Preparations and Properties of Magnesium, Copper, Zinc and Cadmium Dichalcogenides

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The preparations and properties of MX_2 compounds (M = Mg, Cu, Zn, Cd; X = O, S, Se, Te) have been investigated. Structural data for the FeS_2-p type phases MgO_2 and $MgTe_2$ are reported.

The structure type FeS_2-p (p = pyrite) and FeS_2-m (m = marcasite) occur mainly among the transition metal dipnictides and dichalcogenides, and some thirty years ago, these compounds were believed to constitute the complete family. However, the FeS_2-p type structure has later been reported for NaO_2,[1,2] MgO_2,[3] $MgTe_2$,[4] ZnO_2,[5] ZnS_2,[6] $ZnSe_2$,[6] CdO_2,[7,8] CdS_2,[6] $CdSe_2$,[6] SiP_2[9] and $SiAs_2$.[9] (For NaO_2 the FeS_2-m type also occurs as a low temperature modification.[1,2]) The present communication concerns preparations and properties of compounds with general formulae MgX_2, CuX_2, ZnX_2 and CdX_2 (X = O, S, Se, Te).

EXPERIMENTAL

Starting materials were *inter alia p.a.* grade $Mg(NO_3)_2.6H_2O$, $Zn(NO_3)_2.4H_2O$, $Cd(NO_3)_2.4H_2O$, $CuSO_4.5H_2O$, and H_2O_2 (30 %, zur Analyse) from E. Merck AG, 99.8 % Mg, 99.997 % Cu, 99.999 % Zn, 99.9998 % Cd, 99.99 % S, and 99.999 % Te from Koch-Light Laboratories, and 99.995+ % Se from Bolidens Gruvaktiebolag. The preparational details for the compounds in question are given in the result section.

All samples were examined microscopically (including scanning electron microscopy) and by powder X-ray (Guinier) diffraction [$CuK\alpha_1$ radiation, KCl (a = 6.2919 Å) as internal standard] at room temperature (unit cell dimensions derived by applying the method of least squares). Density measurements were carried out pycnometrically

with kerosene as displacement liquid. DTA/DTG data were collected with a Mettler Recording Vacuum Thermoanalyzer, using ∼60 mg samples, a heating rate of generally 2 °C/min, and Pd or Al_2O_3 powder as reference material.

The magnetic susceptibilities were measured by the Faraday method (maximum field 8 kØ) using ∼30 mg samples. Room temperature powder neutron diffraction data were obtained using cylindrical sample holders of vanadium and neutrons of wavelength 1.877 Å from the reactor JEEP II. The nuclear scattering lengths (in 10^{-12} cm) b_{Mg} = 0.516, b_O = 0.578 and b_{Te} = 0.580 were taken from Ref. 10. The least squares profile refinement programme of Rietveld[11] was applied in the fitting of the variable parameters.

RESULTS

In the presentation of the results it is convenient to group the compounds according to the nonmetal (X) rather than the metal (M) components. The conventional nomenclature (peroxides) will be used for the MO_2 compounds despite the fact that analogy with the MS_2, MSe_2 and MTe_2 compounds would call for the designation dioxides. However, it should be emphasized that the distinction in nomenclature reflects a formal privilege of the oxides, which is not rooted in structural and bonding peculiarities within the FeS_2-p type family.

A brief survey of the present and earlier findings on these MX_2 compounds is given in Table 1.

(i) *Peroxides.* The recipes described in Refs. 3, 5, 7 and 8 were tried for the preparation of the peroxides MO_2 (M = Mg, Zn, Cd). The most convenient method proved to be the slow precipitation from solutions of H_2O_2, $M(NO_3)_2$ and NH_3/NH_4NO_3. The precipitation rate can be

Table 1. Survey of preparations and structures for MgX_2, CuX_2, ZnX_2 and CdX_2 chalcogenides.

MX_2	Initially from aqueous solution	Sealed silica capsule technique	High pressure — high temperature means
MgO_2	FeS_2-p; Ref. 3 and this work		
MgS_2		No reaction; this work	
$MgSe_2$		FeS_2-p; this work	
$MgTe_2$		FeS_2-p; Ref. 4 and this work	
CuO_2	No compound; fast decomp. of H_2O_2		
CuS_2	FeS_2-m; this work	No reaction; this work	FeS_2-p, FeS_2-m; Refs. 6 and 13
$CuSe_2$		FeS_2-m; Ref. 14	FeS_2-p, FeS_2-m; Refs. 6 and 13
$CuTe_2$		No reaction; this work	FeS_2-p; Refs. 6 and 13
ZnO_2	FeS_2-p; Ref. 5 and this work		
ZnS_2	X-ray amorpheous; this work	No reaction; this work	FeS_2-p; Ref. 6
$ZnSe_2$		No reaction; this work	FeS_2-p; Ref. 6
$ZnTe_2$		No reaction; this work	$Cd(OH)_2(?)$; Ref. 6
CdO_2	FeS_2-p; Refs. 7, 8 and this work		
CdS_2	X-ray amorpheous; this work	No reaction; this work	FeS_2-p; Ref. 6
$CdSe_2$		No reaction; this work	FeS_2-p; Ref. 6
$CdTe_2$		No reaction; this work	

partly controlled by adjustment of pH, no detectable precipitation being observed when $pH < \sim 5$. By careful addition of NH_3 the most favourable conditions were found at pH ≈ 6.5. [The continuous, homogeneous generation of NH_3 through hydrolysis of urea produces CO_2, which should be avoided, see also Ref. 12. The use of an ammonium acetate buffer (pH ≈ 7) gave poorer results (more contaminations and more diffuse X-ray powder diagrams).] Ageing of the precipitates for about three weeks in contact with the mother liquor improved the crystallinity. Very little further improvement resulted from the prolongation of the ageing cure. A newed treatments of the precipitates

with fresh hydrogen peroxide solutions gave no significant improvement.

The samples were (in succession) washed with hydrogen peroxide solution, alcohol and ether. This treatment and subsequent drying in a (P_4O_{10}) desiccator did not remove all adsorbed water. On the other hand, drying in air at $110-120$ °C for about two days seems sufficient to take away the water. An even better drying technique is to use a stream of (H_2O and CO_2 free) oxygen, increasing the temperature slowly from ambient to 300 °C for MgO_2, and 160 °C for ZnO_2 and CdO_2. This improved the sharpness of the X-ray powder patterns considerably, in particular for MgO_2. The unit cell edges for MgO_2, ZnO_2 and CdO_2 were determined as $a = 4.8441(6)$, 4.868(5) and 5.311(6) Å, respectively.

Structural data for MgO_2 (as derived by the neutron diffraction/profile refinement technique) are listed in Table 2, the pycnometric density being 3.18 g/cm³. The quality of the ZnO_2 and CdO_2 samples did not justify structure determination. Moreover, the contact with kerosene and/or the evacuation under kerosene produce decomposition and hence prevent density measurements.

M was established as MO after decomposition and "active" oxygen was determined by iodometric titration with standard thiosulfate solution. Excellent accordance with the formula MO_2 was obtained for the "oxygen dried" samples. The decomposition temperatures reported in the litera-

Table 2. Structural data for MgO_2 and $MgTe_2$.

	MgO_2	$MgTe_2$
a (Å)	4.8441(6)	7.0212(5)
x	0.4114(4)	0.3875(5)
6 $Mg-X$ (Å)	2.083(2)	2.941(4)
1 $X-X$ (Å)	1.487(5)	2.736(10)
6 $X-Mg-X$ (°)	92.43(8)	94.14(10)
6 $X-Mg-X$ (°)	87.57(8)	85.86(10)
3 $Mg-X-Mg$ (°)	110.59(9)	115.14(12)
3 $Mg-X-X$ (°)	108.33(13)	102.94(13)
6 $X-X$ (Å)	2.883(5)	4.007(10)

ture (*cf.*, *e.g.*, Ref. 12) were presently confirmed by DTA and quenching experiments as about 360, 210 and 200 °C for MgO_2, ZnO_2 and CdO_2, respectively.

The MO_2 compounds are all white, and when only desiccator drying has been employed they show diamagnetic behaviours. After drying in air at $110-120$ °C, weak paramagnetic susceptibilities were recorded at room temperature. It has been suggested[3,5,7] that this should reflect the reaction $3MO_2 + 2H_2O \rightleftarrows 2M(OH)_2 + M(O_2)_2$. The formation of superoxides $M(O_2)_2$ would indeed be consistent with the paramagnetic behaviour. However, drying in oxygen *(vide supra)* produced only diamagnetic materials. Since the paramagnetic effect (and thereby the amount of possible superoxide) is very small and we had no other means to detect superoxides, the problem could not be pursued any further.

(ii) *Disulfides.* The sealed silica capsule technique was tried to synthesize the MS_2 compounds of $M = Mg$, Cu, Zn and Cd from $MS + S$. However, this endeavour was in vain. We have also tried to prepare the disulfides for $M = Cu$, Zn and Cd from aqueous sulfate solutions by adding NH_4HS_2 solution under various conditions. The resulting precipitates were allowed to stay in contact with the mother liquor for varying amounts of time, were washed with NH_4HS solution, water, alcohol and ether. Subsequently they were dried and outgassed in vacuum-desiccators at room temperature before being sealed in evacuated pyrex tubes and heated at various temperatures. For $M = Zn$ and Cd only the known MS compounds, S and some X-ray amorphous materials (containing M and S) resulted. For $M = Cu$, however, long-term annealings at $70-80$ °C produced (in addition to uncreated $CuS + S$) an orthorhombic phase: $a = 4.651(3)$, $b = 5.793(3)$, $c = 3.532(2)$ Å. The small amounts of impure sample available prevented structural refinement by the powder neutron diffraction method, but from the intensities on the Guinier photographs, there is no doubt that the structure is of the FeS_2-*m* type. X-Ray diffraction photographs taken above room temperature reveal that very little expansion occurs until the material decomposes at 90 ± 5°C (confirmed by DTA and quenching experiments).

Hinze and Neuhaus[13] have reported the preparation of an FeS_2-*m* type phase during high pressure – high temperature experiments on disproportion reactions of Cu_2S below ~ 64 kbar. Their unit cell

dimensions $a = 4.60$, $b = 5.66$ and $c = 3.52$ Å, suggest very strongly that this is the sample phase as we have obtained. (The domain of the FeS_2-*p* type modification of CuS_2 appears to be ≥ 64 kbar.[6,13] The isostructural phases of ZnS_2 and CdS_2 are obtained similarly by the application of high pressure – high temperature means.[6])

(iii) *Diselenides.* As for the disulfides of Zn and Cd, the syntheses of the corresponding MSe_2 compounds apparently require the application of the high pressure – high temperature technique. $CuSe_2$ with the FeS_2-*m* type structure is, on the other hand, easily made[14] by the sealed silica capsule technique. (Hinze and Neuhaus[13] have reported that Cu_2Se disproportionates into Cu and $CuSe_2$ with FeS_2-*m* type structure at pressures between 37 and 44 kbar. At pressures above 44 kbar the FeS_2-*p* type modification of $CuSe_2$ is formed.) Somewhat surprisingly, we have also succeeded in making small amounts of rather impure $MgSe_2$ (together with excess, unreacted $MgSe + Se$ and MgO) according to this method. $MgSe_2$ crystallizes cubically with $a = 6.500(6)$ Å, and the structure is almost certainly of the FeS_2-*p* type. However, the $MgSe_2$ phase is very difficult to handle (protection gas is, *e.g.*, needed during the X-ray exposures) and it is extremely sensitive to humidity and air. The present $MgSe_2$ sample appears to decompose to MgSe and Se at ~ 280 °C.

(iv) *Ditellurides.* Among the probable MTe_2 compounds, we only succeeded in making $MgTe_2$ by the sealed silica capsule technique, using heat treatments at 400 to 500 °C (two intervening crushings) and finally slow cooling to room temperature. (Small amounts of MgO and unreacted Te were found in the capsules after the syntheses. The Te impurity was removed before the samples were further examined.)

Structural data for $MgTe_2$ (according to the neutron diffraction/profile refinement technique) are given in Table 2. The observed density is 5.30 g/cm³. The results compare reasonably well with those reported earlier.[4]

REFERENCES

1. Carter, G. F. and Templeton, D. H. *J. Am. Chem. Soc. 75* (1953) 5247.
2. Ziegler, M., Rosenfeld, M., Känzig, W. and Fischer, P. *Helv. Phys. Acta 49* (1976) 57.
3. Vannerberg, N. G. *Ark. Kemi 14* (1959) 99.
4. Yanagisawa, S., Tashiro, M. and Anzai, S. *J. Inorg. Nucl. Chem. 31* (1969) 943.
5. Vannerberg, N. G. *Ark. Kemi 14* (1959) 119.
6. Bither, T. A., Bouchard, R. J., Cloud, W. H., Donohue, P. C. and Siemons, W. J. *Inorg. Chem. 7* (1968) 2208.
7. Vannerberg, N. G. *Ark. Kemi 10* (1956) 455.
8. Hoffman, C. W. W., Ropp, R. C. and Mooney, R. W. *J. Am. Chem. Soc. 81* (1959) 3830.
9. Donohue, P. C., Siemons, W. J. and Gilson, J. L. *J. Phys. Chem. Solids 29* (1968) 807.
10. *The 1976-compilation of the Neutron Diffraction Commission.*
11. Rietveld, H. M. *J. Appl. Crystallogr. 2* (1969) 65.
12. Vol'nov, I. I. *Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals*, Plenum, New York 1966.
13. Hinze, E. and Neuhaus, A. *Naturwissenschaften 56* (1969) 136.
14. Kjekshus, A., Rakke, T. and Andresen, A. F. *Acta Chem. Scand. A 28* (1974) 996.