
01 Jan 1974

X-Ray Powder Data And Unit Cell Parameters Of MgCl₂.6H₂O

Charles A. Sorrell

Missouri University of Science and Technology

Roy R. Ramey

Follow this and additional works at: https://scholarsmine.mst.edu/matsci_eng_facwork

 Part of the [Ceramic Materials Commons](#)

Recommended Citation

C. A. Sorrell and R. R. Ramey, "X-Ray Powder Data And Unit Cell Parameters Of MgCl₂.6H₂O," *Journal of Chemical and Engineering Data*, vol. 19, no. 1, pp. 31 - 32, American Chemical Society, Jan 1974.

The definitive version is available at <https://doi.org/10.1021/je60060a023>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Materials Science and Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

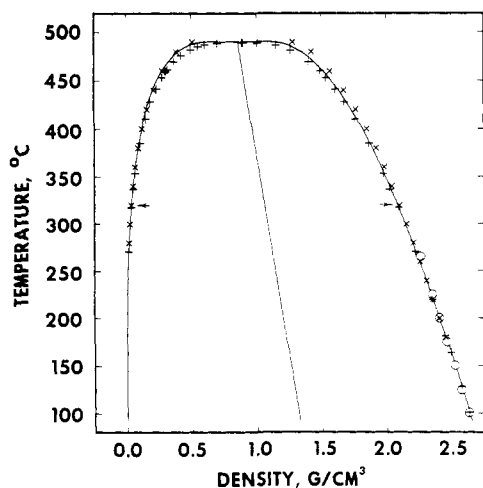


Figure 1. Coexistence curve for aluminum bromide
 —, Calculated from Equations 10 and 11; O, Biltz and Voight (1); X, Zhuravlev (10); +, Johnson et al. (4). Arrows indicate highest experimental temperature reached in present work

temperature. Indeed, the experimental points observed by Johnson et al. lie slightly below Equation 10 at temperatures above our highest temperature. Similarly, Zhuravlev's liquid density data lie slightly above our Equation 10, also above our highest temperature. These data are shown in Figure 1.

Safety

The same precautions should be taken as were reported previously (5) for the containment of liquids above their normal boiling points in glass vessels.

Nomenclature

a_i = empirical coefficients
 A = constant, a function of a_2 and a_3

b_i = empirical coefficients
 B = constant, a function of a_3
 d = density of AlBr_3 vapor
 D = density of AlBr_3 liquid
 m_i = mass of AlBr_3 in i th tube
 n = number of individual experimental measurements
 Q = positive difference between rectilinear diameter and d or D
 T_i = total enclosed volume in i th tube
 t = temperature in degrees centigrade
 t_c = critical temperature
 V_i = liquid AlBr_3 volume in i th tube
 z_i = residual; function to be treated by least-squares fitting
 ρ = overall tube average density; i.e., m/T
 ρ_c = density at critical temperature
 ρ_m = rectilinear diameter; i.e., $(d + D)/2$
 σ = standard deviation in Q
 τ = distance from critical temperature, i.e., $t_c - t$
 ϕ = fraction of total tube volume occupied by liquid; i.e., V/T

Literature Cited

- (1) Biltz, W., Voight, A., *Z. Anorg. Allgem. Chem.*, **126**, 39 (1923).
- (2) Boston, C. R., in "Advances in Molten Salt Chemistry," Chap. 3, J. Braunstein, G. Mamantov, and G. P. Smith, Eds., Plenum Press, New York, N.Y., 1971.
- (3) Fischer, W., Rahfs, O., Benze, B., *Z. Anorg. Allgem. Chem.*, **205**, 1 (1932).
- (4) Johnson, J. W., Silva, W. J., Cubicciotti, D., *J. Phys. Chem.*, **72**, 1664 (1968).
- (5) King, L. A., Seegmiller, D. W., *J. Chem. Eng. Data*, **16**, 23 (1971).
- (6) Rotinjan, L., Suchodski, W., *Z. Phys. Chem.*, **87**, 635 (1914).
- (7) Seegmiller, D. W., Fannin, Jr., A. A., Olson, D. S., King, L. A., *J. Chem. Eng. Data*, **17**, 295 (1972).
- (8) Seegmiller, D. W., Rhodes, G. W., King, L. A., *Inorg. Nucl. Chem. Lett.*, **6**, 885 (1970).
- (9) "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand. Circular 500, p 731, 1952.
- (10) Zhuravlev, D. I., *Zh. Fiz. Khim.*, **10**, 325 (1937).

Received for review May 29, 1973. Accepted September 19, 1973.

X-Ray Powder Data and Unit Cell Parameters of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Charles A. Sorrell¹ and Roy R. Ramey

Department of Ceramic Engineering, University of Missouri, Rolla, Mo. 65401

Detailed X-ray powder data for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were obtained by diffractometry by use of $\text{CuK}\alpha$ radiation at 22°C. The data were indexed on a bimolecular monoclinic unit cell, space group C2/m, with $a = 9.858 \pm 0.001 \text{ \AA}$; $b = 7.107 \pm 0.001 \text{ \AA}$; $c = 6.069 \pm 0.001 \text{ \AA}$; $\beta = 93^\circ 47' \pm 10'$. Calculated density was 1.591 g/cm^3 , compared with a measured density of $1.593 \pm 0.003 \text{ g/cm}^3$.

The structure of magnesium chloride hexahydrate, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, was determined by Andress and Gundermann (1), who reported a bimolecular unit cell, space group C2/m, with $a = 9.90 \pm 0.03 \text{ \AA}$; $b = 7.15 \pm 0.03 \text{ \AA}$; $c = 6.10 \pm 0.03 \text{ \AA}$; $\beta = 94^\circ \pm 20'$. The only available X-ray powder data appeared in the original Hanawalt et al. compilation (3) and was subsequently included in the "Powder Diffraction File" (5). Comparison of the struc-

ture factors calculated by Andress and Gundermann with the powder data indexed by J. V. Smith indicates the incomplete nature of the powder data. This, coupled with the relatively low precision of the reported unit cell parameter measurements, prompted acquisition of the data reported in this work.

X-Ray Procedures

Powder data were acquired at 22°C by conventional methods by use of a General Electric XRD-700 recording diffractometer with $\text{CuK}\alpha$ radiation generated at 50 kVp and 20 Ma. Flat recessed sample holders machined from Lucite were used. Samples containing approximately 20% high-purity rock crystal quartz as an internal standard were scanned from 2° to $60^\circ 2\theta$ at a rate of 0.2° per min, which permitted measurement of 2θ values to the nearest 0.01° . Samples containing no internal standard were then scanned, following alignment on the (020) line of the chloride, to provide complete interplanar spacing and intensity data.

¹ To whom correspondence should be addressed.

Table I. X-Ray Powder Diffraction Data for MgCl₂·6H₂O at 22°C

hkl	2θ _{obsd}	d _{obsd}	d _{calcd}	I/I ₁
110 ^a	15.38	5.760 ₉	5.760 ₇	14
111	20.87	4.256 ₂	4.256 ₉	9
111 ^a	21.70	4.095 ₃	4.095 ₄	100
201	22.52	3.948 ₀	3.947 ₆	13
201	24.05	3.700 ₂	3.699 ₉	4
020 ^a	25.06	3.553 ₃	3.553 ₅	26
021	29.14	3.064 ₄	3.064 ₈	1
002	29.50	3.027 ₈	3.027 ₉	2
310 ^a	30.01	2.977 ₅	2.977 ₂	23
220 ^a	31.05	2.880 ₁	2.880 ₃	58
311	32.78	2.732 ₀	2.737 ₇	39
112 ^a			2.724 ₀	
202	33.88	2.645 ₇	2.658 ₀	69
221 ^a			2.641 ₁	
112 ^a			2.638 ₅	
311	34.35	2.610 ₆	2.610 ₅	3
221 ^a	35.01	2.562 ₉	2.562 ₉	6
202	35.83	2.506 ₁	2.505 ₅	1
400 ^a	36.53	2.459 ₇	2.459 ₁	6
401	38.59	2.333 ₀	2.332 ₈	5
022	39.08	2.304 ₈	2.304 ₇	39
130 ^a			2.303 ₁	
401 ^a	40.48	2.228 ₃	2.227 ₇	27
312	41.23	2.189 ₅	2.189 ₆	2
131	41.76	2.162 ₉	2.163 ₉	3
131 ^a	42.18	2.142 ₃	2.141 ₇	9
222	42.50	2.127 ₀	2.128 ₅	2
312	43.91	2.061 ₉	2.061 ₉	6
222 ^a	44.21	2.048 ₆	2.047 ₇	11
330	47.48	1.914 ₈	1.920 ₂	6
203			1.912 ₃	
421	48.23	1.886 ₈	1.887 ₄	4
132 ^a	49.36	1.846 ₂	1.846 ₉	23
203	49.96	1.825 ₄	1.825 ₅	2
331	50.39	1.810 ₉	1.810 ₃	4
040 ^a	51.40	1.777 ₆	1.776 ₈	19
023	52.08	1.756 ₀	1.755 ₂	3
422 ^a	53.15	1.723 ₂	1.725 ₅	10
223	54.49	1.683 ₉	1.684 ₀	2
422	56.08	1.639 ₉	1.640 ₉	2
241 ^a	56.76	1.621 ₈	1.620 ₂	4
332 ^a	57.86	1.593 ₉	1.594 ₀	4

^a Lines reported by "Powder Diffraction File," No. 1-0431.

Sample Preparation

Initial measurements were made with Fisher ACS Certified MgCl₂·6H₂O crystals covered with plastic wrap (Dow Handi-Wrap) to prevent absorption of atmospheric water. It proved to be impossible, however, to grind the crystals to a sufficiently small particle size, less than 270 mesh, necessary for reliable intensity measurements without excessive absorption of water. Detailed measurements were made, therefore, with Dow flake MgCl₂·6H₂O, con-

sisting of aggregates of fine crystals. Measured 2θ values for the two materials were identical. Integrated intensities were obtained from the diffractometer recording chart by counting squares.

Density Measurements

Density of Dow flake MgCl₂·6H₂O was measured by suspension in liquid mixtures at 22°C. Densities of the pure liquids and mixtures were determined by pycnometric comparison with water. Flakes were floated on bromoform (ρ = 2.865); xylene (ρ = 0.863) was added a few drops at a time, and the mixture was agitated. When a few of the flakes remained suspended with all others floating because of included air, the density of the liquid was determined by pycnometer. When flakes were placed in carbon tetrachloride (ρ = 1.585), some floated, some sank, and some remained suspended because of differences in porosity. Bromoform was added a drop at a time, the mixture was agitated, and the flakes were observed. When none remained on the bottom and some were in suspension, the density of the liquid was determined by pycnometer.

Results

Measured diffraction angles, 2θ, interplanar spacings, d_{obsd}, and relative intensities, I/I₁, are given in Table I.

Initial indexing was accomplished by comparing observed interplanar spacings with those calculated from the unit cell parameters of Andress and Gundermann (1). After identification of the (400), (020), and (002) lines and the (201) (201) pair, precise lattice parameters were calculated by Ito's method (2, 4). Diffraction angles and interplanar spacings were then recalculated, and all lines in the pattern were identified. Agreement between calculated and observed values is excellent. The revised lattice parameters are a = 9.858 ± 0.001 Å; b = 7.107 ± 0.001 Å; c = 6.069 ± 0.001 Å; β = 93° 47' ± 10'.

Indexing is in agreement with the reported space group, C2/m, in that h + k = 2n for all lines. Relative intensities are reasonably close to reported values (3). The unit cell volume is 424.27 Å³, and the calculated density, ρ_x, is 1.591 g/cm³. Densities determined by suspension in xylene-bromoform and carbon tetrachloride-bromoform mixtures were 1.593 and 1.594, respectively. Within reasonable experimental limits, therefore, the density data are in agreement. The value obtained, 1.593 ± 0.003, is considerably higher than that obtained from the X-ray data of Andress and Gundermann (1), 1.568, and that reported in the "Handbook of Chemistry and Physics" (6), 1.569.

Literature Cited

- (1) Andress, K. R., Gundermann, J., *Z. Kristallogr.*, **87A**, 345 (1934).
- (2) Azaroff, L. V., Buerger, M. J., "The Powder Method in X-Ray Crystallography," pp 106-17, McGraw-Hill, New York, N.Y., 1958.
- (3) Hanawalt, J. D., Rinn, H. W., Frevel, L. K., *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).
- (4) Ito, T., "X-Ray Studies on Polymorphism," pp 187-228, Maruzen, Tokyo, Japan, 1950.
- (5) Joint Committee on Powder Diffraction Standards, "Powder Diffraction File," No. 1-0431, Philadelphia, Pa., 1960.
- (6) Weast, R. C., Ed., "Handbook of Chemistry and Physics," 52nd ed., p B-106, Chemical Rubber Co., Cleveland, Ohio, 1971-72.

Received for review June 11, 1973. Accepted October 15, 1973.