JOURNAL OF SOLID STATE CHEMISTRY 12, 80–83 (1975)

Preparation and Properties of $LnMX_3$, where Ln = Rare Earths, Bi; M = Ta, Nb, Ti, V, and X = S, Se*

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Received January 31, 1974

Compounds were prepared of the general formula $LnMX_3$ (where Ln = all rare earths or Bi, X = S, and M = Ta or Nb; Ln = La through Tb, X = S, and M = Ti or V; Ln = La through Gd, X = Se, and M = Ta or Nb; Ln = La, X = Se, and M = Ti or V).

They were prepared by reaction of the elements in evacuated silica tubes with iodine as a mineralizing agent. They form as black shiny lamella crystals which exhibit plastic deformation, good thermal and hydrolytic stability, low coefficients of friction, and metallic conductivity. The crystal structures have subcells like $PbNbS_3$ but the actual cells are larger and more complex. $LaTiS_3$ is isotypic with $LaCrS_3$.

Introduction

Reported chalcogenides of general formula $LnMS_3$ include $LaMS_3$ (M = Cr, Mn, Fe and Co) (*1*), $LnCrS_3$ (*2*), $LnAlS_3$ (*3*), and $LnCrSe_3$ (*4*).

$LnCrS_3$ exhibit lamella-type crystal habits and large monoclinic cells (*1*, *2*). Compositions in this series are semiconductors.

Compounds of the general formula $M^{II}M^{IV}S_3$ include $BaM^{IV}S_3$ which have perovskite-type structures for M^{IV} = Zr, Hf (*5*) and $BaNiO_3$-type structures for M^{IV} = Ti and V (*5*, *6*). The compounds $PbTiS_3$, $PbNbS_3$, and $PbTaS_3$ exhibit tetragonal crystal structure and metallic conductivity (*7*, *8*). No compounds have been reported of the formula $LnMX_3$ (M = Ti, V, Nb, Ta, and X = S, Se).

Experimental

All reactions were carried out with the elements and a catalytic amount of I_2 in dried, evacuated silica tubes, the insides of which were coated with carbon by pyrolysis of toluene. Rare earths of about 99.9% purity were obtained commercially. The more active rare earths, La through Eu, were cut in a N_2-filled dry box and weighed under N_2. The rare earths Gd through Yb and Y were obtained as lumpy sponges or filings and could be handled in air. Elemental Ti, V ,Nb and Ta of between 99.9 and 99.99% purity were used in powdered form for convenience. Sulfur and Se were 99.999% pure.

The elements were placed in the tubes with about 0.05 g I_2. The tubes were evacuated, quickly sealed and heated in natural gradient furnaces. The tubes measured about 15 mm o.d./12 mm i.d. × 6 in. and were positioned in the furnaces so that the ends containing the elements were near the centers of the furnaces while the other ends were at the furnace openings. They were initially heated at low temperature until the S reacted. After all the S was taken up, they could be heated at any temperature up to the softening point of silica. A typical heating cycle is described as follows. The center of the furnace was heated between 400 and 600°C for about 48 hr, then about 800°C for 24 hr. When all the S was

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* Contribution No. 2114.

Printed in Great Britain

taken up, the entire tube was heated between 1000 and 1200°C for 24–72 hr. At any stage of heating, the tube could be removed and shaken to better mix the reactants. In some cases, when all S or Se was taken up, the tubes were opened, the products ground in an agate mortar, resealed in a silica tube, and reheated.

The products generally formed as a mass of small black crystals with some larger (~0.5 cm) platelike crystals. The products were identified by X-ray powder diffraction. Since all distinguishable regions (small and large crystals) showed the same powder pattern, the stoichiometry was assumed to be that of the starting ratio. In some cases, large black flakes were separated to be sure of having a single phase, and analysed.

Electrical resistivities were measured by a four-probe method on single crystals.

Results and Discussion

Figure 1 illustrates the combinations of elements which form isotypic $LnMX_3$-type phases. Not included are $BiNbS_3$ and $BiTaS_3$. Since rare earths exhibit a regular decrease in ionic radii with increasing atomic number, combinations lying between Ln ions marked + may be assumed to be possible by interpolation. An exception is $EuTiS_3$ which forms a different structure, no doubt due to the stability of Eu^{2+}.

The extent of phase formation under the conditions described is related to the anion to cation radius ratio.

The phases are isotypic in a qualitative sense, and more X-ray characterization is desirable. All phases have powder patterns which resemble those of $PbNbS_3$ and $PbTaS_3$, reported to be tetragonal (*8*) ($PbNbS_3$, $a = 4.07$ Å, $c = 11.92$ Å). All the peaks in the powder patterns could not be indexed with analogous tetragonal cells. The powder patterns of several phases are shown in Table I. Because the crystalline habit is flaky and exhibits easy plastic deformation, single crystal studies were not possible for most compositions. Crystals of $LaTiS_3$ and $YbTaS_3$ were less bendable than other members of the series and were used for single crystal determinations of the cell size and space group. The cells could not be unambiguously derived because of suspected twinning. The tentative cells have dimensions:

$LaTiS_3$ $a = 5.9$ Å $b = 17.18$ A $c = 11.2$ A
$\beta = 95°$.
$YbTaS_3$ $a = 5.6$ Å $b = 14.2$ Å $c = 11.8$ Å
$\beta = 91°$.

The cell of $LaTiS_3$ is like that reported for $LaCrS_3$ (*2*). Although all the subcells are similar, many variations appear to be possible, probably due to various stacking sequences. Güinier camera data of $PbNbS_3$ also showed peaks not indexable, using the reported tetragonal cell.

Since the powder patterns of the bulk materials were the same as powder patterns from ground crystals, the materials are single phase with stoichiometry of the reactants. Chemical analysis on crystals separated from the bulk showed fairly good correspondence,

$LnMS_3$

M	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Ti	+					+			+							
V	+					+			+							
Nb	+	+				+	+	+			+			+		
Ta	+	+				+		+						+		+

$LnMSe_3$

M	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Ti	+															
V	+															
Nb	+							+								
Ta	+							+								

FIG. 1. Compounds prepared of formula $LnMX_3$; X = S, Se + indicates compound was prepared)

TABLE I

Some Debye-Scherer Powder Patterns of $LnMX_3$ Phases

$PbNbS_3$		$LaTaS_3$		$SmTaS_3$		$YbTaS_3$		$LaNbSe_3$		$LaTiS_3$	
I_{obsd}	d_{obsd}	I_{obsd}	d_{obsd}	I_{obsd}	d_{obsd}	I_{obsd}	d_{obsd}	I_{obsd}	d_{obsd}	I_{obsd}	d_{obsd}
20	11.51	60	11.321	50	11.173	30	10.964	80	12.303	30	3.859
60	5.934	70	5.711	60	5.620	65	5.527	60	11.818	100	3.741
100	3.953	100	3.813	100	3.741	35	3.823	25	6.083	100	2.931
70	2.965					100	3.691	45	5.961	80	2.860
						30	3.440				
80	2.877	10	2.880	30	2.825	30	2.731	40	4.034	50	2.799
80	2.808	5	2.805	20	2.761	20	2.683	80	3.986	50	2.461
10	2.596	10	2.668	10	2.533	10	2.615	60	3.019	20	2.315
20	2.373	10	2.576	40	2.262	60	2.239	100	2.995	10	2.175
70	2.332	10	2.422	2	1.987	35	2.217	30	2.960	70	2.044
5	2.067	50	2.298	40	1.873	10	1.975	70	2.913	60	1.810
10	2.031	5	2.039	20	1.762	20	1.940	100	2.399	30	1.701
10	1.981	40	1.910			10	1.919	10	2.249		
20	1.836	10	1.796			35	1.847	20	2.122		
								20	2.092		
								40	1.999		

considering the sample size. The possibility of some nonstoichiometry is not excluded.

Analysis. Calcd for $GdNbS_3$: 45.50% Gd, 26.82% Nb, 27.76% S. Found: 43.39% Gd, 24.48% Nb, 23.34% S. Calcd for $BiNbS_3$: 52.50% Bi, 23.34% Nb, 24.16% S. Found: 54.9% Bi, 25.04% Nb, 25.43% S. Calcd for $SmNbS_3$: 27.36% Nb, 28.34% S. Found: 25.7% Nb, 27.97% S.

The materials are unexpectedly stable in dilute HCl, considering the instability of Ln_2S_3 toward hydrolysis. Thermally they decompose at elevated temperature. Figure 2 shows the results of TGA on several samples in air. As can be seen, these compositions are more stable than lubrication grade MoS_2, The Ta compositions are the most stable.

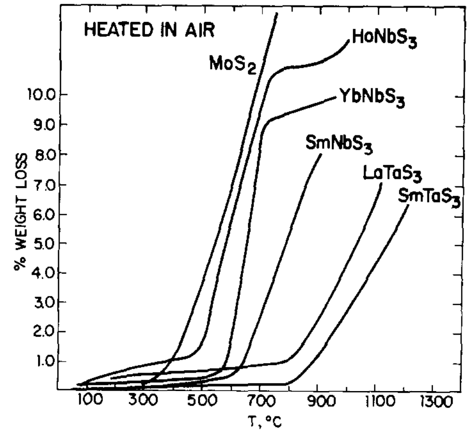

Fig. 2. Percent Wt. loss of some $LnMX_3$ phases vs temperature when heated in air.

Because of the crystalline habit, it was proposed that these materials may be useful as solid lubricants. Tests of coefficient of friction were made on 325 mesh powders. The results are as follows: $SmNbS_3$, 0.21; $HoNbS_3$, 0.22; $GdTaS_3$, 0.21; $GdNbS_3$, 0.60. In comparison we observed values between 0.1 and 0.18 for commercial lubrication grade MoS_2.

TABLE II

Electrical Resistivities on $LnMX_3$

Material	ρ298 K in Ω-cm	ρ4.2 K in Ω-cm
$LaTaS_3$	3.9×10^{-4}	1.1×10^{-4}
$YbTaS_3$	1.6×10^{-4}	2.5×10^{-5}
$LaTaSe_3$	1.5×10^{-4}	4.0×10^{-5}
$GdTaS_3$	1.1×10^{-4}	4.3×10^{-5}
$LaTiS_3$	2.2×10^{-4}	6×10^{-5}
$SmNbS_3$	4×10^{-4}	2×10^{-4}

Metallic conductivity was observed on all crystals measured. The results are shown in Table II.

In comparison, $LnCrX_3$ compositions are semiconductors. The semiconduction can be understood in terms of a combination of Ln^{3+} and octahedral Cr^{3+}. These ions should have their remaining electrons on low lying states. The metallic conduction of $LnMX_3$ is probably due to the presence of M ions in trivalent states having their remaining electrons in high lying levels available for conduction.

Note added in proof. Emission spectroscopy of $CeTaS_3$ and $BiNbS_3$ showed only 50–250 ppm.

Acknowledgments

We wish to thank Mr. D. W. Reutter for sample preparations, C. M. Foris for determining cell dimensions, Dr. J. F. Whitney and his staff in the X-ray diffraction section, Mr. H. W. Williams for TGA measurements, Mr. H. A. Selz for determining coefficients of friction, Mr. R. J. Berndt for S analysis, Mr. W. M. Kipp for cation analyses, and Mr. J. L. Gillson for electrical measurements.

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