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High-Pressure Synthesis of Rare Earth Dimanganese Compounds with the $MgZn_2$ (Laves) Structure¹

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Laves structures of the $MgZn_2$ type were synthesized for $GdMn_2$, $TbMn_2$, $DyMn_2$, $HoMn_2$, $Y Mn_2$, and $YbMn_2$ under high-temperature and high-pressure conditions. All but the Yb compound were previously known only in the $MgCu_2$ structure. $YbMn_2$ had not been prepared before this work. Also the synthesis of $ErMn_2$ was verified and $SmMn_2$ was prepared at high pressure.

Introduction

The rare earth dimanganese ($RE Mn_2$) compounds are known to exhibit some interesting changes in crystal structure as the atomic number of the rare earth

varies.³ Both the light and heavy rare earths (at 1 atm) form $RE Mn_2$ compounds in the C14 ($MgZn_2$) Laves structure while the intermediate rare earths form $RE Mn_2$ compounds in the C15 ($MgCu_2$) Laves structure. This information is summarized in Table I as are, also, the high-pressure results of this paper.

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TABLE I
 CRYSTAL STRUCTURES OF REMn₂ COMPOUNDS^a

	Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1 atm	H	C	X	X	H	H	X	C,H	X	C	C	C	C	C,H	H	X	H
High pressure		H			X	X		H		H	H	H	H	H	H	H	H

^a H, C14 (MgZn₂) type (hexagonal); C, C15 (MgCu₂) type (fcc); and X, no known compound.

LaMn₂ and CeMn₂ have not been prepared. PrMn₂ has been reported in the C14 phase⁴ but Oesterreicher reports that he could not duplicate this reported result. Rather, he obtained an α Mn type and a Th₆Mn₂₃ type.^{5,6}

By application of high pressure simultaneously with high temperature, we have synthesized the MgZn₂ type structure for the dimanganides of Gd, Tb, Dy, Ho, and Y which were previously known only in the MgCu₂ structure and also YbMn₂ which was previously unknown. The compound SmMn₂, which has reportedly been synthesized at 1 atm in both Laves phases, could not be prepared by us at pressures below 50 kbar. Neither could we prepare the previously reported NdMn₂ in the pressure range covered by this work.

Experimental Section

The syntheses were carried out by application of high temperature at high pressure to a stoichiometric mixture of the elements in a tetrahedral anvil apparatus.^{7,8} The procedure and sample geometry were the same as has been described previously.⁹ Runs were carried out at 1300–1400° for 1 min followed by rapid quenching to room temperature and then release of pressure. Run times up to 2 hr and temperatures up to 2000° at 70 kbar were tried on the Nd–Mn system without success.

The rare earth metals were obtained from Research Chemicals, Inc., Burbank, Calif. Manganese was obtained from Baker Chemical Co. The metals were filed or crushed in air and particles passing a 100-mesh sieve were used for synthesis.

Products from the runs were crushed between two polished WC blocks and loaded in 0.5-mm glass capillaries; X-ray diffraction patterns were obtained with a 143.2 mm diameter Debye–Scherrer camera on a G. E. XRD-5 unit. Chromium (λ 2.29092 Å) radiation and V₂O₅ filters were used. Lattice parameters were obtained by a least-squares fit of 12–24 d values depending upon the pattern. The MgZn₂ type structures were identified by comparison of the X-ray diffraction patterns with the pattern for ErMn₂ of Wernick and Haszko.¹⁰ All diffraction lines were indexed to the MgZn₂ structure except for GdMn₂ which showed some weak lines from an unidentified impurity. It was concluded that the products were single phase.

Results

Table II shows the lattice parameters and calculated densities obtained in this study. These parameters give a smooth transition between the previously reported values for the light and heavy REMn₂ hexagonal compounds.

The minimum pressure required for synthesis of the MgZn₂ structure is shown in Figure 1. Although the synthesis of MgZn₂-type dimanganides of Pr, Nd, and Sm has been reported at 1 atm,^{3,4} we could not synthe-

 TABLE II
 LATTICE PARAMETERS OF HEXAGONAL REMn₂ COMPOUNDS

	a_0 , Å	c_0 , Å	Density, g/cm ³
ErMn ₂	5.274 ± 4	8.626 ± 6	8.86
HoMn ₂	5.316 ± 2	8.672 ± 3	8.60
DyMn ₂	5.356 ± 3	8.744 ± 5	8.33
TbMn ₂	5.390 ± 3	8.786 ± 5	8.08
GdMn ₂	5.447 ± 3	8.893 ± 5	7.76
SmMn ₂	5.501 ± 2	8.968 ± 4	7.36
YbMn ₂	5.233 ± 3	8.561 ± 5	9.26
YMn ₂	5.404 ± 7	8.848 ± 10	5.90

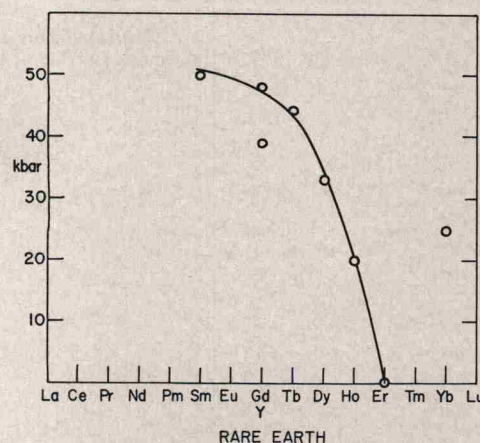


Figure 1.—Minimum pressure required for the synthesis of hexagonal REMn₂.

size SmMn₂ below 50 kbar and could not obtain NdMn₂ or PrMn₂ at any pressure between 10 and 70 kbar.

Discussion

Laves phases of AB₂ compounds are known with d_A/d_B ratios from 1.05 to 1.68 and it has been shown that there is no correlation between Laves structure type and the atomic diameter ratio.¹¹ Since all rare earth dimanganide compounds fall within this range of diameter ratios, the existence of the structure transition from hexagonal to cubic and back to hexagonal as the atomic number of the rare earth increases (1 atm synthesis) shows that other effects must be more important in determining which Laves structure is stable in this series.

The densities of the MgCu₂ and the MgZn₂ structures calculated from lattice parameters obtained at 1 atm are virtually identical and there is no reason to suspect a significant difference in compressibility of the two structures. Therefore, density differences do not seem to be a determining factor in forming one structure type in preference to another as has been found in other systems.¹²

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