

# Structural studies of zinc ammonium sulphate and magnesium ammonium sulphate mixed crystals – By X-ray diffraction

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## ARTICLE DETAILS

### Article History

Published Online: 15 April 2019

### Keywords

x-ray, zinc, sulphate, cubic mineral.

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## ABSTRACT

The cubic mineral langbeinite  $K_2Mg_2(SO_4)_3$  and its isomorphs  $A^{+1}B^{+2}(SO_4)_3$  where  $A^{+1} = K, Rb, Cs, Te, NH_4^+$  and  $B^{+2} = Mg, Ca, Zn, Mn, Fe, Co$  and  $Ni$  are known for their ferro electric properties. The zinc ammonium sulphate magnesium ammonium sulphate mixed crystals of varying proportions are grown by solution technique and the characterization studies are carried out. By knowing the cell parameters from the available ASTM index for the pure crystals and by adopting the Reitveld refinement procedure from their atomic positions, the h, k, l values of the pure crystals are calculated. From the calculated h, k, l values, the cell parameters of the pure crystals and the X-ray powder diffraction pattern of the mixed crystals, the cell 'n' programme is generated and cell parameters of the mixed crystals are calculated. Some of the calculated values are checked by single crystal analysis. The X-ray Laue pattern is taken and this confirms the single crystallinity and  $P2_1/a$  monoclinic nature. The gradation in the cell parameters is analysed and discussed.

## 1. Introduction

The cubic mineral langbeinite  $K_2Mg_2(SO_4)_3$  and its isomorphs  $A^{+1}B^{+2}(SO_4)_3$  where  $A^{+1} = K, Rb, Cs, NH_4^+$  and  $B^{+2} = Mg, Ca, Zn, Cd, Mn, Fe, Co$  and  $Ni$  are known for their electro optical properties. In the above series only the ferro electricity of  $(NH_4^+)_2Cd_2(SO_4)_3$  was reported by Jona and Pepinsky

In the present work, the zinc ammonium sulphate and magnesium ammonium sulphate pure crystals are synthesized and the purity of the samples are checked by their standard physical properties. The pure crystals Zn/Mg ammonium sulphate mixed crystals of transparent nature are grown by solution technique. As so far no attempt has been made to grow and characterize these materials, the crystals are grown and X-ray powder diffraction studies are carried out and the results are discussed.

### Experimental Details

Zinc ammonium sulphate and magnesium ammonium sulphate pure crystals are synthesized by homogenizing the equimolar solutions of the respective sulphate salts and suddenly quenching in ice. The salts are recrystallized and the purity of the zinc ammonium sulphate and magnesium ammonium sulphate is checked by the standard physical properties like melting point, density, refractive index, solubility etc.,

Appropriate amounts of zinc ammonium sulphate and magnesium ammonium sulphate are mixed in the proportion of 0.1, 0.25, 0.333, 0.5, 0.666. The crystals are grown by solution technique. The crystals grown are transparent and opaque. X-ray powder diffraction pattern of the mixed crystals are taken. The cell parameters of the pure crystals of zinc ammonium sulphate and magnesium ammonium sulphate are

taken from the ASTM index (1, 2) and as the h, k, l values are not available for both the systems, the Reitveild Refinement procedure (5, 6) is adopted to find out the h, k, l valued from their atomic position. From this determines crystallographic data, the cell parameters are calculated by indexing h, k, l values in to the cell programme.

### Results and Discussions

For taking the powder diffraction pattern the characteristic X-ray radiation e.g.  $CuK\alpha$  is used so that the wavelength  $\lambda$  is known. Thus from the Bragg's equation  $n\lambda = 2d \sin \theta$ , the inter planar values from the X-ray powder diffraction patterns.

The crystals belonging to monoclinic system are optically biaxial. The powder diffraction pattern of the pure crystals of Tutton salts mixed crystals having composition 'a' values 0.1, 0.25, 0.333, 0.5, 0.666 are taken. The diffraction data in the form of a list of 'd' values are obtained. The 'd' values are arranged in the order of decreasing intensity of the powder lines.

These data are then matched against standard data and if the two match, the identification is accomplished. The standard data are available in the cards provided by American Chemical Society for Testing and Materials (ASTM). As in the standard data h, k, l values for zinc ammonium sulphate and the standard itself for magnesium ammonium sulphate is not available, by assuming the positions of the atoms, cell parameters,  $P2_1/a$  with monoclinic system.

A good correlation is found between the calculated values of the cell parameters and single crystal analysis. X-ray Laue pattern confirmed the single crystallinity and the crystal belong to monoclinic. The irregularity in the cell parameters shows the random occupation of  $Zn^{2+}$  in the lattice sites.

**X-ray powder data for magnesium sulphate**

S. No	2θ		d	h	k	l	a	b	c	β
1	17	8"	5.2155	1	2	0	9.324	12.597	6.211	107° 8"
2	21	36"	4.1141	1	1	1				
3	24		3.7078	1	3	0				
4	26	24"	3.3759	1	3	1				
5	29	42"	3.0079	1	3	1				
6	32	42"	2.7388	1	4	1				
7	42	12"								

**Table 1 X-ray powder data for zinc ammonium sulphate**

S. No	2θ		d	h	k	l	a	b	c	β
1	14	15"	6.1936	0	2	0	9.223	12.5	6.237	106° 52"
2	17	24"	5.0965	1	2	0				
3	21	24"	4.1521	2	0	1				
4	23	36"	3.7698	1	3	0				
5	29	30"	3.0279	2	1	1				
6	35	6"	2.5566	2	3	1				
7	42	12"								

**Table 2 X-ray diffraction pattern data of mixed crystals determination of cell parameters Zn/Mg ammonium sulphate crystals (a = 0.1)**

S. No	2θ		d	h	k	l	a	b	c	β
1	16	42"	5.3085	1	2	0	7.3913	14.0025	7.2403	107° 20"
2	21	30"	4.1329	1	1	1				
3	23	36"	3.7697	1	3	0				
4	26	24"	3.3759	1	3	1				
5	28	24"	3.1425	1	3	1				
6	33	42"	3.0079	1	4	1				

**Table 3 X-ray diffraction pattern data of mixed crystals determination of cell parameters Zn/Mg ammonium sulphate crystals (a = 0.25)**

S. No	2θ		d	h	k	l	a	b	c	β
1	17	6"	5.1852	1	2	0	8.8539	12.2934	7.2025	107° 22"
2	19	48"	4.4838	1	1	1				
3	24	36"	3.6187	1	3	0				
4	26	36"	3.4270	1	3	1				
5	29	24"	3.0379	1	3	1				
6	31	54"	2.8053	1	4	1				

**Table 4 X-ray diffraction pattern data of mixed crystals determination of cell parameters Zn/Mg ammonium sulphate crystals (a = 0.333)**

S. No	2θ		d	h	k	l	a	b	c	β
1	17	12"	5.1553	1	2	0	9.2187	12.6513	6.3788	107° 21"
2	21		4.2302	1	1	1				
3	23	18"	3.8176	1	3	0				
4	26		3.4270	1	3	1				
5	29	24"	3.0379	1	3	1				
6	32		2.7968	1	4	1				

**Table 5 X-ray diffraction pattern data of mixed crystals determination of cell parameters Zn/Mg ammonium sulphate crystals (a = 0.5)**

S. No	2θ		d	h	k	l	a	b	c	β
1	17	6"	5.1852	1	2	0	9.9295	12.4318	6.2334	107° 22"
2	21	6"	4.2104	1	1	1				
3	23	18"	3.8176	1	3	0				
4	26		3.4270	1	3	1				
5	29	18"	3.0481	1	3	1				
6	32	42"	2.7467	1	4	1				

**Table 6 X-ray diffraction pattern data of mixed crystals determination of cell parameters Zn/Mg ammonium sulphate crystals (a = 0.666)**

S. No	2θ		d	h	k	l	a	b	c	β
1	14		6.3256	0	2	0	9.1153	12.615	6.5376	106° 86"
2	17	6"	5.1852	1	2	0				
3	22	12"	4.0042	2	0	1				
4	23	18"	3.8176	1	3	0				
5	29	18"	3.0481	2	1	1				
6	35		2.5636	2	3	1				
7	41	30"	2.1759	2	5	0				
8	50	6"	1.8207	4	2	1				

**Cell parameters for the mixed crystals**

Concentration	Cell parameter			
	a	b	c	β
0.1	7.3913	14.0025	7.2403	107.205
0.25	8.8539	12.2934	7.2025	107.222
0.333	9.2187	12.6513	6.3788	107.217
0.5	9.9295	12.4318	6.2334	107.220
0.666	9.1153	12.6156	6.5376	107.862

**ASTM data for magnesium ammonium sulphate generated by reitveild refinement procedure**

l	3.30	5.37	4.21	4.26	3.01														
	100	96.80	78.72	62.80	55.30	d	l/lo	h	k	l	d	l/lo	h	k	l				
System Monoclinic S.G.C <sub>2</sub> <sup>5</sup> H P2 <sub>1</sub> /a S.G.C2H P21/a						5.9	10.6	0	0	1	2.46	38.29	3	3	1				
						5.37	96.8	0	1	1	2.226	19.14	2	4	1				
						5.14	46.81	1	2	0	2.159	14.89	0	4	2				

Colour colourless	4.21	78.72	2	0	1	2.1	20.2	4	2	0
	4.2	62.76	2	1	0	1.91	13.8	3	1	3
	3.8	100	1	3	0	1.764	10.63	5	1	0
	3.4	19.1	1	3	1	1.73	9.57	3	5	1
	3.15	45.7	0	4	0	1.64	5.3	5	3	0
	3.01	55.3	1	1	2	1.26	5.3	4	6	1
	2.78	47.9	1	2	2					

ASTM data for zinc ammonium sulphate mixed crystals by reitveld refinement procedure

System Monoclinic  a = 9.224 b = 12.5 c = 6.237 $\beta = 106^{\circ}52''$ colour colourless	3.76	4.167	5.38	3.02	2.43	Zinc ammonium sulphate									
	100	74.84	59.35	57.42	37.42	d	l/lo	h	k	l	d	l/lo	h	k	l
						7.19	9	1	1	0	1.98	8.4	0	0	3
						6.24	25.86	0	2	0	1.95	9	3	5	1
						5.38	59.35	0	1	1	1.85	8	2	6	1
						4.20	74.8	2	0	1	1.81	6.5	1	1	3
						3.76	100	1	3	0	1.76	5.2	3	5	2
						3.02	57.42	1	1	2	1.62	4	4	4	1
						2.79	25.81				1.56	3.2	2	0	4
						2.43	37.42	3	3	1					
						2.21	21.29	2	4	1					
						2.15	17.4	0	4	2					

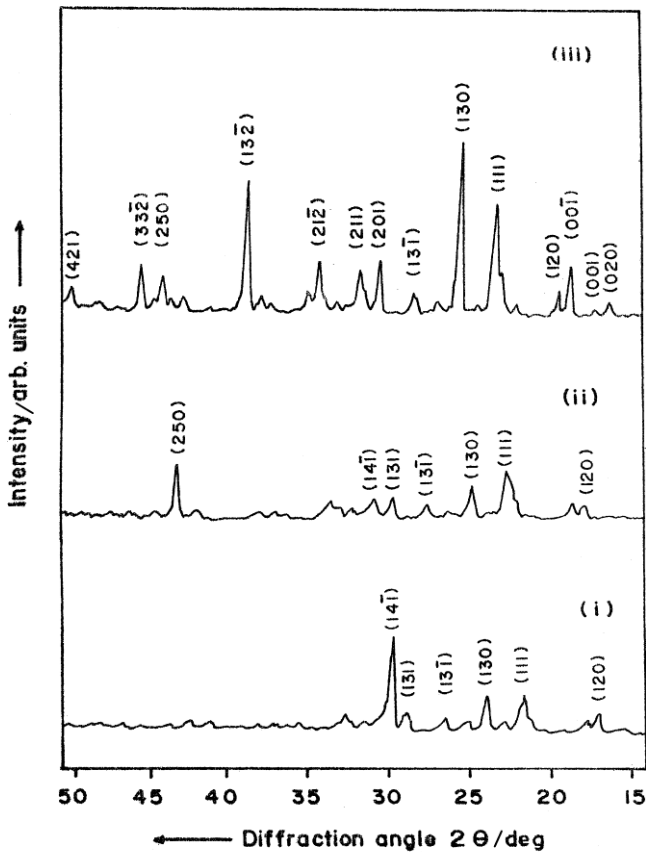


Fig 6 X ray diffraction pattern for  
 (i) magnesium ammonium sulphate  
 (ii) 0.1 zinc magnesium ammonium sulphate  
 (iii) 0.25 zinc magnesium ammonium sulphate

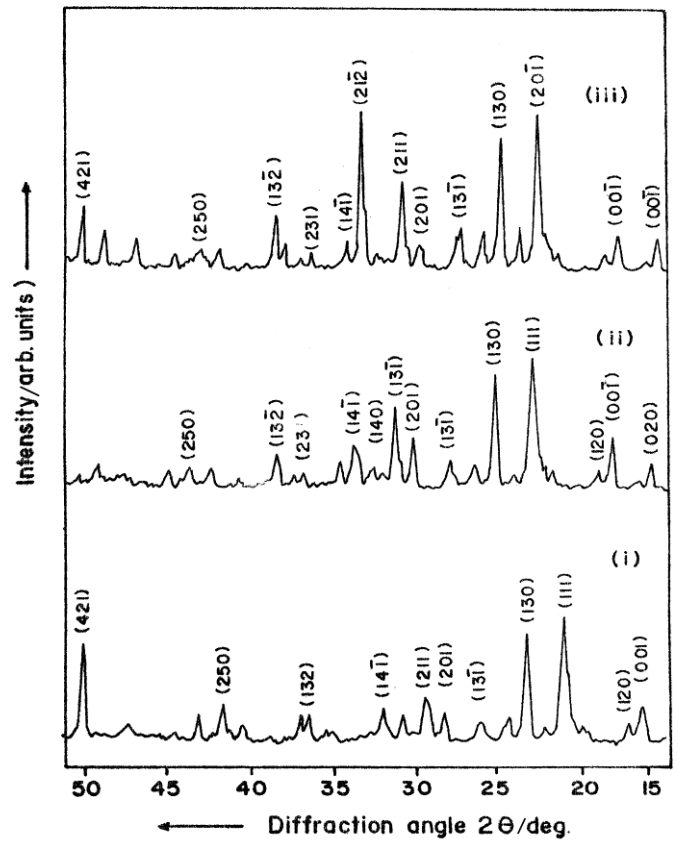


Fig 7 X ray diffraction pattern for  
 (i) 0.33 zinc magnesium ammonium sulphate  
 (ii) 0.5 zinc magnesium ammonium sulphate  
 (iii) 0.66 zinc magnesium ammonium sulphate

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