Mat. Res. Bull. Vol. 11, pp. 227-232, 1976. Pergamon Press, Inc.
Printed in the United States.

TRANSITION OF SULFOSPINEL TO Th_3P_4 TYPE PHASE UNDER PRESSURE

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(Received May 22, 1975; Refereed)

ABSTRACT

Sulfospinels AB_2S_4 (A=Mg, Mn, B=Tm, Yb) were treated at 1000°C and 55 kbar for 1h. The X-ray powder diffractions were completely indexed by assuming that the products were isostructural with Th_3P_4. The results of density measurements showed a good agreement with those calculated from the X-ray data. No magnetic ordering was observed in temperatures down to 77K.

Introduction

In compound AB_2S_4, various types of structures are found when different combinations of cations are chosen. The representative structures are Ag_2HgI_4, spinel, NiAs and Th_3P_4 types (1, 2). High pressure experiments on these phases reveal that some of them convert to denser structures such as from spinel to NiAs type (3). It is commonly accepted that the coordination numbers of constituent elements in a substance are enhanced by compression and those of cations in spinel type phase increase from (4, 6) to (6, 6) in the above-mentioned example. Since Th ions in Th_3P_4 are located in dodecahedral sites, the cations in the compounds with Th_3P_4 type structure have the highest coordinations in AB_2S_4. No high pressure experiment, however, has ever been reported in which AB_2S_4 transforms from spinel or NiAs to the Th_3P_4 type phase. Some experiments were attempted to investigate this possibility of phase transformation. The results will be reported here.

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TABLE 1

X-ray powder and density data of AB_2S_4 treated at 1200°C and 55 kbar. The calculated d-spacings were obtained by assuming the crystal structure of Th_3P_4 type. The calculated densities were obtained from the lattice constants mentioned in this table.

			$MgTm_2S_4$		$MgYb_2S_4$		$MnTm_2S_4$		$MnYb_2S_4$	
	hkl	I	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
X-ray data	211	s	3.356	3.355	3.351	3.353	3.356	3.356	3.353	3.348
	220	vw	2.899	2.905						
	310	vs	2.601	2.599	2.597	2.597	2.601	2.599	2.598	2.594
	321	s	2.197	2.196	2.194	2.195	2.197	2.197	2.193	2.192
	420	s	1.839	1.838	1.837	1.837	1.837	1.838	1.834	1.834
	332	w	1.752	1.752	1.751	1.751	1.752	1.752	1.749	1.749
	510 431	w	1.612	1.612	1.611	1.611	1.611	1.612	1.609	1.609
	611 532	w	1.333	1.333	1.332	1.332	1.334	1.333	1.330	1.331
	620	vw	1.299	1.299	1.299	1.299	1.300	1.300		
	541	vw	1.268	1.268	1.267	1.267	1.269	1.268		
			a=8.218 Å		a=8.213 Å		a=8.220 Å		a=8.202 Å	
Densities			D_{meas}	D_{calc}	D_{meas}	D_{calc}	D_{meas}	D_{calc}	D_{meas}	D_{calc}
			5.8	5.87	5.9	5.98	6.2	6.23	6.3	6.37

Experimental

The starting material of AB_2S_4 (A=Mg, Mn, B=Tm, Yb) was prepared by mixing the powders of MgO, $MnCO_3 \cdot xH_2O$ and B_2O_3 in the molar ratio. Both MgO and $MnCO_3$ were guaranteed reagent prepared by Merck. The B_2O_3 was made by Shin-etsu Chemical Co Ltd with the purities of 99.9%. Each material was heated at 1200°C for 1h in the flow of H_2S. The sample was cooled, ground and heated in an evacuated silica tube with a small amount of sulfur at 1200°C for 24h. The material obtained in this manner was confirmed to possess the spinel type structure by X-ray diffraction. The starting material was then treated at 1200°C and 55 kbar using the high pressure device described by Yanagisawa et al (4). After the treatment for 1h, the sample was cooled down to room temperature and taken out of the pressure cell.

The product was examined by an ore microscope and X-ray powder diffraction. The diffractometer was scanned with 0.5°/min. The powder data were recorded using the Ni-filtered Cu-Kα radiation. The error in the calculation of d-spacings was within ±0.003Å. The density was measured with a pycnometer. The weight of sample used for the density measurement was about 0.1g, which is the amount produced in one run of high pressure experiment. Three results of measurements using different samples were averaged and the final density was obtained, the error being less than 3%. The magnetic susceptibility was measured in the temperature range from 77K to 300K using the device described by Shimada et al (5). The absolute value was determined by the use of Mohr's salt as a standard. The electric conductivity at room temperature was obtained by a conventional four probe technique. The distance between two probes was 0.25mm. The sample taken out of the pressure cell was trimmed

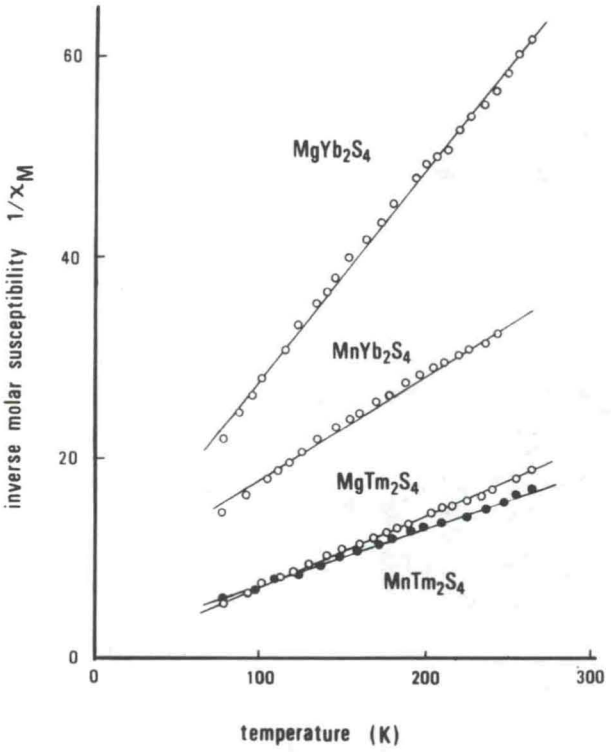


FIG. 1

reciprocal of molar susceptibility as a function of temperature in the range from 80K to 300K.

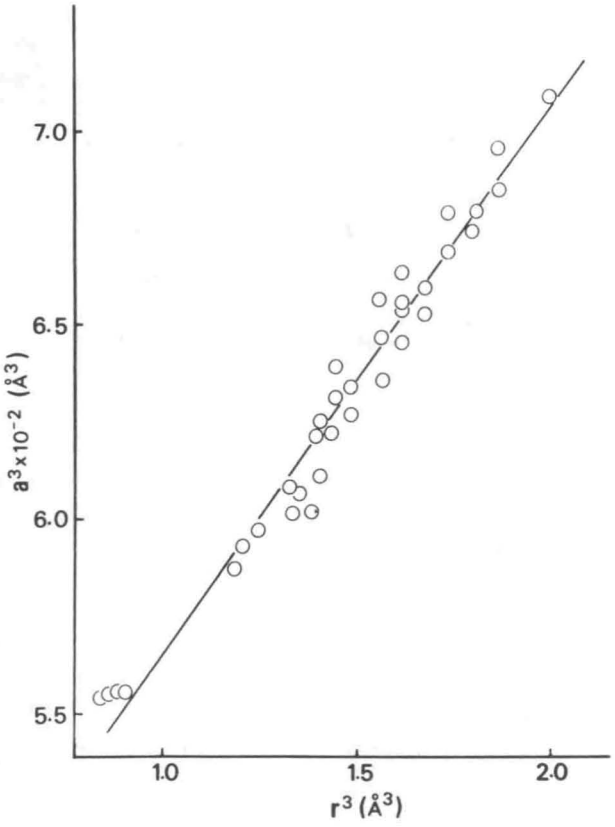


FIG. 2

Relation between unit cell volume a^3 and parameter r^3 in compounds AB_2S_4 with Th_3P_4 type structure. the parameter r is defined as $r=(r_A+2r_B)/3$ where r_A and r_B are The ionic radii of cation A and B respectively.

in the shape of cylinder 2.8mm in diameter and 3mm long.

Results

The observations under an ore microscope showed that the products always consisted of a single phase. The X-ray powder diffraction patterns were similar to Th_3P_4. Assuming that this structure was correct, the lattice constants were calculated. Table 1 is the X-ray data of the products. A good agreement between the observed and the calculated values is seen in every case. The measured and theoretical densities are also tabulated in this Table. A consistency is found between these two values.

The changes in magnetic susceptibility with temperature are illustrated in Fig. 1. The electric conductivities of all samples were in the order of 10^{-11} to 10^{-14} per ohm-cm at room temperature.

Considerations and Discussions

The X-ray data indicate that spinel type AB_2S_4 (A=Mg, Mn; B=Tm, Yb) transforms to a Th_3P_4 type phase under pressure. Good agreement between observed and theoretical densities is another proof that the high pressure products crystallize in the Th_3P_4 type. The volume change accompanied with the transition is in the order of 15.5% in $MnTm_2S_4$ to 15.9% in $MnYb_2S_4$. This new phase reverted to spinel type on heating at 1200°C for 2h in a sealed silica tube. The coordinations of cations in spinel are 4 and 6 folded. In Th_3P_4, all cations are in the dodecahedral site. Consequently, the increase of coordination number accompanied with the transition is seen in the present experiments.

Flahaut (3) finds a relation between ionic radii of cations and lattice constants of compounds AB_2S_4 with Th_3P_4 type. This relation is revised by using more recent values of radii reported by Schannon and Prewitt (6) and is shown in Fig. 2. When the relation is extrapolated towards the smaller side of the radii, it crosses the position corresponding to the compounds investigated in the present work. It is reasonable, therefore, that AB_2S_4 crystallizes to Th_3P_4 type structure under pressures when A=Mg, Mn and B=Tm, Yb. It is also predicted that the compounds such as $CdLu_2S_4$ or $CaLu_2S_4$ form the Th_3P_4 type phase under some adequate conditions of synthesis and their lattice constants would be about 8.3Å.

The changes of magnetic susceptibilities with temperature appear to obey the Curie-Weiss' law, indicating that all products behave paramagnetically in temperatures down to 77K. The molar Curie constants, C_m, are obtained in the same way as those described by Longo and Raccah (7) and also by Suchow and Ando (8). The values are listed in Table 2 together with the paramagnetic Curie temperatures and C_m of the same compounds with spinel structure.

The calculated Curie constants are obtained by the assumption that no magnetic interactions exist between adjacent ions. The difference between the observed and calculated values are small. This fact suggests that no magnetic long-range ordering exists in Th_3P_4 type phases and this configuration is also observed in spinel type phases as seen in Table 2.

TABLE 2

Molar Curie constant, C_m, and paramagnetic Curie temperature, θ, of AB_2S_4 with Th_3P_4 and spinel type structures. The calculated Curie constants are the sum of Curie constants of individual ions given by the following relations (5), (6):

$C_m(\text{ind}) = \mu^2_{\text{eff}}/2.84^2$ where

$\mu_{\text{eff}}(\text{Tm, Yb}) = g\sqrt{J(J+1)}$ and $\mu_{\text{eff}}(\text{Mn}) = g\sqrt{s(s+1)}$.

	Th_3P_4 type		Spinel type		C_m
	C_m	θ(K)	C_m	θ(K)	Calc.
$MgTm_2S_4$	14.6	- 8	14.7	-17	14.2
$MgYb_2S_4$	4.9	-39	4.4	-60	5.1
$MnTm_2S_4$	17.1	-26	18.0	- 3	18.6
$MnYb_2S_4$	9.1	-63	10.0*	-54	9.5

* ref.(5) C_m= 9.52 θ=-50~-60
ref.(6) C_m=10.1 θ=-30

Acknowledgment

This work was partly supported by a Scientific Research Fund from the Ministry of Education.

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