The Crystal Structure of Magnesium Arsenate, $Mg_{8.5}As_3O_{16}$

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Single crystals of magnesium arsenate have been grown from a PbO–As_2O_5 eutectic by flux crystallization of a ceramic preparation having an initial composition of $6MgO \cdot As_2O_5$. The crystals are rhombohedral, space group $R\bar{3}m$, with hexagonal unit cell parameters $a = 6.0278(6)$ and $c = 27.600(3)$ Å. A three-dimensional structural analysis using automatic diffractometer data has been completed and refined by full-matrix least-squares procedures to a residual $R = 0.049$ ($R_w = 0.059$) with a data–parameter ratio of 36 in the final anisotropic refinement. The structure analysis indicated that magnesium arsenate has the composition $Mg_{8.5}As_3O_{16}$ and is isostructural with the previously reported $Co_8As_3O_{16}$. The structure is based upon a cubic close-packed oxygen array with charge balance achieved in magnesium arsenate through partial occupancy of a unique magnesium site occurring in an arsenic-substituted MgO-type layer.

Introduction

The composition magnesium arsenate, $6MgO \cdot As_2O_5$, has been reported (*1*) as a red-emitting phosphor when activated by tetravalent manganese. Its emission spectrum has been investigated (*1, 2*) and compared with manganese-activated magnesium fluorogermanate (*3, 4*). As part of a program investigating the structural parameters of manganese(IV)-activated phosphor systems (*5–8*), we have prepared single crystals and have determined the crystal structure of magnesium arsenate.

Experimental

Preparation and Analysis

Magnesium arsenate was prepared by standard ceramic techniques. Magnesium oxide (Mallinckrodt Analytical Reagent) and arsenic pentoxide (Fisher Certified Reagent) in a 6:1 mole ratio with one m/o manganese carbonate (Fisher Certified Reagent) added as an activator were mixed and ground under acetone. After removal of the acetone at 110°C, the mixture was fired in a platinum crucible at 1000°C in air for 1 hr, reground and fired for 16 hr at 1200°C.

A suitable high temperature flux for crystal

growth was found to be an eutectic in the PbO–As_2O_5 system occurring at approximately 83 m/o PbO–17 m/o As_2O_5 (*9*). 33.67 g of this eutectic mixture (0.150 "moles") and 7.08 g of the phosphor composition $6MgO \cdot As_2O_5$ (0.015 moles) were mixed and packed into a 25 cm³ platinum crucible. The tightly covered crucible was placed in a silicon carbide resistance-heated furnace, held at 1225°C for 4 hr, cooled at a rate of 8°C/hr to 600°C, and then removed from the furnace. To protect the platinum crucible, dry oxygen was passed through the furnace. The arsenate crystals were removed from the flux by leaching with hot, very dilute hydrochloric acid and by ultrasonic cleaning in water.

A semiquantitative emission spectrographic analysis[1] of the flux-grown crystals revealed the following approximate weight percent impurities: manganese (0.1–1.0%), platinum (0.01–0.10%), and lead (<0.03%). Quantitative analysis was undertaken for magnesium and arsenic both by chemical and neutron activation analysis. In weight percents, the crystal analyses were:

	Found	Calculated ($Mg_{8.5}As_3O_{16}$)
Mg	29.6 ± 1.5	30.06
As	32.7 ± 1.5	32.70.

[1] Analyses were performed by Dr. J. Roth of the Materials Science Center's Analytical Facility.

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These analytical results clearly support the proposed stoichiometry $Mg_{8.5}As_3O_{16}$ (*vide infra*).

X-Ray Diffraction Data

The flux-grown crystals appeared mostly as hexagonal plates ranging up to several millimeters across. The pale yellow crystals fluoresced strongly under ultraviolet excitation with the red emission characteristic of tetravalent manganese. Because of the relatively high linear absorption coefficient of the material for $MoK\alpha$ radiation, a specimen suitable for data collection was prepared by grinding a crystal to an accurate sphere of 0.016(1) cm in diameter.

From Weissenberg, and precession photographs, it was determined that the Laue symmetry was $\bar{3}m$ and that the only systematically absent reflections corresponded to $-h + k + l \neq 3n$. The possible space groups consistent with these data are $R\bar{3}m$, $R32$ and $R3m$. No measurable piezoelectric effect could be detected using a sensitive Giebe–Scheibe detector designed by H. Diamant.

Lattice parameters were determined in a PICK II least-squares refinement program using 52 reflections within the angular range $45° < |2\theta| < 71°$; centering was performed automatically on a Picker FACS-I four-circle diffractometer using $MoK\alpha_1$ radiation. In the hexagonal system the lattice parameters are $a = 6.0278(6)$ and $c = 27.600(3)$ Å. Transforming to rhombohedral indices and performing the least-squares refinement yielded the values $a = 9.836(1)$ Å and $\alpha = 35.68(2)°$ for the rhombohedral unit cell. The numbers in parentheses represent the standard deviation in the last reported figure.

A density, $\rho_0 = 3.96(1)$ g/cm^3, was determined by the buoyant force method on approximately 42 mg of selected single crystals. A Cahn electrobalance (Model G) was used for both dry and wet (CCl_4, Fisher Scientific Company, Spectroanalyzed Grade) weighings. Based upon the hexagonal unit cell contents (*vide infra*), $Mg_{25.5}As_9O_{48}$, the calculated density, $\rho_c = 3.941$ g/cm^3.

The diffraction intensities were measured using Zr filtered $MoK\alpha$ radiation at a take-off angle of 2.5° with the diffractometer operating in the θ–2θ scan mode. The scans were run at the rate of 1° 2θ per minute over a range of 1.5° with allowance for dispersion, and with 40 sec background counts taken at both ends of the scan. Of the 1339 independent data investigated in the angular region $2\theta \leqslant 104°$, a total of 1285 were retained as objectively observed with

$|F_o| > 0.670\sigma_F$, where σ_F is defined by $\sigma_F = 0.02|F_o| + [C + k^2B]^{1/2}/(2|F_o|L_P)$. The total scan count is C, k is the ratio of scanning time to the total background scanning time, and B is the total background count. At a period of 50 reflections throughout the entire data collection, three reflections were monitored as standards. There was no evidence of crystal degradation and no random variation in intensity greater than 1.5% was observed. The data were corrected for Lorentz and Polarization effects and absorption corrections (*10*) were applied for a spherical crystal having $\mu R = 0.80$. The maximum absorption correction applied to any reflection was 6.8% of $|F_o|$.

Determination of the Structure

A preliminary examination of the hexagonal lattice parameters indicated a unit cell containing twelve close-packed oxygen layers with the c-axis as the stacking direction, and four closest-packed atoms per layer. Based upon this close-packed model, a Patterson map was calculated using intervals of $\frac{1}{6}$ along the a-axis and $\frac{1}{48}$ along c, thus enabling all possible interacting vectors between octahedral and tetrahedral interstices and packing atoms to appear.

In anticipation of the Patterson synthesis, an analysis of several simple packing schemes was made in which it was observed that an occupied tetrahedral hole gives rise to a set of $00z$ vectors characteristic of its packing environment. Such vectors join the tetrahedral site to close-packed atoms at definite distances above and below it. (Occupancy of an octahedral site above or below the tetrahedral hole gives rise to an identical set of vectors.) In magnesium arsenate, the presence of Patterson vectors of the $00z$ type with only values of z being $\frac{3}{48}$, $\frac{9}{48}$, $\frac{15}{48}$, and $\frac{21}{48}$ precludes all but cubic closest packing. Examination of the Patterson quickly yielded the proper orientation of the stacking sequence; the entire map could be interpreted in terms of special positions in the space group $R\bar{3}m$ (*11*). The stoichiometry of the compound at this stage was $Mg_9As_3O_{16}$, showing an excess of one positive charge per formula unit.

Refinement of the Structure

A full-matrix least-squares refinement (*12*) of the positional parameters, isotropic temperature factors, and the metal occupancy factors was initially undertaken in the space group $R\bar{3}m$. Zerovalent scattering factors were used for

magnesium, arsenic, and oxygen *(13)*; anomalous scattering terms were included for magnesium and arsenic *(14)*. Isotropic extinction corrections according to Zachariasen's analysis *(15)* were also applied, the maximum correction being 9.0% of $|F_c|$ for the 02,16 reflection in the final refinement. In the early cycles of refinement the only atom whose multiplicity showed significant deviation from unit occupancy was magnesium in the *e* symmetry position of the space group [labeled Mg(1)] where an approximate 20% vacancy was indicated. In subsequent refinements all metal multiplicities except that of Mg(1) were set to their full occupancy values and held constant. Upon convergence of the isotropic refinement the standard residual $R = \sum ||F_o| - |F_c||/\sum |F_o|$ had the value of 0.056 with a data to parameter ratio of 64. The resulting stoichiometry, $Mg_{8.4}$-As_3O_{16}, was checked by performing two additional cycles of least-squares refinement in which all atom multiplicities were allowed to vary; only that of Mg(1) indicated any deviation from unit occupancy.

With the large amount of data available it is possible to refine the structure in the noncentrosymmetric space groups $R32$ and $R3m$, while maintaining excellent data to parameter ratios. Table I shows weighted $(1/\sigma_{F_o}^2)$ and unweighted residuals and the corresponding data to parameter ratios for the isotropic and anisotropic refinements in all three space groups. The starting point for the refinements in the acentric space groups was the set of refined coordinates obtained in $R\bar{3}m$ plus additional shifts to remove the atoms from centrosymmetric positions.

While Hamilton's ratio test *(16)* indicates $R3m$ as the statistically correct space group, there are objections to this choice on other grounds. A comparison of the refined positional parameters in the three space groups shows that in every case where an atomic position from the centric space group is refined according to the less restrictive

symmetry requirements of the acentric space groups, the errors associated with such parameters increase by an average factor of three, with correlations between these "centrosymmetrically" related parameters ranging from 0.60 to 0.93; atomic positions which are centrosymmetric in the acentric space group $R32$ refine with coordinates and errors identical (well within one ESD) to those in $R\bar{3}m$. Considering the large number of data employed, the observed increases in the estimated standard deviations are clearly much greater than what would be expected for an increase in the number of parameters alone and raises serious doubts about the choice of either noncentrosymmetric space group. It should also be pointed out that the isotropic thermal parameters for two of the oxygen atoms refined in $R3m$ showed unreasonably low values of 0.03(6) and 0.22(4), with the former being nonpositive definite in the anisotropic refinement.

These considerations, together with the fact that the refinement carried out in the more constrained space group $R\bar{3}m$ is completely satisfactory in all respects, led to the choice of the centrosymmetric space group for magnesium arsenate. The residuals for the final anisotropic refinement in the space group $R\bar{3}m$ are $R = 0.049$ and $R_w = 0.059$.[2]

The final X-ray stoichiometry of $Mg_{8.4}As_3O_{16}$ is deficient in positive charge by 0.6 units per triply primitive hexagonal cell. Since there was no evidence of partial occupancy in any other site, we postulate a unit-cell content of $Mg_{25.5}$-As_9O_{48} on the basis of charge balance. The final atomic coordinates and anisotropic thermal parameters are presented in Table II.

Description of the Structure

The structure can best be described in terms of the stacking of close-packed layers along the hexagonal c axis. Fig. 1 shows a net in the xy plane containing a 2×2 block of unit cells with each illustration depicting the cation distribution in a particular layer lying at some multiple of $\frac{1}{12}$

TABLE I

| | Isotropic residuals | | |
	$R\bar{3}m$	$R32$	$R3m$
R	0.056	0.054	0.049
R_w	0.065	0.064	0.057
Data/parameter ratio	64	53	35
	Anisotropic residuals		
R	0.049	0.048	0.045
R_w	0.059	0.057	0.053
Data/parameter ratio	36	28	20

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a-c]

Atom	Site symmetry (11)		$10^4 x$	$10^4 y$	$10^4 z$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As(1)	3(a)	3m	0	0	0	0.24(1)	B_{11}	0.12(1)	$\frac{1}{2}B_{11}$	0	0
As(2)	6(c)	3m	0	0	1919.8(1)	0.30(1)	B_{11}	0.25(1)	$\frac{1}{2}B_{11}$	0	0
Mg(1)[d]	9(e)	2/m	$\frac{1}{2}$	$\frac{1}{2}$	0	0.69(8)	B_{11}	0.39(5)	0.26(4)	0.07(4)	$-B_{13}$
Mg(2)	18(h)	m	4982(2)	$-x$	2452.7(4)	0.43(4)	B_{11}	0.61(2)	0.24(2)	$-0.01(2)$	$-B_{13}$
O(1)	6(c)	3m	0	0	1300(1)	0.47(7)	B_{11}	0.31(6)	$\frac{1}{2}B_{11}$	0	0
O(2)	6(c)	3m	0	0	3795(1)	0.72(8)	B_{11}	0.68(8)	$\frac{1}{2}B_{11}$	0	0
O(3)	18(h)	m	5139(3)	$-x$	1230(1)	0.43(6)	B_{11}	0.68(4)	0.28(3)	$-0.09(3)$	$-B_{13}$
O(4)	18(h)	m	5223(4)	$-x$	3726(1)	0.63(7)	B_{11}	0.36(4)	0.29(4)	0.01(3)	$-B_{13}$

[a] Numbers in parentheses are estimated standard deviations in the last significant figure.

[b] Coordinates of 0 or $\frac{1}{2}$ are determined by site and space group symmetry.

[c] B_{ij}'s in units of Å^2.

[d] Partially occupied site.

of z. Octahedral sites are represented by circles and tetrahedral sites by triangles; the oxygen lattice is omitted for simplicity. At $z = 0$ a substituted MgO-type layer containing As(1) at the origin produces the pattern shown in Fig. 1(a). The magnesium atom in this layer lies on the partially occupied Mg(1) site and the loss of one such atom per two unit cells yields the composition $Mg_{2.5}AsO_4$ for this layer. At $z = \frac{1}{12}$,

the second layer (Fig. 1(b)) is similar to the first with vacancies replacing the arsenic positions. The composition Mg_3O_4 taken with that of the first layer produces a neutrally charged unit $Mg_{5.5}AsO_8$. Sharing faces with the unoccupied octahedral site in the second layer is the tetrahedral As(2) of layer three (Fig. 1(c)). The other As(2) tetrahedron in this sparsely populated layer shares faces with the unoccupied octahedral
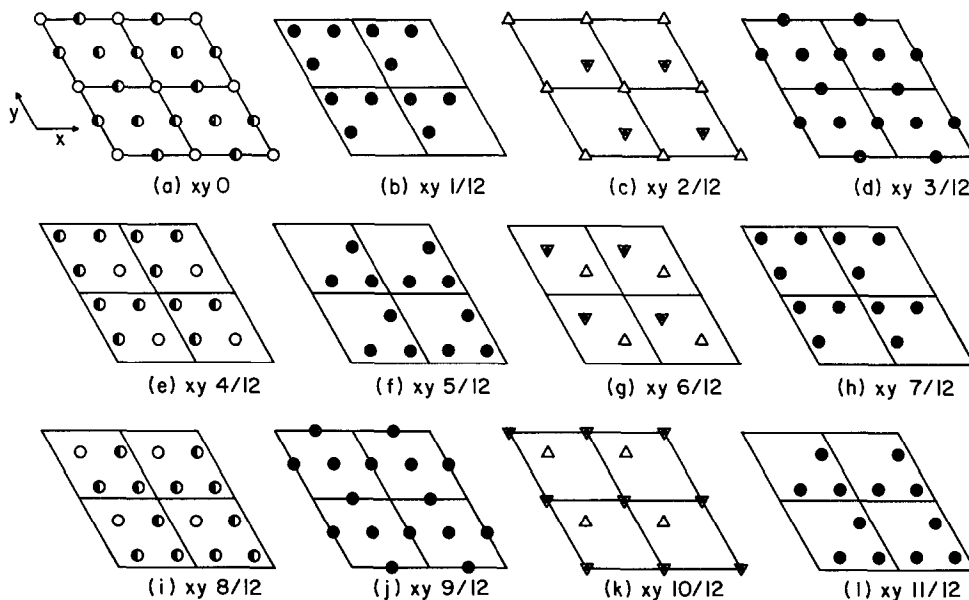

FIG. 1. Metal packing sequence in $Mg_{8.5}As_3O_{16}$. Layers 1–12 are represented by a–l; As(1) = ○, Mg(1) = ◐, Mg(2) = ●, As(2) = ▽ (tetrahedron pointing upward, $+z$) or △ (tetrahedron pointing downward, $-z$). Depending upon their orientations, the As(2) have z coordinates approximately $\pm\frac{1}{48}$ of that indicated in the figure.

TABLE III

BOND DISTANCES, BOND ANGLES, AND POLYHEDRAL EDGE
LENGTHS IN MAGNESIUM ARSENATE[a]

	Distance (Å)	Angle (°)	Edge length (Å)
Arsenic polyhedra			
6x As(1)–O(4)	1.857(2)		
6x O(4)–As(1)–O(4)		89.3(1)	2.612(3)
6x O(4)–As(1)–O(4)		90.7(1)	2.642(3)
As(2)–O(1)	1.712(3)		
3x As(2)–O(3)	1.674(2)		
3x O(1)–As(2)–O(3)		107.6(1)	2.733(3)
3x O(3)–As(2)–O(3)		111.2(1)	2.763(3)
Magnesium polyhedra			
2x Mg(1)–O(2)	2.156(2)		
4x Mg(1)–O(4)	2.159(2)		
4x O(2)–Mg(1)–O(4)		89.1(1)	3.029(1)
4x O(2)–Mg(1)–O(4)		90.9(1)	3.074(3)
2x O(4)–Mg(1)–O(4)		104.6(1)	3.416(3)
2x O(4)–Mg(1)–O(4)		75.4(1)	2.642(3)
Mg(2)–O(1)	2.105(2)		
Mg(2)–O(2)	2.074(2)		
2x Mg(2)–O(3)	2.049(2)		
2x Mg(2)–O(4)	2.127(2)		
2x O(1)–Mg(2)–O(3)		93.4(1)	3.024(1)
2x O(1)–Mg(2)–O(4)		87.3(1)	2.921(3)
2x O(2)–Mg(2)–O(3)		86.9(1)	2.837(3)
2x O(2)–Mg(2)–O(4)		92.2(1)	3.029(1)
O(3)–Mg(2)–O(3)		105.6(1)	3.265(3)
2x O(3)–Mg(2)–O(4)		89.3(1)	2.936(2)
O(4)–Mg(2)–O(4)		75.7(1)	2.612(3)
O(1)–Mg(2)–O(2)		179.4(1)	4.179(3)
2x O(3)–Mg(2)–O(4)		165.0(1)	4.141(3)

[a] Numbers in parentheses are estimated standard
deviations in last figure.

site in layer four (Fig. 1(d)). The combined
composition of the third (As_2O_4) and fourth
(Mg_3O_4) layers produces another neutrally
charged section of the structure. Layers five–
twelve are related to the first four by translations
and complete Fig. 1.

Thus far the structure of magnesium arsenate
has been described in terms of the packing of
idealized cation polyhedra. While this approxi-
mation is generally good for both the octahedral
and tetrahedral arsenic polyhedra, it is somewhat
less accurate in describing the magnesium
environments. The Mg(1) octahedron shares two
opposite edges with As(1) octahedra and the
shorter As(1)–O(4) distances along these shared
edges produce the decreased O(4)–Mg(1)–O(4)
angle (75.4°). The situation for the Mg(2)

octahedron is similar, one edge being shared with
the As(1) polyhedron with the result of an
O(4)–Mg(2)–O(4) angle of 75.7°. No other
significant polyhedral distortions occur in the
structure.

It is worth noting that the average Mg(1)–O
distance is 2.158 Å, while that of Mg(2)–O is
shorter, i.e., 2.088 Å. The incomplete occupancy
of the Mg(1) site with its resulting lower average
positive charge is compatible with a longer
metal–oxygen bond length. Table III presents the
relevant bond lengths, angles and polyhedral edge
lengths.

$Mg_{8.5}As_3O_{16}$ is isostructural with the com-
pound "$Co_8As_3O_{16}$" (17). In this compound the
deficiency in cobalt is found to occur over both
sites while in the magnesium compound the metal
deficiency is here shown to be entirely in the
Mg(1) site. Furthermore, there is no evidence
for the presence of trivalent arsenic in either of
the fully occupied arsenic sites; indeed, the
metal–oxygen distances agree very well with
those calculated from the recently tabulated radii
for four- and six-coordinated pentavalent arsenic
(18).

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