A STUDY ON ELECTRICAL PROPERTIES OF PURE AND KDP, ADP DOPED ZnSO4.7H2O SINGLE CRYSTAL

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Abstract:

Zinc Sulphate heptahydrate (ZSHH) possesses wide range of applications in the field of telecommunication, solar systems for solar energy storage, coagulation bath for rayon and optical information storage devices. Crystallization of heptahydrate sulphate material such as zinc vitriol ($ZnSO_4.7H_2O$) of high purity has become an important field of research for both academic and industrial applications in various areas like medical, agricultural and chemical industry. To be useful in various applications, crystals must have the appropriate properties which depend on the particular substance and the impurities and defects present. In this project work growth of pure $ZnSO_4.7H_2O$ crystals and KDP and ADP doped $ZnSO_4.7H_2O$ crystals with different concentrations have been undertaken by using solution growth, slow evaporation methods. And we studied the various properties of the grown crystals. The aim of this work is to study the effect of impurity on various properties of the $ZnSO_4.7H_2O$ crystals.

1.Introduction

Zinc sulphate heptahydrate (merenosite), $ZnSO_4.7H_2O$, belongs to the hexagonal crystal system having a hexagonal molecular unit cell of dimensions (abc) and is isomorphism with $MgSO_4.7H_2O$ and $NiSO_4.7H_2O$. The crystal is white in color. It is soluble in water and its solubility at $20°$ is 46.0 parts by weight per 100 parts by weight of water [6,7]. The molecular weight and density are 287.54 and 7.13 (kg/m^3) in 10^3 respectively. Zinc sulphate heptahydrate is used in agriculture industries as mixmicronutrient fertilizers [8]. The pure zinc sulphate crystals were grown at low temperature from aqueous solutions (Kasatkin 2002, Ramalingom et al. 2001, Sgualdino et al. 1987, Tomas et al. 1969). At room temperature around $34°C$, the solubility was found to be 92.41 gm/50 ml. The compound is found to be thermally stable up to $70°C$. The first weight loss occurs in the range of $70°$ to $120°C$ due to the loss of six water molecules with a sharp endothermic peak in the DTA spectrum. The sample suffers a second weight loss at $260°C$ due to the loss of SO_3 molecule and half of a water molecule leaving $ZnO.1/2(H_2O)$.

Potassium dihydrogen orthophosphate (KDP) belongs to scalenohedral class of tetragonal crystal system. It exhibits an electric dipole moment even in the absence of external electric field. It undergoes a transition from polarized phase into an unpolarized phase at Curie temperature. It consists of domain with parallel and antiparallel polarization separated by domain walls. When an electric field is applied domains that are favorably oriented with respect to this field grow at the expense of others. The favorably oriented domains can nucleate and grow until the whole crystal becomes a single domain. When cooled below 122K (Curie temperature) [18] KDP changes to a crystal hybrid in which there is a breakup of the single crystal into sub-crystalline regions. When the hybrid crystal is warmed above the Curie temperature, the sub-crystalline unit's merge. KDP is insoluble in alcohol but soluble in water.

The molecular weight of KDP is 136.09. The refractive index of KDP is 1.5095 which is slightly less than that of glass. The density of the crystal is 1.338 g/cc [19]. Its resistivity is of the order if 10^{-6} ohm meter. The dielectric constant is ~ 10.

Ammonium dihydrogen orthophosphate (ADP) ($NH_4H_2PO_4$) is an interesting and useful material for science and industry. It belongs to the scalenohedral class of tetragonal crystal system. It is colourless and isomorphous with potassium dihydrogen orthophosphate(KDP). It has a tetragonal structure very similar to that of Zircon and has the tetramolecular unit cell having dimensions [20] given as a=b=7.510 Å and c=7.564 Å, has a ratio c/a=1.0072 Å. The molar volume of ADP is 6.4225×10^{-5} m^3. Each ammonium has four hydrogen bonds linked with oxygen of phosphate lattice. The layers of hydrogen bonds are lying closely in ab planes. The hydrogen ions in the ammonium lattice have only fixed positions, while the hydrogen ions connecting the phosphate groups have two positions along the hydrogen bond. ADP is soluble in water. The solubility at 0, 10, 20, 30, 40, 50, 60, 70, 80 and 100° C are 22.7, 29.5, 37.4, 46.4, 56.7, 82.5, 118 and 173 parts by weight per 100 parts by weight of water respectively [19]. ADP is antiferroelectric and the curie temperature T_c is -125°C [18]. The molecular weight and density are respectively 115.03 and 1.803 g/cc. Its melting point is 150°C (ie) at 150°C, the compound decomposes. It has the refractive indices 1.525 and 1.475 along unique axis and perpendicular directions respectively.

2. Experimental Details

The methods of crystal growth can be classified into four categories: i) growth from solid, ii) growth from melt, iii) growth from vapour and iv) growth from solution. It is very much necessary to prepare large specimens of crystalline material such that there is a complete crystallographic continuity across a given specimen in all directions. The two principal reasons for the artificial growth of single crystals are, many physical properties of solids are obscured or complicated by the effect of grain boundaries and the full range of tensor relationships between applied physical causes and observed effect can be obtained only if the full internal symmetry of the crystal structure is maintained throughout the specimen. Crystals intended for practical and technical applications should have a well developed morphology and contains a low density of defects such as inclusions, dislocations, etc. Among the several methods available to grow single

crystals, solution growth occupies a prominent place owing to its versatility and simplicity. Crystals of materials which exhibit structural transformation while cooling from the melting point or which decompose on heating can be grown by solution growth if suitable solvents are available. The process of solution growth now yields good quality crystals for a variety of applications. Moreover, growth of crystals from solution at room temperature has many advantages over other growth methods, since the rate of crystallization is very slow and growth is carried out at room temperature the concentration of structural imperfections in solution grown crystal is relatively low. So, this method is widely used to grow bulk crystals.

A good solvent for crystal growth should have the following properties: (i) A sufficient solubility of the material in it; (ii) Moderately reversible solubility of the material; (iii) Useful habit of crystal grown from it; (iv) No corrosion of growth apparatus; (v) Low vapour pressure at the growth temperature; (vi) Low toxicity and inflammability; (vii) Low viscosity; (viii) Cheap in pure state; etc. In general, organic solvents are volatile, toxic and inflammable. Water is considered to be the best choice because of its low viscosity, low toxicity, easy availability in the pure state and cheapness. Also, it is inert to a variety of glasses, plastics and metals and provides a reasonably wide range for the selection of growth temperature in comparison with other solvents. A solvent in which the solute has a solubility between 10 to 60% may be considered suitable for crystal growth.

In temperature gradient method ,the material to be grown as crystal is transported from a hot region to a cooler region where the solution is super-saturated and the required crystal grows.
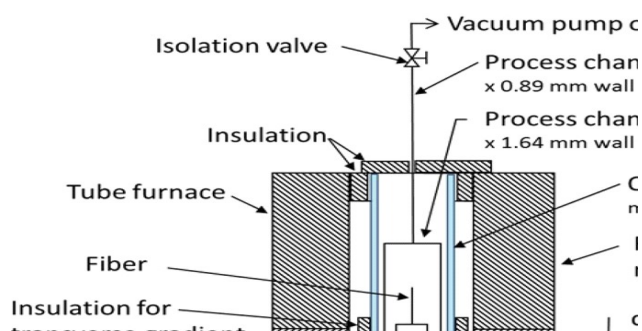

A simple apparatus is schematically shown in Figure. When pumped, super-saturated solutions tend to nucleate. When the solution saturated at T+ΔT is pumped directly to growth vessel, undissolved particles are transferred to the growth region. Such problems can be overcome by using crystallizers having three-vessel growth system. The temperature of the saturator vessel is normally 10°C above the crystallizer and the solution temperature in the super-heater vessel is much higher than the saturator. When crystal growth is taking place, the solution flows from super-heater vessel to the crystallizer and then to the saturator and returns to the super-heater vessel.

The Sankaranarayanan – Ramasamy (S-R) method is a recently established one [27, 28] by which growth of single crystals with specific orientation and 100% solute-crystal conversion efficiency can be achieved. A simple experimental set up is schematically shown in Figure.

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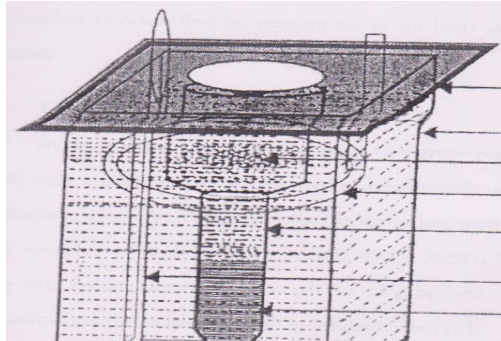
The set up consists of a growth ampoule made of glass with seed mounting pad. The inner growth ampoule is holded and protected by an outer glass shield tube. A ring heater positioned at the top of the growth ampoule is connected to the temperature controller. It provides the necessary temperature for solvent evaporation. The temperature around the growth ampoule is controlled with the aid of a temperature controller. This temperature is selected based on the solvent used. Depending on the growth rate of the crystal grown, the ring heater is moved downwards using a translation mechanism.

In slow (free) evaporation method, the solution loses particles which are weakly bound to other components and, therefore, the volume of the solution decreases. By utilizing the difference between the evaporation rates of the solvent and solute, an excess of the given solute can be established. Vapour pressure of the solvent above the solution is normally higher than that of the solute. Therefore, the solvent evaporates more rapidly and the solution becomes super-saturated. It is necessary and sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. Technically this method is very simple but considered to be useful for a very long time. Evaporation is permissible into the atmosphere for non-toxic solvents such as water.
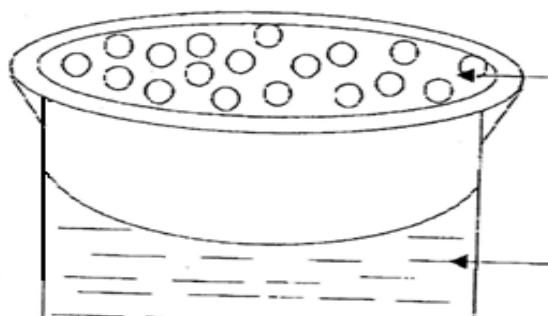
For toxic and inflammable solvents, precautions are taken to avoid the leakage of solvent vapour into the atmosphere. The crystallization rate depends on the rate of solvent evaporation. Figure shows the schematic diagram of a simple apparatus for growth by this method with few holes in the lid. Evaporation rate can be controlled by changing the total area of the holes in the lid. In sophisticated growth systems, evaporation is controlled by passing air or an inert gas at a required rate over the solution.

Analytical reagent (AR) grade samples of $ZnSO_4.7H_2O$ (ZSH), KDP and ADP along with double distilled water were used for the growth of single crystals by the free (slow) evaporation method. ZSH was added with KDP and ADP in three different impurity concentrations, viz. 0.001, 0.002, 0.003 mol% and pure ZSH crystals was also grown. Supersaturated aqueous solutions were prepared and allowed to evaporate (equilibrate) at the room temperature (33°C). In all the growth experiments the volume of the solution kept in the growth cell (100 ml beaker) was constant (20 ml). The crystals were grown in the unstirred condition.

The amount of solute (m) in grams for preparing the required supersaturated solution may be obtained by using the formula

<div align="center">(In gram units)</div>

Where, M - is the molecular weight of the solute (M=287.54 for ZSH)

x – is the supersaturated concentration in molar units (x=3.2M in the present study)

v – is the required volume of the solution (v=40 ml in the present study)

　　　　The aqueous solution of a particular supersaturated concentration (x) of the substance was prepared by dissolving the required amount (m) of the solute in slightly insufficient volume of solvent at a temperature slightly higher than the experimental temperature. Then the solution was transferred to a measuring jar and the volume was made 40 ml by adding the required amount of solvent. The supersaturation was obtained by cooling naturally to the experimental temperature of 33°C.

　　　　For a solution of ZSH added with KDP and ADP, the required amount of impurity (dopant) solute (KDP and ADP) was also added and dissolved along with the pure ZSH solute individually. If the molecular ratio of ZSH and dopant was 1:P, the amount of dopant (KDP & ADP) required in grams (m') was calculated using the formula

　　　　(in gram units)

where,

M – is the molecular weight of the solute (M=136.09 for KDP & M=115.03 for ADP)

P – is the mole fraction of dopant in the doping ratio

x – is the supersaturated concentration in molar units (x=3.2M in the present study)

　　　　In the present work the impurity used is KDP and ADP and the doping ratio's used in the present study are

Molecular Ratio of $ZnSO_4.7H_2O$ and KDP

$ZnSO_4.7H_2O$	:	KDP
1	:	0.000(Pure $ZnSO_4.7H_2O$)
1	:	0.001

1	:	0.002
1	:	0.003

Molecular Ratio of $ZnSO_4.7H_2O$ and ADP

$ZnSO_4.7H_2O$	:	ADP
1	:	0.000(Pure $ZnSO_4.7H_2O$)
1	:	0.001
1	:	0.002
1	:	0.003

The dielectric constant is one of the basic electrical properties of solids. The measurement of dielectric constant ($_r$) and dielectric loss ($\tan\delta$) as a function of temperature (T) and frequency (f) is of interest both from theoretical point of view and from the applied aspects. Practically, the presence of a dielectric between the plates of a condenser enhances the capacitance. Essentially, $_r$ is the measure of how easily a material is polarized in an external electric field.

The AC electrical measurement of dielectric constant has its own utility. It provides information about certain defects in the crystal; particularly in the case of doped and mixed crystals the measurements yield interesting information about relaxation effects.Operation of electro-optic devices is based on the Pockel's effect, in which the change in the dielectric constant Δ_r, is a linear function, of the applied field [52].

The dielectric constant of a material is generally composed of four types of contributions, viz. ionic, electronic, orientational and space charge polarizations. All these may be active at low frequencies. The amount of power losses in a dielectric under the action of the voltage applied to it is generally known as dielectric losses. When considering the dielectric losses we usually mean the losses precisely under an alternating voltage. The dielectric loss angle is also an important parameter both for the material of a dielectric and an insulated portion. If a dielectric is subjected to an alternating field E there is a phase lag between the applied field and the displacement. Hence the dielectric constant is described as a complex quantity:

$= ' - i''$ and

$'' / ' = \tan\delta$

Where, $\tan\delta$ is called the dielectric loss factor. The capacitance and dielectric loss ($\tan\delta$) were measured by the conventional parallel plate capacitor method for all the seven crystals grown using an LCR meter Agilent 4284A with a range of frequency 1kHz at various temperatures ranging from 40-75C in a way similar to that followed by Freeda and his co-workers. The observations

were made while cooling the sample and the temperature was controlled to an accuracy of ±0.1C. The dimensions of the crystals were measured using a travelling microscope (L.C. = 0.001 cm). Air capacitances were also measured for the thickness equal to that of the crystals. Since the variation of air capacitance with temperature was found to be negligible, air capacitance was measured only at room temperature. The dielectric constant of the crystal was calculated using the well-known relation,

$_r = C_c / C_a$

Where, C_c is the capacitance of the crystal and C_a is the capacitance of the air medium of the same dimension as that of the crystal. The AC electrical conductivity (σ_{ac}) was calculate using the relation,

$$\sigma_{ac} = _{0r}\omega\tan\delta,$$

where $_0$ is the permittivity of free space (8.85×10^{-12} $C^2N^{-1}m^{-2}$) and ω is the angular frequency ($\omega = 2f$).

3.Result and discussion

Pure and impurity added crystals grown were found to be colorless highly transparent and with less defects. The $ZnSO_4.7H_2O$ crystals grown in the present work are shown by the photographs provided in. The morphology of all the grown crystals is similar to the morphology of $ZnSO_4.7H_2O$.

Photograph of the grown crystals[From top a. Pure ZnSO₄.7H₂O;
b. 0.001 mole% KDP added; c. 0.002 mole% KDP added; d. 0.003 mole% KDP added;
e. 0.001 mole% ADP added; f. 0.002 mole% ADP added; g. 0.003 mole% ADP added]

Powder X-ray Diffractometers patterns of pure and doped $ZnSO_4.7H_2O$ crystals obtained are shown in Fig (a) to (g). The powder XRD patterns indicate the crystallinity of the grown crystals. The observed patterns are found to be similar to that available in the literature for $ZnSO_4.7H_2O$ crystals. In addition, it has been found that KDP and ADP addition does not lead to any serious lattice distortion.

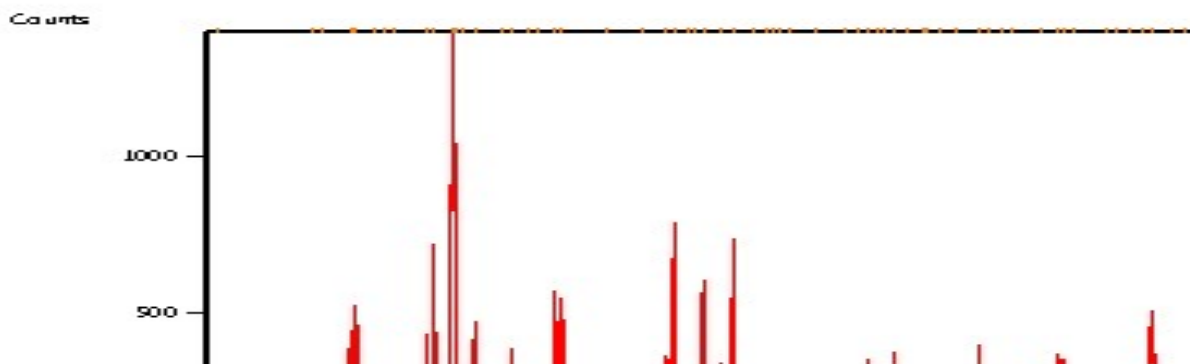**Fig (a) The powder XRD pattern for pure ZnSO$_4$.7H$_2$O**
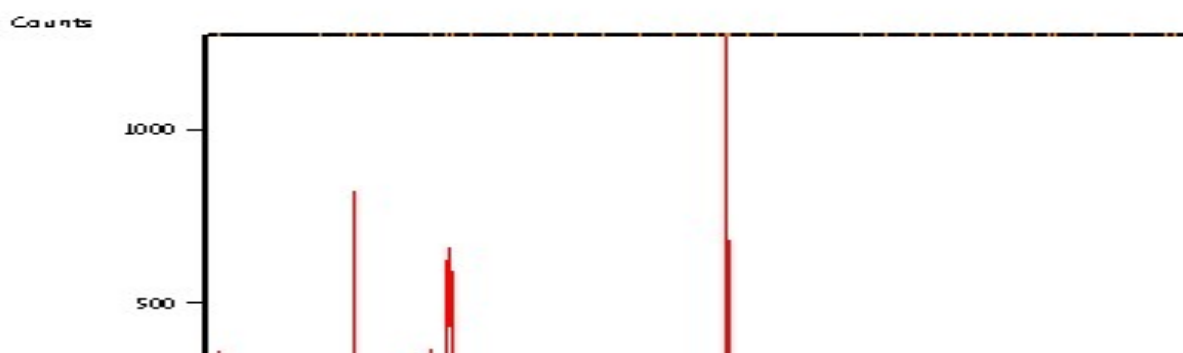

Fig (b) The powder XRD pattern for KDP (0.001 mole%) added ZnSO$_4$.7H$_2$O crystal

Fig (c) The powder XRD pattern for KDP (0.002 mole%) added ZnSO$_4$.7H$_2$O crystal

Fig (d) The powder XRD pattern for KDP (0.003 mole%) added $ZnSO_4.7H_2O$ crystal

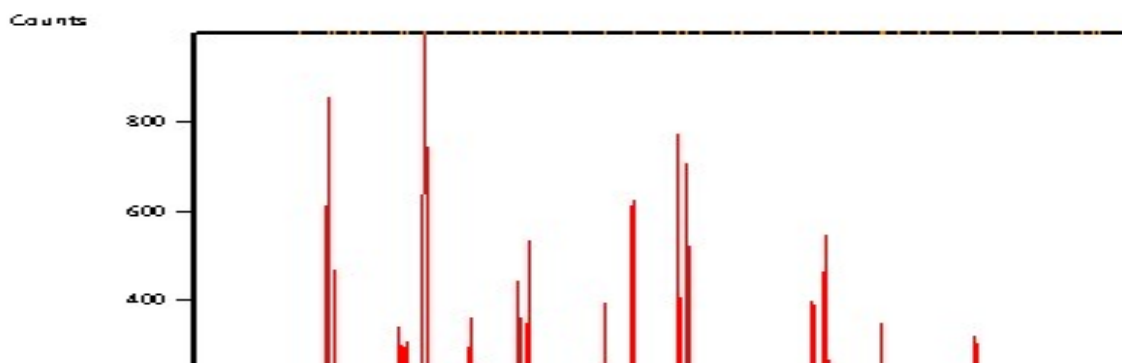**Fig (e) The powder XRD pattern for ADP (0.001 mole%) added**

Fig (f) The powder XRD pattern for ADP (0.002 mole%) added $ZnSO_4.7H_2O$ crystal

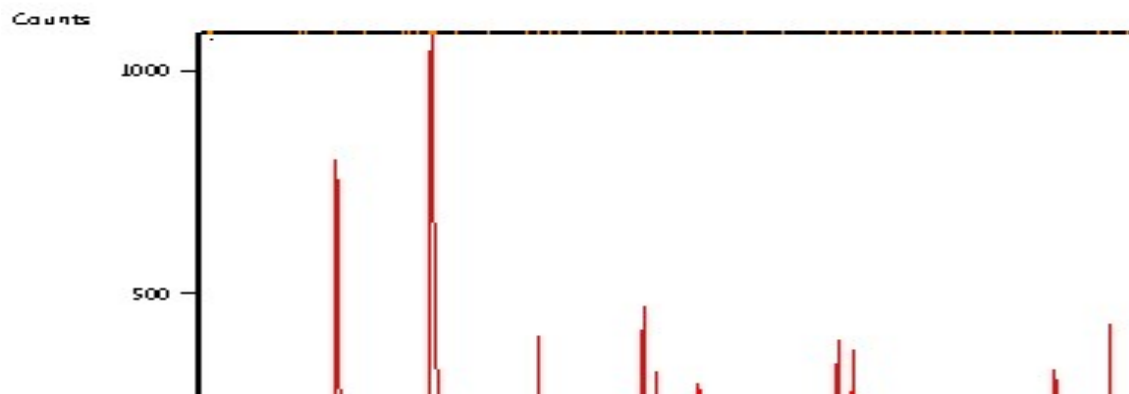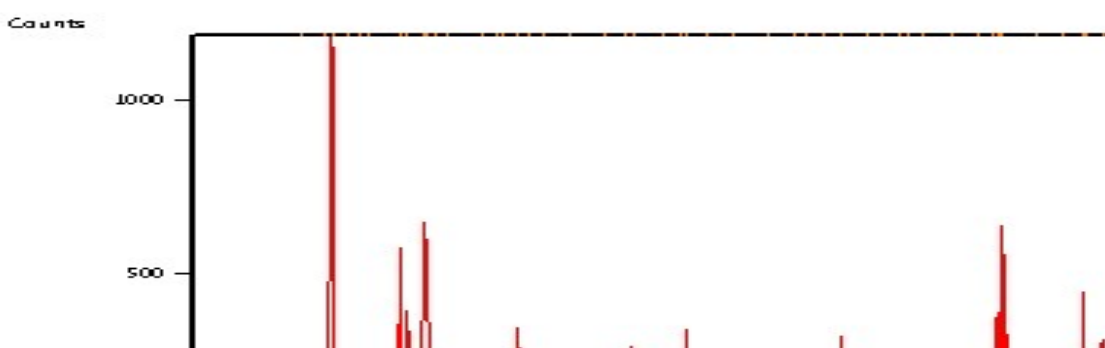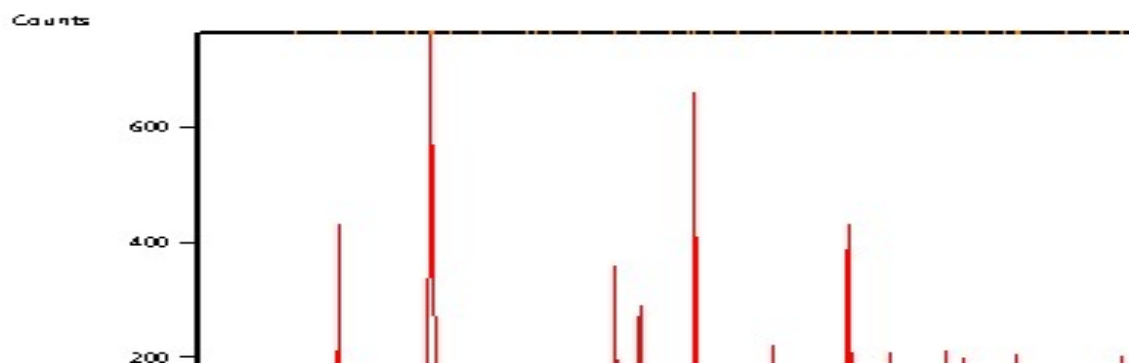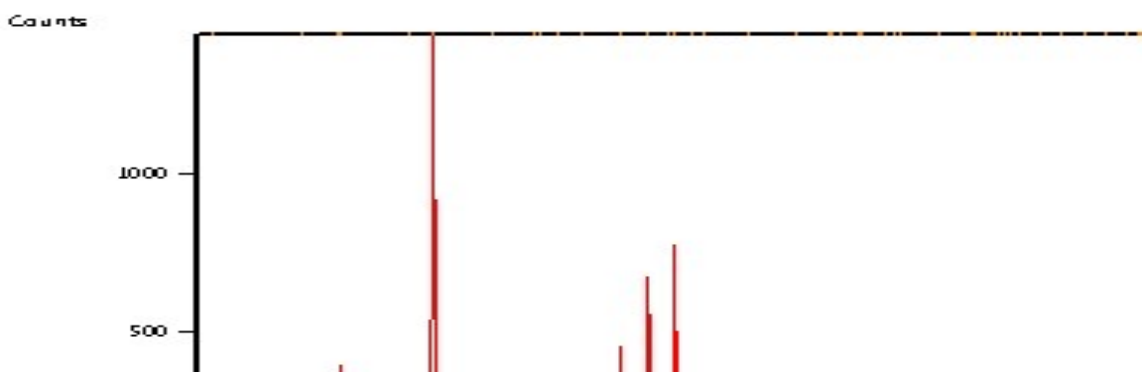**Fig (g) The powder XRD pattern for ADP (0.003 mole%) added ZnSO₄.7H₂O crystal**

The Bragg's diffraction peaks were indexed for the orthorhombic system with the space group $P2_12_12_1$. The observed prominent peaks confirm the crystalline property of the grown pure and doped $ZnSO_4.7H_2O$ crystals. The (h k l) planes satisfy the general reflection conditions of space group observed from the structure determination of the crystal. The PXRD pattern for pure $ZnSO_4.7H_2O$ (Fig(a)) obtained in the present study is well matched with the reported one and confirms the material of the grown crystal [Anderson et al. 2005]. The PXRD patterns obtained for the various concentrations of KDP and ADP added $ZnSO_4.7H_2O$ crystals (Fig(b) to (g)) are well matched with the pure $ZnSO_4.7H_2O$ also some intensity are slightly shifted and newly raised; this indicates that the added impurity molecules considered in the present study entered in to the $ZnSO_4.7H_2O$ lattice and it do not disturb the crystal structure of $ZnSO_4.7H_2O$ lattices. Thus, the variations in lattice parameters, intensity of peaks and decrease in unit cell volume with the increase of KDP and ADP concentration in $ZnSO_4.7H_2O$ crystals clearly indicate that KDP and ADP could be incorporated into the pure $ZnSO_4.7H_2O$ crystal lattices. The calculated lattice parameter value for pure $ZnSO_4.7H_2O$ is well matched with the reported one from the literature [55].

The lattice parameters observed for pure and doped ZnSO₄.7H₂O crystals

System (Impurity in mole% in the solution)	Lattice Parameters			
	a (Å)	b (Å)	c (Å)	Volume (Å³)
a) For pure $ZnSO_4.7H_2O$	11.8377	12.0732	6.8188	974.54
b) For KDP added $ZnSO_4.7H_2O$				
0.001	11.8294	12.0941	6.7589	966.97
0.002	11.7986	12.0724	6.7649	963.57

0.003	11.6542	12.1013	6.8178	961.52
c) For ADP added $ZnSO_4.7H_2O$				
0.001	11.7844	12.0696	6.8017	967.43
0.002	11.5627	12.0380	6.8458	952.88
0.003	11.5338	12.0369	6.8236	947.33

It can be noticed, that the addition of KDP and ADP in $ZnSO_4.7H_2O$ leads to dissimilar lattice contraction/expansion in 'a', 'b' and 'c' direction. In spite of the increase/decrease in 'a' or 'b' or 'c' the overall cell volume decreases with the concentration of KDP and ADP increases in $ZnSO_4.7H_2O$ lattices. The lattice parameter decrease in one direction is compromised by the increased lattice on other direction. Hence the overall uniform unit cell volume contraction takes place with the increase of concentration of KDP and ADP in $ZnSO_4.7H_2O$ lattices, it indicates that the dopant enter into the crystal lattice of $ZnSO_4.7H_2O$.

The electrical parameters, viz, dielectric constant (ε_r), dielectric loss ($\tan\delta$) and AC electrical conductivities (σ_{ac}) observed in the present study are increased with the increase in temperature for all the grown crystals with the corresponding frequency of the AC applied for all the systems considered in the present study.

Dielectric constant for pure and KDP doped $ZnSO_4.7H_2O$ at a frequency of 1kHz

Temperature (C)	r			
	Pure	**0.001 mole%**	**0.002 Mole%**	**0.003 mole%**
40	5.181	5.186	5.205	5.238
45	5.270	5.292	5.348	5.560
50	5.305	5.365	5.465	5.683
55	5.401	5.484	5.529	5.725
60	5.510	5.515	5.690	5.793
65	5.632	5.682	5.715	5.821
70	5.768	5.779	5.785	5.905
75	5.917	6.017	6.112	6.268

Dielectric constant for pure and ADP doped $ZnSO_4.7H_2O$ at a frequency of 1kHz

Temperature (C)	r			
	Pure	**0.001 mole%**	**0.002 mole %**	**0.003 mole%**
40	5.181	5.198	5.222	5.315
45	5.270	5.315	5.356	5.482
50	5.305	5.382	5.486	5.721
55	5.401	5.492	5.562	5.926
60	5.510	5.605	5.720	6.011
65	5.632	5.710	5.753	6.125
70	5.768	5.789	5.812	6.234
75	5.917	6.150	6.206	6.385

AC conductivity (10^{-6} mho/m) for pure and ADP doped $ZnSO_4.7H_2O$ crystals at constant frequency of 1kHz

Temperature (C)	AC conductivity (10^{-6} mho/m)			
	Pure	**0.001 mole%**	**0.002 mole%**	**0.003 mole%**
40	0.0425	0.0395	0.0291	0.0401
45	0.0467	0.0462	0.0320	0.0475
50	0.0475	0.0568	0.0329	0.0675
55	0.0645	0.0723	0.0403	0.0869
60	0.0783	0.0943	0.0424	0.1443
65	0.0987	0.1157	0.0436	0.3419
70	0.1235	0.1291	0.0458	0.4928
75	0.1552	0.2426	0.0508	0.5831

Variation of AC conductivity (10^{-6} mho/m) with temperature

for pure and KDP doped ZnSO$_4$.7H$_2$O crystal

Fig Variation of AC conductivity (10^{-6} mho/m) with temperature for pure and ADP doped ZnSO$_4$.7H$_2$O crystal

4.Conclusion

Crystal growth and characterization forms a frontier area of research in science and technology. Zinc Sulphate heptahydrate is a widespread evaporate mineral and has played a number of roles of scientific interest over the last four centuries. Crystals growth of heptahydrate sulphate material such as ZSH of high purity has become an important field of research for both academic interest and industrial applications. Doping (addition of impurity molecules), even at lower concentrations in the parent solute of the solution used for the crystal growth has considerable effect on the growth kinetics and other properties of the crystals grown. Earlier workers have shown that impurity addition to ZSH makes it a more interesting material. In the present study, with an aim of discovering new useful materials, we have grown ZSH single crystals by the free evaporation method and investigated the effect of two simple inorganic impurities [KDP and ADP] added (impurity added in the ZSH solution used for the growth of crystals) with impurity concentration ranging from 0.001 to 0.003 mole%) on their various properties. A total of seven crystals were grown and characterized.

X - ray diffraction data were collected from powder samples of crystals using an automated X - ray diffractometer. The reflections were indexed and the lattice parameters were determined. The observed decrease of lattice volume with impurity addition (KDP & ADP) indicates that the impurity molecules have entered into the lattice of ZSH crystals.

AC electrical measurements were carried out by using the parallel plate capacitor method at various temperatures with a fixed frequency of 1 kHz. The dieletric constant($_r$), dielectric loss factor (tan) and AC electrical conductivity ($_{ac}$) were determined to understood the dielectric nature of the grown crystals. The results obtained indicate that the grown crystals exhibit a normal dielectric behaviour. Also, the conduction in these crystals is understood to be due to the protonic movement. Thus the ZSH crystal is expected to be useful in microeletronics industry.

Attempts can be made to identify suitable dopants which could provide lower dielectric constant values and thereby enhance the utility of these crystals in the micro electronics industry. In addition, suitable depants should be identified to enhance its utility as a material for long term heat storage in heat storage systems. Moreover, attempts can be made to improve the electrical transport via super protonic transport by forming complex materials of ZSH with hydrogen phosphates for its utility as a solid electrolyte in fuel cells.

5.References

1**.** P. Santhana Raghavan and P. Ramasamy (1999) *Crystal growth processes and methods* (KRU Publication, Kumbakonam]

2. J.C. Brice (1986) *Crystal Growth Processes* [John Wiley and Sons, New York]*"1976 Crystal Growth and Materials"* (**Vol. 11** of Current Topics in Materials Science), **918 pages**, editors E. Kaldis and H.J. Scheel, North-Holland Publ. Comp., Amsterdam - New York (1977).

3. *"Crystal Growth and Epitaxy"*, Proceedings of 34eme Cours de Perfectionnement de 1' Association Vaudoise des Chercheurs en Physique "Croissance de Cristaux et de Couches Epitaxiales pour Applications Electroniques et Optiques" (held at Grimentz March 16-21, 1992), **418 pages**, editor H.J. Scheel (1993)

4. *"First International School on Crystal Growth Technology: Book of Lecture Notes"* (Beatenberg September 5-16, 1998), editor H.J. Scheel, REPRO-EPF Lausanne (1998), **806 pages**.

5. C. Mahadevan, D. Irene Lathe and V. Umayourbhagan (1999) *J. Indian Cheim. Soc*., **Vol. 76, pp. 335**.

6. B.E. Warren (1969) X-ray Diffraction [Addision Wesley, California]

7. www.m.exportersindia.com

8. P.G. de Gennes and J.Prost. *The Physics of Liquid Crystals*. Clarendon Press, Oxford, Second, Paperback edition, (1995).

9. M.J. Stephen and J.P. Straley, *Physics of Liquid Crystals.* Rev. Mod. Phys., **46: 617-704,** (1974)

10. K.R. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (2000) **2275**.

11. H. Olivier - Bourbigou, L. Magna, J. Mol. Cat. A 182-183 (2002) **419**.

12. J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) **3667**.

13. J.F. Liu, G.-B. Jiang, Y.-G. Chi, Y-Q. Cai, J.-T. Hu, Q.-X. Zhou, Anal. Chem. 75 (2003) **5870**.

14. J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) **156**.

15. S. Carda-Broch, A. Berthod, D.W. Armstrong, Anal. Bioanal. Chem. 375 (2003) **191**.

16. R.A. Laudise, *'The Growth of Single Crystals'*, Prentice Hall, New Jersey, (1970).

17. E.C. Subbarao (1973) Ferroelectrics, 5, **267**.

18. J.A. Dean (edn.) (1979) *Lange's Handbook of Chemistry*, 12th edn. [Mc Graw Hill Book Company, New York].

19. R.W.G. Wyckoff (1960) Crystal Structures, Vol. 3, II. Edn. [Interscience, New York], **p. 160**.

20. B.R. Pamplin (Ed.) (1980) Crystal Growth (2nd edn.) [Pergamon, Oxford]

21. A.A. Chernov (1984) Modern Crystallography III. Crystal Growth [Springer, Berlin]

22. J.C. Brice (1986) *Crystal Growth Processes* [John Wiley and Sons, New York]

23. J.W. Mullin (1993) Crystallization [Bvtterworth - Heinemann, Oxford]

24. K. Sangwal (1994) *Elementary Crystal Growth* [Saan Publishers, Lublin]

25. K. Byrappa and T. Ohachi (2002) *Crystal Growth Technology* [Springer - Verlag, Berlin]

26. K. Sankaranarayanan and P. Ramasamy (2005) J. Cryst. Growth 280, **467**.

27. S. Balamurugan, M. Lenin, G. Bhagavannarayana and P. Ramasamy (2007) Cryst. Res. Technol. 42, **151**.

28. Cullity B.D (1978). *Elements of X-Ray Diffraction* (2nd ed.). Reading, Massachusetts: Addison-Wesley Publishing Company. ISBN 0-534-55396-6.

29. Drenth J (1999) *Principles of Protein X-ray Crystallography*. New York: Springer - Verlag. ISBN 0-387-98587-5.

30. Giacovazzo C (1992). *Fundamentals of Crystallography*. Oxford: *Oxford University Press*, ISBN 0-19-855578-4.

31. Brady, John B., and Boardman, Shelby, J., (1995), *Introducing Mineralogy Students to X-ray Diffraction Through Optical Diffraction Experiments Using Lasers.* Jour. Geol. Education, **v. 43#5**, **471-476**.

32. C. Mahadevan (1986) J. Crystallogr. Spectrosc. Res. [Renamed as J. Chem. Crystallogr.] 16, **347**.

33. Brady, John B., Newton, Robert M., and Boardman, Shelby J., (1995), New Uses for Powder X-ray Diffraction Experiments in the Undergraduate Curriculum. Jour. Geol. Education, **v. 43#5, 466-470**.

34. Dutrow, Barb, (1997), *Better Living Through Minerals X-ray Diffraction of Household Products*, in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, Mineralogical Society of America, **p. 349-359**.

35. Hovis, Guy. L., (1997), *Determination of Chemical Composition, State of Order, Molar Volume, and Density of a Monoclinic Alkali Feldspar Using X-ray Diffraction,* in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, Mineralogical Society of America, **p. 107-118**.

36. Brady, John B., (1997), Making Solid Solutions with Alkali Halides (and Breaking Them), in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, Mineralogical Society of America, **p. 91-95**.

37. Perkins, Dexter, III, and Sorensen, Paul, Mineral Synthesis and X-ray Diffraction Experiments, in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, Mineralogical Society of America, **p. 81-90**.

38. Hogan, C.M. (1969). *"Density of States of an Insulating Ferromagnetic Alloy"*. Physical Review 188 (2): **870**.