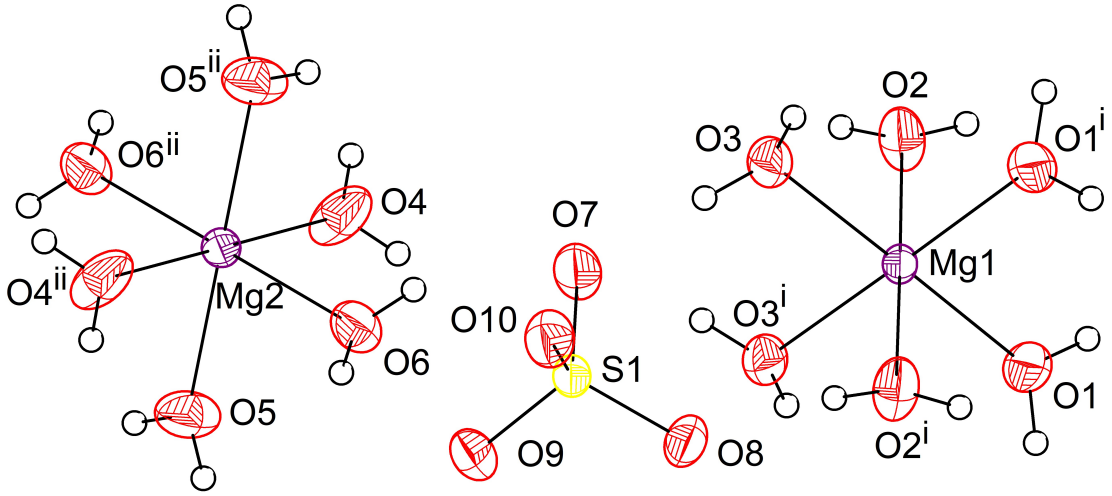
# Comments on the paper "Crystallization of inorganic nonlinear optical zinc di-magnesium chloro sulphate (ZDMCS) single crystal"

Bikshandarkoil R. Srinivasan, Megha S. Deshpande
School of Chemical Sciences, Goa University, Goa 403206, India Email: srini@unigoa.ac.in

**Graphical abstract**

$ZnSO_4 \cdot 7H_2O + 2\ MgCl_2 \cdot 6H_2O \rightarrow [Mg(H_2O)_6](SO_4)$ and NOT ~~ZDMCS~~




**Highlights**

# The title paper is critiqued

# Many points of criticisms are highlighted

# Experimental data reported in the title paper are discussed

# Zinc di-magnesium chloro sulphate is in fact magnesium sulphate hexahydrate

## Abstract

The authors of the title paper (Optics & Laser Tech **88** (2017) 147-151) claim to have grown a so-called inorganic nonlinear optical zinc di-magnesium chloro sulphate (ZDMCS) single crystal formulated as Zn 2($MgCl_2$) $SO_4$. A critical analysis of the title paper is presented to show that the reported experimental data are not in agreement with the proposed formula of ZDMCS. In this letter to Editor, we prove that ZDMCS is in fact, the well-known crystal magnesium sulphate hexahydrate having formula $MgSO_4 \cdot 6H_2O$.



Keywords: *crystal growth; zinc di-magnesium chloro sulphate; crystal structure; optical materials and properties; magnesium sulphate hexahydrate*


## Introduction

Recently we chanced to read the title paper [1] published online in *Optics & Laser Technology*. A study of the crystallization of new nonlinear optical (NLO) crystals is an active area of research due to several possible applications of NLO materials. However, an inspection of the article by Arivuselvi and Kumar [1] reveal that the experimental data of the growth of the ZDMCS crystal as well as its characterization and the presentation of the results do not meet scientific standards. In the following comment we prove i) the claims in the title paper are erroneous and ii) ZDMCS crystal is in fact $MgSO_4 \cdot 6H_2O$ based on a single crystal structure determination.

## A so-called zinc di-magnesium chloro sulphate (ZDMCS) crystal is in fact $MgSO_4 \cdot 6H_2O$

The authors of the title paper claim to have grown single crystals of ZDMCS **I** by slow evaporation of an aqueous solution containing zinc sulphate heptahydrate and magnesium chloride hexahydrate in 1:2 mole ratio as per the following chemical reaction

$$ZnSO_4 \cdot 7H_2O + 2MgCl_2 \cdot 6H_2O \rightarrow Zn\ 2(MgCl_2)\ SO_4 + 13H_2O\uparrow \quad ..(1)$$

The reaction scheme (equation 1) envisages removal of all water molecules in the starting materials. Such a dehydration process referred to by authors as spontaneous evaporation of water has not been reported for Mg(II) salts to date [2]. It is well documented that Mg(II) compounds crystallizing from aqueous solution contain the octahedral $[Mg(H_2O)_6]^{2+}$ cation. Several structurally characterized

examples containing the hexaaquamagnesium(II) dication are archived in the Cambridge Structural Database (CSD) [3]. For the chlorides and sulphates of Mg(II) and Zn(II) in aqueous solutions no dehydration reaction is expected to occur at room temperature, in the absence of a dehydrating agent.

Instead of reporting the quantities of the reagents employed for crystal growth, and the amount of ZDMCS obtained, authors described following details of filter paper "*The supersaturated solutions was filtered using 0.1 μm porosity WHATMANN filter paper and*..". Under the heading, 'single and powder crystal XRD', authors reported "*The structure of zinc di-magnesium chloro sulphate crystal was confirmed by single crystal X-ray diffraction studies. The grown crystal belongs to the tetragonal crystal system and the cell parameters are a=11.96 Å, b=11.96 Å, c=6.87 Å, α=90°, β=90°, γ=90° and volume=983 Å$^3$*." No other refinement results or the space group a CIF file for the single crystal work was reported. This discussion contradicts the authors claim in the abstract where it was mentioned "*The single crystal X-ray diffraction studies confirmed that the grown crystal belongs to the system of trigonal*".

In their discussion of UV-visible study authors reported, "*From these spectrums it is evident that ZDMCS crystal has UV lower cut off wavelength at 203 nm which suggests that the grown crystal is suitable for second harmonic generation*" without taking into consideration that the primary requirement for second harmonic generation is that the material under study should crystallize in a non-centrosymmetric space group.

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The questionable nature of ZDMCS can also be evidenced from the infrared (IR) spectral discussion. The authors assigned an IR band at 592.15 cm$^{-1}$ for S-Cl stretching vibration without taking into consideration that the S atom is the central atom of the sulphate moiety to which the four oxygens are bonded and hence there can be no such S-Cl vibration. In addition, the following claim "*The very broad band observed at 3091.89 cm$^{-1}$ is due to stretching vibration incorporation of Mg$^{2+}$ ions present in the sample*" can be considered truly remarkable for suggesting IR spectrum as a tool to find the presence of Mg$^{2+}$ ions. The authors claim to have performed elemental analysis and the EDAX spectrum confirms the presence of elements within the material (Table 1). For ZDMCS an unusual

formula Zn 2($MgCl_2$) $SO_4$ was proposed. Although the reason for writing the formula with a blank space after Zn and a blank space after 2($MgCl_2$) is not very clear, a comparison of the experimentally found elemental % with that calculated for the proposed formula reveals a clear mismatch.

The above given discussions reveal that the characterization data do not provide any proof whatsoever for the proposed formula of ZDMCS proving that the claims in the title paper are erroneous. With a view to determine the exact nature of the so-called ZDMCS single crystal, we reinvestigated its crystal growth by dissolving $ZnSO_4.7H_2O$ (1.0 g, 3.47 mM) and $MgCl_2.6H_2O$ (1.4 g, 6.94 mM) in a 1:2 molar ratio in ~50 ml of distilled water. As reported in the title paper, the reaction mixture was continuously stirred for 1 h at room temperature and filtered. The clear filtrate was left undisturbed to facilitate slow evaporation of the solvent. After more than a month, crystalline product was obtained. We did not take any special efforts to grow large crystalline blocks since the product had several X-ray quality crystals. We isolated the crystals by filtration by washing with a small amount of cold water and drying in air. We labelled the product as compound **1** and used a small crystal for single crystal structure determination using a Bruker D8 Quest Eco diffractometer. Details of data collection and refinement results are given in Table 2.

Compound **1** crystallizes in the centrosymmetric monoclinic space group *C2/c* and its structure consists of an unique tetrahedral sulphate anion located in general position and two crystallographically independent octahedral $[Mg(H_2O)_6]^{2+}$ cations with the Mg(II) ions situated in special positions. A view of the crystallographic packing in the [0 1 1] plane reveals alternating layers of octahedral cations and tetrahedral anions (Fig. 1). The structure protocol and checkCIF result of the single crystal study are given as Supplementary material.

From the single crystal study, the formula can be inferred as magnesium sulphate hexahydrate $[Mg(H_2O)_6](SO_4)$. This composition is that of the Mg mineral hexahydrite. The structure of $[Mg(H_2O)_6](SO_4)$ was first reported in the 1960s [4] and our structure model is in good agreement with literature data. It is interesting to note that an aqueous reaction of zinc sulphate heptahydrate and magnesium chloride hexahydrate in 1:2 mole ratio results in an exchange of sulphate anions of zinc to

afford a new product and the formation of magnesium sulphate hexahydrate. The chlorides of Mg and Zn remain in solution. Based on this the chemistry of the crystal growth reaction can be written as follows

$$ZnSO_4 \cdot 7H_2O + 2\ MgCl_2 \cdot 6H_2O \rightarrow [Mg(H_2O)_6](SO_4) \quad ..(2)$$

& not ~~ZDMCS~~

The above reaction of a Mg(II) product containing coordinated aqua ligands is not only in accordance with the chemistry but also can explain the IR spectral features pertaining to the presence of water (-OH vibration) and sulphate. Since the crystal obtained by us is a centrosymmetric solid, we did not measure its second harmonic generation (SHG) efficiency. While we do not wish to comment on the SHG measurements in the title paper, it is to be noted, that claims of discovering SHG response in centrosymmetric crystals have been commented [5-7]. Due to improper characterization, the dielectric properties of ZDMCS, Vicker's microhardness study etc. have no scientific merit and hence not commented.

Before concluding this critique, we wish to mention that the title paper is poorly presented and contains numerous errors other than the ones discussed above. The references at the end of the manuscript are not numbered. There are 27 citations which is two more than the 25 cited references. Although authors mentioned single crystal and powder XRD, no powder data was discussed. The temperature of unit cell measurement is not given. Unit cell data without any esd are reported. In the absence of the refinement results, and a CIF file it is not clear if any measurement was actually performed. While it is mentioned that a double beam instrument was used for recording the UV-Vis spectrum, it is not clear what sample was used as reference or if any reference was used at all. While it is not clear if the IR spectrum was recorded to an accuracy of 0.01 $cm^{-1}$ some of the assignments are questionable.

## Conclusions

In summary, we have proved that a so-called zinc di-magnesium chloro sulphate crystal is in fact, magnesium sulphate hexahydrate $[Mg(H_2O)_6](SO_4)$. The present comment once again highlights the

importance of single-crystal structure refinement data and not unit cell parameters for compound characterization. In this context, we wish to suggest that leading international journals should make submission of CIF file to a database a prerequisite for publication of papers reporting crystal growth studies.

## Supplementary Material

Deposition Number 2043322 contains the supplementary crystallographic data of magnesium sulphate hexahydrate reported in this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

## Acknowledgements

BRS acknowledges the Department of Science & Technology (DST) New Delhi for the sanction of a Bruker D8 Quest Eco single crystal diffractometer to the School of Sciences (formerly Department of Chemistry) Goa University under the DST-FIST programme.

## References

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2] F.A. Cotton, G. Wilkinson, P.L. Gaus, Basic Inorganic Chemistry, 3rd edition 2007, Wiley-India.

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4] A. Zalkin, H. Ruben and D. H. Templeton, The crystal structure and hydrogen bonding of magnesium sulfate hexahydrate, Acta Crystallogr. **17** (1964) 235-240.

5] B.R. Srinivasan, N. U. Parsekar, R. A. Apreyan & A. M. Petrosyan, On the second harmonic generation activity in centrosymmetric crystals, *Molecular Crystals & Liquid Crystals*, **680** (2019) 75-84.

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7] B.R. Srinivasan, Comments on the paper "Growth and characterization of inorganic non linear optical Barium Calcium Borate (BCB) crystal" *Materials Letters* **283** (2021) 128738.

Table 1. Elemental analytical data for a so-called ZDMCS crystal Zn $2(MgCl_2)$ $SO_4$

| Elemental % | Zn | Mg | Cl | S | O | Total % |
|---|---|---|---|---|---|---|
| Calculated for the formula Zn $2(MgCl_2)$ $SO_4$ | 18.59 | 13.82 | 40.29 | 9.11 | 18.19 | 100.0 |
| Experimentally found by EDAX for a so-called ZDMCS | 2.59 | 69.78 | 0.35 | 0.1 | 27.23 | 100.05 |

**Table 2** Crystal data and structure refinement for **1**

| | |
|---|---|
| Empirical formula | $MgSO_{10}H_{12}$ |
| Formula weight (g $mol^{-1}$) | 228.47 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | *C*2/c |
| Unit cell dimensions | |
| *a* (Å) | 10.1238(10) |
| *b* (Å) | 7.2225(7) |
| *c* (Å) | 24.485(3) |
| $\alpha = \gamma$ (°) | 90 |
| $\beta$ (°) | 98.250(3) |
| Volume ($Å^3$) | 1771.8(3) |
| Z | 8 |
| $D_{calc}$ ($mg/m^3$) | 1.713 |
| Absorption coefficient ($mm^{-1}$) | 0.465 |
| F(000) | 960 |
| Crystal size ($mm^3$) | 0.336 x 0.159 x 0.112 |
| θ range for data collection (°) | 3.363 to 28.371 |
| Limiting indices | $-13 \le h \le 13$, $-9 \le k \le 9$, $-32 \le l \le 32$ |
| Reflections collected /unique | 12454 / 2206 [R(int) = 0.0232] |
| Completeness θ = 27.00° | 99.2 % |
| Absorption correction | Multi scan |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2206 / 0 / 159 |
| Goodness of fit on $F^2$ | 1.073 |
| Final R indices [$I>2\sigma(I)$] | R1 = 0.0293, wR2 = 0.0774 |
| R indices (all data) | R1 = 0.0318, wR2 = 0.0800 |
| Largest diff. peak and hole (e $Å^{-3}$) | 0.399 and -0.450 |
| CCDC deposit no | 2043332 |

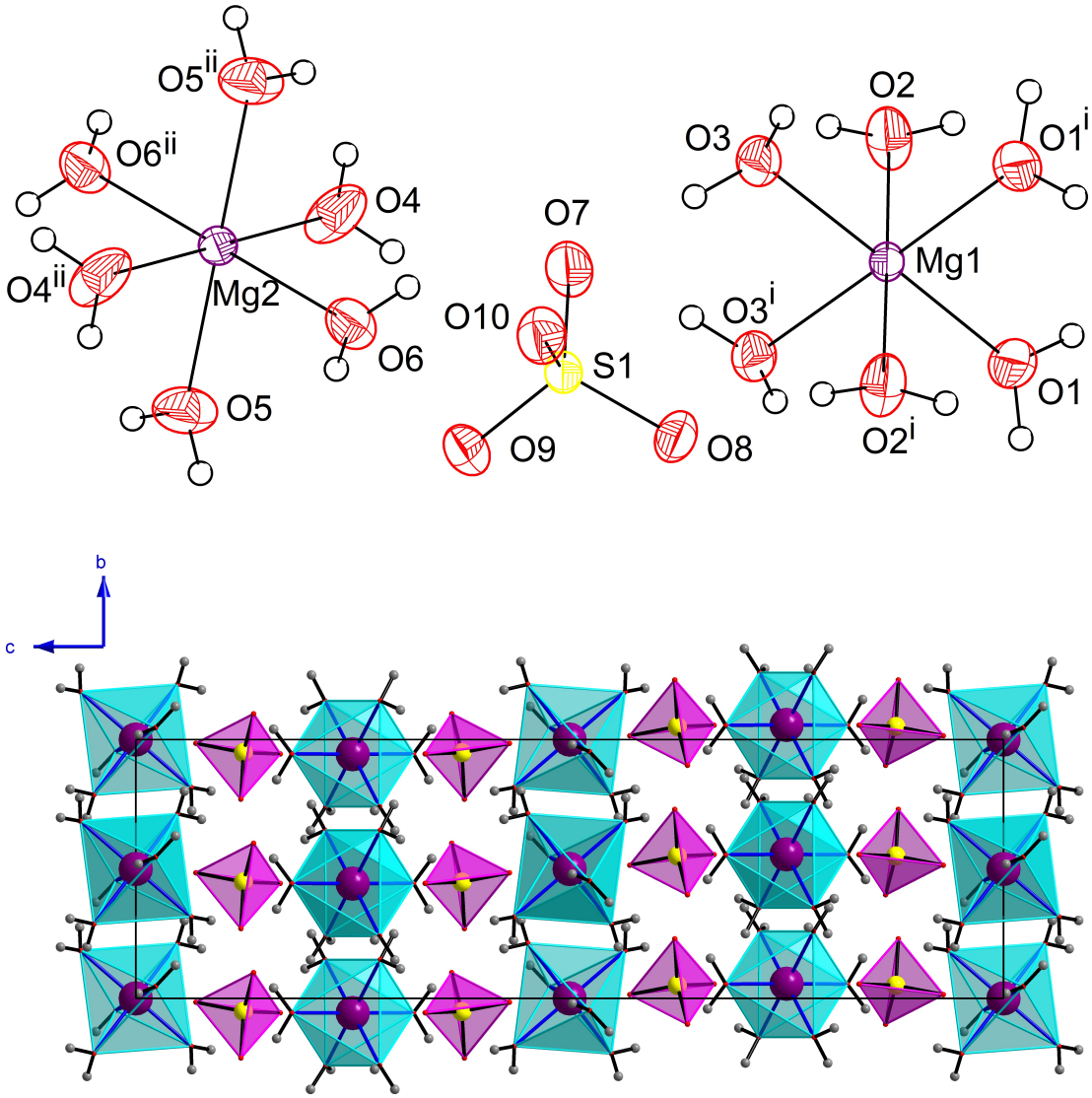


Fig. 1 Crystal structure of $MgSO_4 \cdot 6H_2O$ showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level for all non hydrogen atoms. Symmetry code: i) -x+1,y,-z+1/2 ii) -x+1,-y,-z+1 (**Top**). The crystallographic packing of **1** viewed along *a* axis shows alternating layers of $[Mg(H_2O)_6]^{2+}$ octahedra and $(SO_4)^{2-}$ tetrahedra (**bottom**).

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Supplementary Material for ONLINE version

The following pages contain

i) Structure protocol of magnesium sulphate hexahydrate (pages 2 to 7)

ii) CheckCIF/PLATON report of the CIF file of the crystal structure detrmined by us (pages 8 to 10)

# CRYSTAL STRUCTURE PROTOCOL

Table 1. Crystal data and structure refinement for $Mg(H_2O)_6.SO_4$.

| | | |
|---|---|---|
| Identification code | $Mg(H_2O)_6.SO_4$ | |
| Empirical formula | $H_{12}MgO_{10}S$ | |
| Formula weight | 228.47 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | *C*2/c | |
| Unit cell dimensions | a = 10.1238(10) Å | α= 90° |
| | b = 7.2225(7) Å | β= 98.250(3)° |
| | c = 24.485(3) Å | γ = 90° |
| Volume | 1771.8(3) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.713 $Mg/m^3$ | |
| Absorption coefficient | 0.465 $mm^{-1}$ | |
| F(000) | 960 | |
| Crystal size | 336 x 159 x 112 $mm^3$ | |
| Theta range for data collection | 3.363 to 28.371°. | |
| Index ranges | $-13 \le h \le 13$, $-9 \le k \le 9$, $-32 \le l \le 32$ | |
| Reflections collected | 12454 | |
| Independent reflections | 2206 [R(int) = 0.0232] | |
| Completeness to theta = 25.242° | 99.2 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2206 / 0 / 159 | |
| Goodness-of-fit on $F^2$ | 1.073 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0293, wR2 = 0.0774 | |
| R indices (all data) | R1 = 0.0318, wR2 = 0.0800 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.399 and -0.450 $e.Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $Mg(H_2O)_6.SO_4$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 6345(1) | 5505(1) | 3759(1) | 24(1) |
| Mg(1) | 5000 | 10566(1) | 2500 | 19(1) |
| Mg(2) | 5000 | 0 | 5000 | 21(1) |
| O(1) | 3596(1) | 10552(2) | 1799(1) | 39(1) |
| O(2) | 6122(1) | 12587(2) | 2190(1) | 37(1) |
| O(3) | 3890(1) | 8504(2) | 2819(1) | 33(1) |
| O(4) | 4608(2) | 1847(2) | 4363(1) | 54(1) |
| O(5) | 6881(1) | -459(2) | 4772(1) | 45(1) |
| O(6) | 5851(1) | 2131(2) | 5482(1) | 38(1) |
| O(7) | 5172(1) | 5557(2) | 3335(1) | 45(1) |
| O(8) | 5934(1) | 5147(2) | 4306(1) | 38(1) |
| O(9) | 7255(1) | 4007(2) | 3642(1) | 33(1) |
| O(10) | 7045(1) | 7301(2) | 3788(1) | 37(1) |

Table 3. Bond lengths [Å] and angles [°] for $Mg(H_2O)_6.SO_4$.

| | |
|---|---|
| S1-O7 | 1.4604(11) |
| S1-O10 | 1.4752(11) |
| S1-O9 | 1.4761(11) |
| S1-O8 | 1.4825(13) |
| Mg1-O2 | 2.0604(12) |
| Mg1-O2#1 | 2.0604(12) |
| Mg1-O1#1 | 2.0644(12) |
| Mg1-O1 | 2.0644(12) |
| Mg1-O3 | 2.0838(12) |
| Mg1-O3#1 | 2.0838(12) |
| Mg2-O4#2 | 2.0481(13) |
| Mg2-O4 | 2.0481(13) |
| Mg2-O6 | 2.0521(12) |
| Mg2-O6#2 | 2.0521(12) |
| Mg2-O5 | 2.0865(13) |
| Mg2-O5#2 | 2.0866(13) |
| O1-H1A | 0.83(3) |
| O1-H1B | 0.87(3) |
| O2-H2A | 0.83(3) |
| O2-H2B | 0.82(4) |
| O3-H3A | 0.86(3) |
| O3-H3B | 0.91(3) |
| O4-H4A | 0.77(3) |
| O4-H4B | 0.80(3) |
| O5-H5A | 0.84(3) |
| O5-H5B | 0.80(3) |
| O6-H6A | 0.79(3) |
| O6-H6B | 0.81(3) |
| | |
| O7-S1-O10 | 110.37(7) |
| O7-S1-O9 | 110.34(7) |
| O10-S1-O9 | 110.18(7) |
| O7-S1-O8 | 109.99(8) |
| O10-S1-O8 | 107.73(7) |
| O9-S1-O8 | 108.16(7) |
| O2-Mg1-O2#1 | 89.77(8) |

| | |
|---|---|
| O2-Mg1-O1#1 | 87.69(5) |
| O2#1-Mg1-O1#1 | 92.71(6) |
| O2-Mg1-O1 | 92.71(6) |
| O2#1-Mg1-O1 | 87.69(5) |
| O1#1-Mg1-O1 | 179.44(8) |
| O2-Mg1-O3 | 179.19(5) |
| O2#1-Mg1-O3 | 90.75(5) |
| O1#1-Mg1-O3 | 91.66(5) |
| O1-Mg1-O3 | 87.93(5) |
| O2-Mg1-O3#1 | 90.75(5) |
| O2#1-Mg1-O3#1 | 179.19(5) |
| O1#1-Mg1-O3#1 | 87.93(5) |
| O1-Mg1-O3#1 | 91.66(5) |
| O3-Mg1-O3#1 | 88.74(7) |
| O4#2-Mg2-O4 | 180.00(12) |
| O4#2-Mg2-O6 | 91.76(6) |
| O4-Mg2-O6 | 88.24(6) |
| O4#2-Mg2-O6#2 | 88.24(6) |
| O4-Mg2-O6#2 | 91.76(6) |
| O6-Mg2-O6#2 | 180.0 |
| O4#2-Mg2-O5 | 90.90(6) |
| O4-Mg2-O5 | 89.10(6) |
| O6-Mg2-O5 | 87.08(5) |
| O6#2-Mg2-O5 | 92.92(5) |
| O4#2-Mg2-O5#2 | 89.10(6) |
| O4-Mg2-O5#2 | 90.90(6) |
| O6-Mg2-O5#2 | 92.92(5) |
| O6#2-Mg2-O5#2 | 87.08(5) |
| O5-Mg2-O5#2 | 180.00(8) |
| Mg1-O1-H1A | 120.1(17) |
| Mg1-O1-H1B | 123.5(18) |
| H1A-O1-H1B | 110(2) |
| Mg1-O2-H2A | 122.2(16) |
| Mg1-O2-H2B | 130(3) |
| H2A-O2-H2B | 107(3) |
| Mg1-O3-H3A | 114(2) |
| Mg1-O3-H3B | 118.1(16) |
| H3A-O3-H3B | 107(2) |

| | |
|---|---|
| Mg2-O4-H4A | 121.3(17) |
| Mg2-O4-H4B | 131.2(18) |
| H4A-O4-H4B | 106(2) |
| Mg2-O5-H5A | 124(2) |
| Mg2-O5-H5B | 122(2) |
| H5A-O5-H5B | 112(3) |
| Mg2-O6-H6A | 120(2) |
| Mg2-O6-H6B | 120.2(18) |
| H6A-O6-H6B | 105(2) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x+1,-y,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Mg(H_2O)_6.SO_4$.The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 23(1) | 18(1) | 29(1) | -1(1) | -1(1) | 0(1) |
| Mg(1) | 20(1) | 16(1) | 20(1) | 0 | 2(1) | 0 |
| Mg(2) | 20(1) | 20(1) | 23(1) | -2(1) | -1(1) | 0(1) |
| O(1) | 54(1) | 28(1) | 31(1) | -2(1) | -11(1) | 4(1) |
| O(2) | 33(1) | 31(1) | 47(1) | 12(1) | 6(1) | -3(1) |
| O(3) | 34(1) | 26(1) | 38(1) | 7(1) | 8(1) | 1(1) |
| O(4) | 47(1) | 50(1) | 58(1) | 27(1) | -22(1) | -22(1) |
| O(5) | 29(1) | 57(1) | 49(1) | -21(1) | 5(1) | 3(1) |
| O(6) | 34(1) | 34(1) | 42(1) | -13(1) | -7(1) | 7(1) |
| O(7) | 41(1) | 30(1) | 55(1) | -4(1) | -23(1) | 3(1) |
| O(8) | 44(1) | 32(1) | 41(1) | 0(1) | 14(1) | 1(1) |
| O(9) | 34(1) | 29(1) | 36(1) | -2(1) | 5(1) | 8(1) |
| O(10) | 36(1) | 24(1) | 48(1) | 6(1) | -5(1) | -7(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for $Mg(H_2O)_6.SO_4$.

| x | y | z | U(eq) | |
|---|---|---|---|---|
| H(1A) | 3420(20) | 11520(40) | 1624(10) | 59(7) |
| H(1B) | 3440(30) | 9600(40) | 1585(11) | 63(7) |
| H(2A) | 5780(20) | 13490(40) | 2012(9) | 52(6) |
| H(2B) | 6930(40) | 12780(60) | 2243(15) | 115(13) |
| H(3A) | 3390(30) | 8900(40) | 3048(12) | 75(8) |
| H(3B) | 4330(30) | 7500(40) | 2974(10) | 64(7) |
| H(4A) | 5030(20) | 2740(40) | 4353(10) | 52(7) |
| H(4B) | 3960(30) | 1990(40) | 4136(10) | 57(7) |
| H(5A) | 7600(30) | -180(40) | 4970(13) | 70(8) |
| H(5B) | 6990(30) | -1200(40) | 4541(12) | 70(8) |
| H(6A) | 6340(30) | 1910(40) | 5753(11) | 61(7) |
| H(6B) | 5390(30) | 2990(40) | 5563(11) | 63(7) |

## checkCIF/PLATON report

Structure factors have been supplied for datablock(s) znso4_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: znso4_0m

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```
Bond precision:  Mg- O = 0.0014 A        Wavelength=0.71073

Cell:            a=10.1238(10)     b=7.2225(7)        c=24.485(3)
                 alpha=90          beta=98.250(3)     gamma=90
Temperature:     293 K

                 Calculated                Reported
Volume           1771.8(3)                 1771.8(3)
Space group      C 2/c                     C 2/c
Hall group       -C 2yc                    -C 2yc
Moiety formula   H12 Mg O6, O4 S           H12 Mg O10 S
Sum formula      H12 Mg O10 S              H12 Mg O10 S
Mr               228.47                    228.47
Dx,g cm-3        1.713                     1.713
Z                8                         8
Mu (mm-1)        0.465                     0.465
F000             960.0                     960.0
F000'            962.07
h,k,lmax         13,9,32                   13,9,32
Nref             2223                      2206
Tmin,Tmax        0.915,0.949               0.673,0.746
Tmin'            0.855

Correction method= # Reported T Limits: Tmin=0.673 Tmax=0.746
AbsCorr = MULTI SCAN

Data completeness= 0.992          Theta(max)= 28.371

R(reflections)= 0.0293( 2042)     wR2(reflections)= 0.0800( 2206)

S = 1.073                 Npar= 159
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

**Alert level C**

```
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        Mg1 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        Mg2 Check
PLAT480_ALERT_4_C Long H...A H-Bond Reported H2A      ..S1       .       3.02 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        13 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....         4 Note
```

**Alert level G**

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         4 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         1 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

**Validation response form**

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT242_znso4_0m
;
PROBLEM: Low    'MainMol' Ueq as Compared to Neighbors of        Mg1 Check
RESPONSE: ...
;
_vrf_PLAT480_znso4_0m
;
PROBLEM: Long H...A H-Bond Reported H2A      ..S1       .       3.02 Ang.
RESPONSE: ...
;
_vrf_PLAT911_znso4_0m
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600         13 Report
RESPONSE: ...
;
_vrf_PLAT913_znso4_0m
;
PROBLEM: Missing # of Very Strong Reflections in FCF ....          4 Note
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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**PLATON version of 05/12/2020; check.def file version of 05/12/2020**

**Datablock znso4_0m** - ellipsoid plot