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Lattice variation and thermal parameters of $Ni_xMg_{1-x}SO_4·7H_2O$ single crystals

M THEIVANAYAGOM[†] and C MAHADEVAN*

Department of Physics, ST Hindu College, Nagercoil 629 002, India
[†]Sivanthi Aditanar College, Pillayarpuram, Nagercoil 629 501, India

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Abstract. **$Ni_xMg_{1-x}SO_4·7H_2O$ single crystals were grown by the slow evaporation method from aqueous solutions. Density was measured by the floatation method. X-ray diffraction data were collected for powder samples and used for the estimation of lattice variation and thermal parameters like Debye–Waller factor, mean-square amplitude of vibration and Debye temperature. Lattice volumes approximately obey a relation similar to Retger's rule. Values of thermal parameters do not follow any particular order with composition. The results obtained are reported.**

Keywords. **Mixed crystals; X-ray diffraction analysis; lattice parameters; Debye–Waller factors; Debye temperatures.**

1. Introduction

Nickel sulphate heptahydrate, $NiSO_4·7H_2O$ crystal is orthorhombic with a tetra molecular unit cell of dimensions $a = 11·86$, $b = 12·08$ and $c = 6·81$ Åand is isomorphous with $MgSO_4·7H_2O$, $ZnSO_4·7H_2O$ and $NiCrO_4·7H_2O$. The unit cell parameters for magnesium sulphate heptahydrate, $MgSO_4·7H_2O$ crystal are $a = 11·86$, $b = 11·99$ and $c = 6·858$ Å The space group is $P_{2_12_12_1}$with all atoms in the general positions x, y, z; $x, y, z+\frac{1}{2}$; $x+\frac{1}{2}, \frac{1}{2}-y, z$ and $\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$ (Wyckoff 1960).

The molecular weight, mean refractive index and density of $NiSO_4·7H_2O$ are 280·88, 1·483 and 1·948 g/cc, respectively. The crystal is green in colour. The molecular weight, mean refractive index and density of $MgSO_4·7H_2O$ are 246·48, 1·485 and 1·68 g/cc, respectively. The crystal is colourless (Dean 1979).

Several research workers have carried out much work on mixed crystals of cubic systems. But, very limited studies have been done on orthorhombic systems. Mahadevan and his co-workers have reported specific refraction measurements (Jayakumari and Mahadevan 1992) and Debye temperature determination (Jayakumari *et al* 1993) on mixed crystals of $MgSO_4·7H_2O$ and $ZnSO_4·7H_2O$ and nucleation studies on mixed crystals of $NiSO_4·7H_2O$, $MgSO_4·7H_2O$ and $ZnSO_4·7H_2O$ (Perumal and Mahadevan 1993; Shajan and Mahadevan 1996; Sriramachandran and Mahadevan 1996) and on $NiSO_4·7H_2O$ crystal doped with $MgSO_4·7H_2O$ and $ZnSO_4·7H_2O$ (Mahadevan *et al* 1999).

The Debye temperature is derivable from experimental data like specific heat, elastic constants, X-ray and neutron diffraction intensities, etc. It is possible to estimate the Debye temperature from the data like melting points, compressibility and microhardness by the use of semi empirical relations (Srinivas and Sirdeshmukh 1986a). But the values obtained from them are not that much accurate as those from specific heat or elastic constants. These relations have been tested on pure crystals as well as (cubic) mixed crystals. Various methods of determination of Debye temperatures have been discussed in reviews by Blackman (1955), and Alers (1965). An efficient method of determining the Debye temperature is from the Debye–Waller factor obtained from X-ray (powder or single crystal) diffraction data (Srinivas and Sirdeshmukh 1986b; Jayakumari *et al* 1993; Geetakrishna *et al* 1999). By using this method, the Debye temperatures have been estimated for mixed crystals like $AgCl_xBr_{1-x}$ (Srinivas and Sirdeshmukh 1985a), $Mg_xZn_{1-x}SO_4·7H_2O$ (Jayakumari *et al* 1993) and alkali halide mixed crystals (Pathak and Trivedi 1971; Srinivas and Sirdeshmukh 1978, 1985b, 1988; Srinivas *et al* 1987; Geetakrishna *et al* 1999). As this method is suitable for any crystal system, it can be adopted for $Ni_xMg_{1-x}SO_4·7H_2O$.

A research programme on the growth and physical properties of mixed crystals of $NiSO_4·7H_2O$, $MgSO_4·7H_2O$ and $ZnSO_4·7H_2O$ is on hand in this laboratory. As a part of the programme, mixed crystals of $NiSO_4·7H_2O$ and $MgSO_4·7H_2O$ were grown and X-ray diffraction data were collected from powder samples of the grown crystals and used for the estimation of lattice variation and thermal parameters like mean Debye–Waller factor, mean square

*Author for correspondence

amplitude of vibration and Debye temperature. We report here the results obtained in our study.

2. Experimental

Analytical reagent grade (AR) samples of $NiSO_4{\cdot}7H_2O$ and $MgSO_4{\cdot}7H_2O$ along with double distilled water were used in the present investigations. Aqueous solution of $Ni_xMg_{1-x}SO_4{\cdot}7H_2O$ salt was prepared at a supersaturated concentration and taken in the nucleation cell (corning glass vessel) and allowed to equilibrate at the desired temperature. The crystals were grown in the unstirred condition. The temperature and volume were kept constant respectively at 30°C and 25 ml for all crystal growth experiments. Small crystals appeared in the beginning due to slow evaporation and grew larger in considerable finite time. Best crystals were selected from this and used for the measurements. In the present study crystals were grown from six mixed solutions with x values ranging from 0·0 to 1·0 in steps of 0·2.

Densities of the grown crystals were measured by the floatation method and compositions were estimated following the method adopted by Nair and Walker (1971).

X-ray diffraction data were collected from powder samples of crystals using a Ritz automated diffractometer with monochromated CuK_a (l = 1·5418 Å radiation (scan speed 2°/min) and scintillation counter at a temperature of 25 ± 1°C. The reflections were indexed following the procedures of Lipson and Steeple (1970). Processing of the raw intensity data was done following the procedures of Warren (1969). Lattice parameters were determined from the indexed data using high angle reflections.

The mean Debye–Waller factors (B_{obs}) were determined by the Wilson plot method (Wilson 1942). For the calculation of structure factors, the atomic scattering factors were taken from the literature (Cromer and Mann 1968; Ibers and Hamilton 1974).

For pure $NiSO_4{\cdot}7H_2O$ crystal, the structure factor is:

$$F = 4[\, f_{Ni}^{2+} + f_S + 11\, f_O^- + 14\, f_H].$$

For pure $MgSO_4{\cdot}7H_2O$ crystal, the structure factor is:

$$F = 4[\, f_{Mg}^{2+} + f_S + 11\, f_O^- + 14\, f_H].$$

For $Ni_xMg_{1-x}SO_4{\cdot}7H_2O$ mixed crystals, the structure factor is:

$$F = 4[x\, f_{Ni}^{2+} + (1-x)\, f_{Mg}^{2+} + f_S + 11\, f_O^- + 14\, f_H].$$

Experimentally determined Debye–Waller factor, B_{obs} for mixed crystal contains a static component which arises due to disorder caused by the presence of atoms of different sizes at lattice points which are normally occupied by a given type of atom. This disorder enhances the Debye–Waller factor and also the amplitude of vibration. Hence the observed Debye–Waller factor for mixed crystal is written as

$$B_{obs} = B_{thermal} + B_{static}.$$

Following a model due to Dernier *et al* (1976)

$$B_{static} = (r_A - r_B)^2\, x(1-x).$$

Here r_A and r_B are the atomic radii of Ni and Mg atoms, respectively and x is the fraction of $NiSO_4{\cdot}7H_2O$ present in the crystal. $B_{thermal}$ and B_{static} were found out using the above relations for the mixed crystals.

For pure crystals,

$$B_{obs} = (6h^2/mkT)W(x),$$

and for mixed crystals,

$$B_{thermal} = (6h^2/mkT)W(x).$$

Here h is the Planck's constant, k the Boltzmann constant, T the absolute temperature at which X-ray intensities are measured and m the mean atomic mass of crystal. The function $W(x)$ is given by

$$W(x) = [\, j(x)/x]^2 + \tfrac{1}{4}\, x.$$

Here $x = q_D/T$. q_D is the Debye temperature and $j(x)$ is an integral given by

$$j(x) = \int_0^x e^y/(1-e^y)\, dx.$$

The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill (1966). Using the above equations Debye temperatures (q_D) were evaluated. The mean square amplitudes of vibration $\bar{u}^2$ were obtained using the relation (Glusker and Trueblood 1985)

$$B = 8p^2\, \bar{u}^2.$$

3. Results and discussion

All mixed crystals grown (up to a size of about 1 cm) in the present study were found to have the similar morphology as that for pure crystals (see figure 1). All the crystals grown were found to be stable. All the grown crystals except the pure $MgSO_4{\cdot}7H_2O$ were greenish in colour. $MgSO_4{\cdot}7H_2O$ crystals were transparent. Intensity of green colouration decreased with the increase in x value (showing the composition).

The measured densities of the grown crystals are presented in table 1. For the mixed system considered in the present study the densities show linear composition dependence. The densities observed for the pure systems compare well with those reported in the literature (Dean 1979).

Lattice parameters a, b, c and volumes of the mixed crystals estimated in the present study are given in table 1. The estimated standard deviations were also calculated

and presented in table 1. It is found that volumes are approximately additive and the $NiSO_4{\cdot}7H_2O$–$MgSO_4{\cdot}7H_2O$ system approximately represents the mixed system obeying the relation,

$$V = xV_1 + (1 - x)V_2,$$

which is similar to Retger's rule, applied to cubic system. Here, V is the lattice volume of mixed crystals and V_1 and V_2 are the volumes of the end members. The lattice parameters obtained for the end members compare well with those reported in the literature (Wyckoff 1960).

Values of Debye–Waller factors (B_{thermal} and B_{static}), mean square amplitudes of vibration and Debye temperatures are provided in table 2. No particular order was observed in the case of thermal parameters obtained, viz. B, $\bar{u}^2$ and q_D with respect to composition. This is similar to that observed for the $Mg_xZn_{1-x}SO_4{\cdot}7H_2O$ systems (Jayakumari *et al* 1993). No comparison is made with other studies since there is no data available in the literature for the systems considered in the present study.

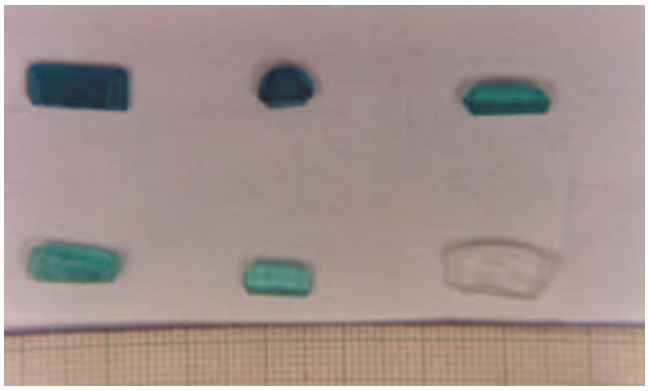

Figure 1. Photograph showing sample crystals. (Top row: from left are $NiSO_4{\cdot}7H_2O$, $Ni_{0\cdot81}Mg_{0\cdot19}SO_4{\cdot}7H_2O$ and $Ni_{0\cdot62}Mg_{0\cdot38}SO_4{\cdot}7H_2O$ and bottom row: from left are $Ni_{0\cdot39}Mg_{0\cdot61}SO_4{\cdot}7H_2O$, $Ni_{0\cdot18}Mg_{0\cdot82}SO_4{\cdot}7H_2O$ and $MgSO_4{\cdot}7H_2O$).

Several relations have been proposed either semi theoretically or empirically to describe the composition dependence of the Debye temperatures of mixed crystals. By assuming the additivity of specific heats and using for the specific heat the low temperature expression from Debye's theory (the Debye T^3 expression), the following relation was obtained

$$q^{-3} = xq_1^{-3} + (1 - x)q_2^{-3},$$

where q_1 and q_2 are the Debye temperatures of the end members and q that of the mixed crystal. This relation is known in literature as the Kopp–Newmann relation (Swalin 1962). Following the same procedure but employing the high temperature expression for specific heat, Nagaiah and Sirdeshmukh (1980) obtained the relation,

$$q^2 = xq_1^2 + (1 - x)q_2^2.$$

Karlsson (1970) and Nagaiah and Sirdeshmukh (1980) respectively, proposed the following relations from empirical considerations

$$q^{-2} = xq_1^{-2} + (1 - x)q_2^{-2},$$
$$q^{-1} = xq_1^{-1} + (1 - x)q_2^{-1}.$$

Recently, Geetakrishna *et al* (1999) have found that the seven alkali halide mixed systems they studied satisfy the Kopp–Newmann relations for the Debye temperatures.

Table 1. Lattice parameters (*a*, *b* and *c*)*, volumes and densities for $Ni_xMg_{1-x}SO_4{\cdot}7H_2O$ crystals.

Sample	*a*(Å)	*b*(Å)	*c*(Å)	Volume (Å^3)	Density (g/cc)
$NiSO_4{\cdot}7H_2O$	11·8600(20)	12·0797(21)	6·8097(3)	975·62	1·878
$Ni_{0\cdot81}Mg_{0\cdot19}SO_4{\cdot}7H_2O$	11·8598(5)	12·0581(8)	6·8348(26)	975·38	1·837
$Ni_{0\cdot62}Mg_{0\cdot38}SO_4{\cdot}7H_2O$	11·8597(18)	12·0271(6)	6·8391(2)	974·90	1·796
$Ni_{0\cdot39}Mg_{0\cdot61}SO_4{\cdot}7H_2O$	11·8596(44)	12·0186(6)	6·8478(13)	974·82	1·745
$Ni_{0\cdot18}Mg_{0\cdot82}SO_4{\cdot}7H_2O$	11·8595(1)	11·9989(38)	6·8479(3)	974·45	1·698
$MgSO_4{\cdot}7H_2O$	11·8594(5)	11·9923(6)	6·8503(28)	974·26	1·661

*e.s.d's are given in parentheses.

Table 2. Thermal parameters for $Ni_xMg_{1-x}SO_4{\cdot}7H_2O$ crystals.

Sample	B_{obs} (Å^2)	B_{thermal} (Å^2)	B_{static} (Å^2)	$\bar{u}^2$ (Å^2)	q_D (K)
$NiSO_4{\cdot}7H_2O$	20·700	–	–	0·262	125·4
$Ni_{0\cdot81}Mg_{0\cdot19}SO_4{\cdot}7H_2O$	28·532	28·512	0·020	0·361	108·0
$Ni_{0\cdot62}Mg_{0\cdot38}SO_4{\cdot}7H_2O$	12·714	12·684	0·031	0·160	164·3
$Ni_{0\cdot39}Mg_{0\cdot61}SO_4{\cdot}7H_2O$	13·103	13·072	0·031	0·165	165·3
$Ni_{0\cdot18}Mg_{0\cdot82}SO_4{\cdot}7H_2O$	10·789	10·770	0·019	0·136	183·8
$MgSO_4{\cdot}7H_2O$	12·950	–	–	0·164	169·6

The above relations are good for mixed crystals of cubic systems and may not be for mixed crystals of orthorhombic systems. The orthorhombic systems studied so far, viz. $Mg_xZn_{1-x}SO_4{\cdot}7H_2O$ and $Ni_xMg_{1-x}SO_4{\cdot}7H_2O$ do not satisfy any of the above relations for the Debye temperatures.

4. Conclusions

$Ni_xMg_{1-x}SO_4{\cdot}7H_2O$ single crystals were grown from aqueous solutions and X-ray powder diffraction analyses were done. The volumes were found to be additive. The obtained thermal parameters do not follow any particular order with respect to composition.

References

Alers G A 1965 *Physical acoustics* (New York: Academic Press) Vol. **3B**

Benson G C and Gill E K 1966 *Tables of integral functions related to Debye–Waller factor* (Ottawa: National Research Council of Canada)

Blackman M 1955 *Handbuch der physik* (Berlin: Springer Verlag) Vol. 7, Part I

Cromer D T and Mann J B 1968 *Acta Crystallogr.* **A24** 321

Dean J A (ed.) 1979 *Lange's handbook of chemistry* (New York: McGraw Hill Book Company) 12 edn

Dernier P D, Weber W and Longinotti L D 1976 *Phys. Rev.* **B14** 3635

Geetakrishna P, Subhadra K G, Kumaraswamy T and Sirdeshmukh D B 1999 *Pramana – J. Phys.* **52** 503

Glusker J P and Trueblood F N 1985 *Crystal structure analysis – A primer* (New York: Oxford University Press) II edn

Ibers J A and Hamilton W C (eds) 1974 *International tables for X-ray crystallography* (Birmingham: Kynoch Press) Vol. IV

Jayakumari K and Mahadevan C 1992 *J. Optics* **21** 22

Jayakumari K, Mahadevan C and Chandrasekaram D 1993 *J. Pure & Appl. Phys.* **5** 331

Karlsson A V 1970 *Phys. Rev.* **B2** 3332

Lipson H and Steeple H 1970 *Interpretation of X-ray powder diffraction patterns* (New York: Macmillan)

Mahadevan C, Irene Latha D and Umayorubhagan V 1999 *J. Indian Chem. Soc.* **76** 335

Nagaiah B and Sirdeshmukh D B 1980 *Indian J. Pure & Appl. Phys.* **18** 903

Nair I R and Walker C T 1971 *Phys. Rev.* **B3** 3446

Pathak P D and Trivedi J M 1971 *J. Phys. C: Solid State Phys.* **4** L219

Perumal S and Mahadevan C 1993 *Nucleation studies on supersaturated aqueous solutions of $Mg_xZn_{1-x}SO_4{\cdot}7H_2O$, V nat. sem. cryst. growth* (Madras: Anna University)

Shajan X S and Mahadevan C 1996 *Nucleation studies on supersaturated aqueous solutions of $Mg_xNi_{1-x}SO_4{\cdot}7H_2O$, Proc. nat. conf. fundam. cryst. growth* (Madras: Anna University) p. 90

Srinivas K and Sirdeshmukh D B 1978 *Pramana – J. Phys.* **10** 17

Srinivas K and Sirdeshmukh D B 1985a *Curr. Sci.* **54** 740

Srinivas K and Sirdeshmukh D B 1985b *Pramana – J. Phys.* **25** 71

Srinivas K and Sirdeshmukh D B 1986a *Indian J. Pure & Appl. Phys.* **24** 95

Srinivas K and Sirdeshmukh D B 1986b *Cryst. Res. & Technol.* **21** 157

Srinivas K and Sirdeshmukh D B 1988 *Pramana – J. Phys.* **31** 221

Srinivas K, Ateequddin M and Sirdeshmukh D B 1987 *Pramana – J. Phys.* **28** 81

Sriramachandran P and Mahadevan C 1996 *Nucleation studies on supersaturated aqueous solutions of $Zn_xNi_{1-x}SO_4{\cdot}7H_2O$, Proc. nat. conf. fundam. cryst. growth* (Madras: Anna University) p. 87

Swalin R A 1962 *Thermodynamics of solids* (New York: John Wiley)

Warren B E 1969 *X-ray diffraction* (California: Addison Wesley)

Wilson A J C 1942 *Nature* **150** 151

Wyckoff R W G 1960 *Crystal structures* (New York: Interscience) II ed. **Vol. 3**, p. 839