaLa}_2\text{MnS}_5$.

TABLE 6
Electrical Properties of BaLa₂MnS₅ at 300 K

ρ (10 ⁻² Ωm)	R_H (10 ⁻⁴ m ³ A ⁻¹ s ⁻¹)	n (10 ²² m ⁻³)	μ (10 ⁻³ m ² V ⁻¹ s ⁻¹)
5.22	- 2.03	3.07	3.89

mobility decreases with increasing temperature ($\sim T^{-0.38}$ slope) in a direction less than the $T^{-3/2}$ slope for electron-phonon scattering (16). The electrical data at 300 K are summarized in Table 6.

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