GROWTH AND CHARACTERIZATION OF EPSOMITE SINGLE CRYSTALS DOPED WITH KCl FROM LOW TEMPERATURE AQUEOUS SOLUTIONS

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ABSTRACT

Highly transparent and well faceted large size epsomite single crystals have been grown in pure form and doped with KCl from aqueous solutions by slow cooling and isothermal evaporation method. The optical quality of the epsomite improves on doping by KCl. Mass growth rates were found to increase with doping of lower concentrations of KCl and then decreases with the higher concentration of KCl. KCl doped epsomite crystal reveals that structures are slightly distorted due to adsorption of Cl^- ion into the crystal lattice. DC conductivity along the growth axis for all of the grown crystals increases with temperature in the range of 25 to 70 ºC and also increases with the KCl concentration. Dielectric constant is found to be almost independent of frequency up to range of 10^6Hz. The dielectric studies show the suitability of these grown crystals for optoelectronic applications.

1. INTRODUCTION

Crystallization of heptahydrate sulphate material such as epsomite ($MgSO_4.7H_2O$) of high purity has become an important field of research for both academic interest and industrial applications in various areas like medical, agricultural and chemical industry (1-3). The epsomite is included in a group of heptahydrate sulphate with the general formula $RSO_4.7H_2O$ (R= Mg, Zn, Ni) (4). $MgSO_4.7H_2O$, as a source of Mg^{2+} ions has wide application in medical (like acute management of cardiac arrhythmia, migraine attacks, spasms in cerebral blood vessels) and agricultural industry (as fertilizer)(2-3). The crystal structure of $MgSO_4.7H_2O$ is orthorhombic. During industrial crystallization, the size and shape of the crystal plays an important factor, since the undesirable habits such as plate like or needle like causes the problems of separating, washing or drying (5). The physical properties such as packing density, agglomeration and re-dissolution mainly depend on the shape of the crystal. The pure epsomite crystals have been grown at low temperature from aqueous solutions (6-8). The presence of the foreign particles in the growth media has long been recognized in changing the growth habits of crystals (9-10). Jibbouri *et al* (9) presented the influence of different additives (KCl, K_2SO_4, NaCl and $MgCl_2$) on the crystallization kinetics of epsomite. They found that the impurities exert influence on the saturation and super-saturation limit. Ramalingom *et al.*(11) have studied the urea doped epsomite crystal at low temperature by slow cooling technique. They found that the addition of urea in the mother solution of epsomite increased the metastable zone width and the structure of the epsomite crystals also changed from orthorhombic into tetragonal. From technological and application point of view, in the present study, an attempt has been made to improve the quality of the epsomite crystal by adding KCl as impurities and to see the influence of impurities on the growth kinetics.

2. EXPERIMENTAL

Growth of single crystals

Analar grade magnesium sulphate heptahydrate, KCl and distilled water were used in the crystallization process. The solubility study of epsomite was performed in water

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solvent. The solubility was found to increase almost linearly with the increase of temperature and have a positive coefficient of solubility. Using the solubility data, a saturated solution of the epsomite compound was prepared and allowed to evaporate at room temperature. The pure magnesium sulphate seed crystals were prepared by the conventional isothermal evaporation method. Colorless and transparent crystals were harvested within 15 days under the isothermal evaporation process. The harvested crystals were recrystallized repeatedly to achieve good quality. KCl was added with epsomite as a dopant material with 0.1, 0.2, 0.4, 0.6, 1.0 and 1.6 molar concentrations. In slow cooling process, crystallization was initiated by decreasing the temperature of the solution at a cooling rate of 0.1 ^{0}C per day. For natural evaporation process, the crystallizers were covered with perporated polyethylene sheet and kept in a dust free chamber. Pure and KCl doped $MgSO_4.7H_2O$ crystals were harvested after a period of 3 to 4 weeks.

Characterization

The infrared spectra of all the grown crystals were recorded by KBr pellet technique at room temperature in the wave number of 4000 to 400 cm^{-1}. X-ray diffraction studies were carried out using a Shimadzu X-ray Diffractometer with MoKα radiation (λ=0.7093A^o) with an operating voltage 30kV and current 20mA. Scanning rate was maintained at 1^o per minute. The DC conductivity measurements were carried out on the grown crystals by two probe method in the temperature range of 25~70ºC. Transparent crystals with the dimensions of 8 mm x 6 mm x 2 mm were cut into a rectangular size and surfaces were coated with silver paint to give good electrical contact between the electrodes. Keithley electrometer was used to measure the current in the samples. The samples, electrodes, leads wires etc. were all well insulated to avoid stray current. The field is applied to perpendicular to c-axis. In this experiment, the applied voltage was kept at 80 volt.

3. RESULTS AND DISCUSSION

Growth rates of the crystal

Mass growth rates of the grown crystals were determined by weighing method $^{(12)}$. The seed crystals of pure $MgSO_4.7H_2O$ were placed in KCl doped $MgSO_4.7H_2O$ solution in a petri-dish and then petri dish was kept in a dust free glass chamber. The weights of the growing crystals were recorded for every 24 hours by a digital balance. After four weeks, the crystals were collected from the solution. The growth rates with respect to the initial mass, G_g, is calculated as Gg = $(m - m_o) / (m_o \Delta t)$, where, m_o is the initial mass, m is the finial mass, and Δt is the growth time.

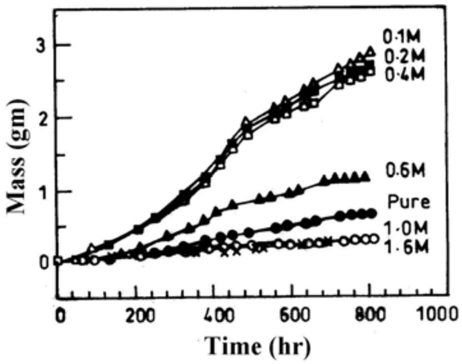


Fig. 1. Mass growth of the pure and doped crystals.

Mass growth rates of seven different samples are presented in Fig. 1. It was observed that the mass growth rate increases initially to a certain limit of KCl concentration (0.1M) and then decreases with the increase of KCl molar concentration. Highly transparent and well faceted large size single crystals were grown by isothermal evaporation process. The addition of KCl increased the quality of the crystals by chemical complexion of trace heavy metal ions like Cd, Zn, Co, Sb etc. present in the solutions by Cl^- ion and thus the complex metal ion cannot get into the crystal lattice.

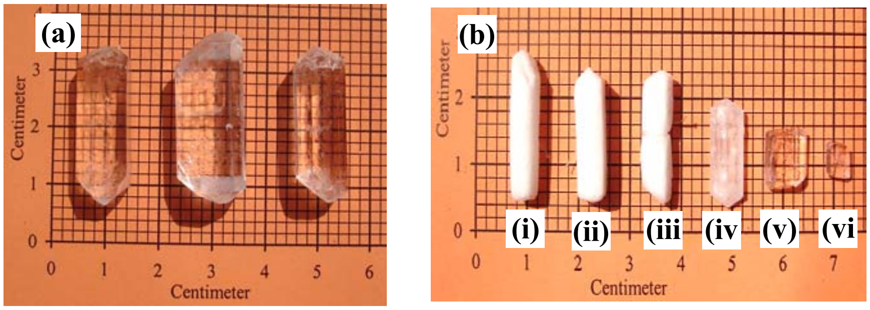


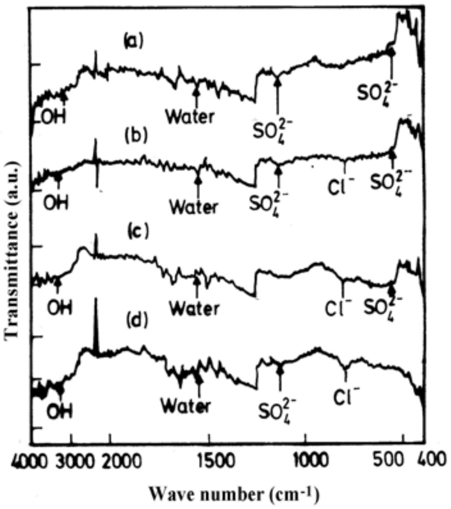
Fig. 2. (a) Single crystals of 0.4 M KCl doped $MgSO_4.7H_2O$, (b) The order of transparency of the single crystals lost due to drying in desiccators (i) 0.1 M KCl (ii) 0.2 M KCl (iii) 0.4 M KCl (iv) 0.6 M KCl (v) 1.0 M KCl (vi) 1.6 M KCl

Influence of KCl

From the application point of view, sustainability of these crystals in adverse environment (especially in the dry and hot atmosphere) has been studied. For testing the effect of dry weather, the pure $MgSO_4.7H_2O$ crystals were kept in a desiccator containing silica gel. After 2~3 days the pure $MgSO_4.7H_2O$ crystals were observed milky-white colour. The crystals became softer but their shape remained unchanged. The grown crystals were completely opaque and lost their transparency, shown in Figure 2 (b). The changes in their transparency and softness are due to the absorption of crystalline water by the silica gel in the dessicator. It was found that 0.1, 0.2, 0.4 M KCl doped crystals lost their transparency fully, 0.6 M lost their transparency partially and for higher concentration (1.6 M) crystals remained unchanged. This implies that Cl^- ion absorbed into the crystal lattice and the presence of higher concentration of Cl^- ion in the crystals is the cause of their unchanged physical properties. The pure $MgSO_4.7H_2O$ crystals as well as doped crystals of lower concentration of KCl are not stable in the dry environment.

Infrared Spectroscopy

The specified bonds are identified by the corresponding wavenumber and the band assignments are mentioned in the spectra (Fig.3). The absorption band at 550 cm^{-1} corresponds to SO_4^{2-} bending vibration. The band at around 650 cm^{-1} represents the presence of Cl^{-1} ion. In the spectrum, the presence of chlorine is very clearly identified and the peak area corresponds to Cl^- ion is increasing with the increase of KCl molar concentration. It seems that Cl^- ion is adsorbed into the lattice sites. The absorption band at 1050 cm^{-1} is assigned for the SO_4^{2-} stretching vibration. Absorption at around 1600 cm^{-1} may be assigned to bending vibration of water molecule. The band at around 3300 cm^{-1} is assigned to O-H stretching vibration of water.



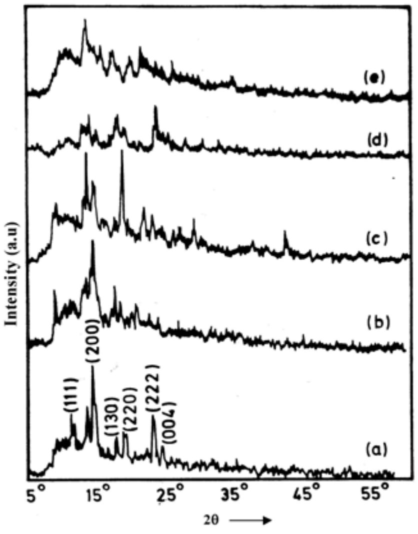


Fig. 3. IR spectroscopy (a) pure $MgSO_4.7H_2O$, (b) 0.1 M KCl doped, (c) 0.2 M KCl doped, (d) 0.6 M KCl doped crystals

Fig. 4. X-ray diffraction patterns (a) pure $MgSO_4.7H_2O$, (b) 0.1 M KCl doped, (c) 0.2 M KCl doped, (d) 0.4 M KCl doped and (e) 0.6 M KCl doped $MgSO_4$. $7H_2O$

X-ray diffraction

X-ray diffraction patterns for the powdered samples are presented in Fig. 4. From the X-ray diffraction pattern the respective data viz. $2\theta_{expt,}$ and relative intensity values for the corresponding hkl planes are presented in Table 1. The X-ray diffraction pattern of the pure and doped $MgSO_4.7H_2O$ single crystals differed in their relative intensities and in the lattice spacing of the crystals. These values are matched well with the ASTM standard values. The reflection peaks are indexed and the deviation in 2θ i.e. $\Delta 2\theta = 2\theta_{exp} - 2\theta_{cal}$ for the experimental and calculated values are given in Table 1. The change in 2θ values suggest that the structures are slightly distorted in comparison to the pure crystal. This may be attributed to the strain on the lattice by the adsorption of Cl^- impurities. For pure sample, the deviation in 2θ values may be due to the presence of natural impurities in the solutions.

Table. 1.
Indexed powder diffraction data for pure and KCl doped $MgSO_4.7H_2O$

Samples		(hkl)	$2\theta_{cal}$(°)	I/I_o %	$2\theta_{exp}$(°)	$\Delta 2\theta$ (°)
$MgSO_4.7H_2O$		111	11.298	55	11.6	+0.302
		002	12.554	35.15	12.600	+0.046
		200	15.710	100	14.560	-1.150
		130	17.424	35	18.100	+0.676
		220	18.885	39	19.150	+0.265
		222	22.746	53	23.350	+0.604
		004	25.183	28	24.840	-0.343
KCl doped $MgSO_4.7H_2O$	**0.1 M**	111	11.298	45	11.350	+0.052
		002	12.554	68.65	13.600	+1.046
		200	15.710	100	14.750	-0.967
		130	17.424	57	17.800	-0.376
		220	18.885	42	18.750	-0.135
		222	22.746	31	22.850	+0.104
		004	25.183	29	24.210	-0.973
	0.2 M	111	11.298	43.27	11.200	-0.098
		002	12.554	59.4	12.5	-0.054
		200	15.710	62.2	16.1	+0.383
		130	17.424	40.6	17.8	+0.376
		220	18.885	100	18.95	+0.065
		222	22.746	49.3	22.300	-0.446
		004	25.183	1.65	24.900	-0.283
	0.4 M	111	11.298	3208	11.500	+0.202
		002	12.554	59.87	12.850	+0.296
		200	15.710	46.05	15.000	-0.717
		130	17.424	80.20	18.00	+0.567
		220	18.885	52.63	19.00	-0.115
		222	22.746	100	23.600	+0.854
		004	25.183	44.7	24.800	-0.383
	0.6 M	111	11.298	3.63	11.250	-0.048
		002	12.554	3.01	13.6	+1.406
		200	15.710	2.56	15.95	+0.233
		130	17.424	2.30	17.79	+0.366
		220	18.885	2.20	18.60	-0.285
		222	22.746	1.80	22.80	+0.054
		004	25.183	1.65	24.90	-0.283

DC conductivity

A graph of DC conductivity vs. temperature is plotted in Fig. 5. It is found that conductivity increases exponentially with temperature and also with the KCl concentrations. Conductivity is found in the order of 10^{-7} mho/m. At low temperature region, conductivity is expected due to the presence of weakly attached impurities and vacancies in the crystal lattice. At high temperature region, the attached water molecule is lost and fracture is developed and conductivity is caused mainly for intrinsic defects.

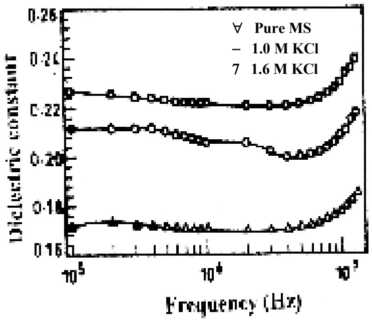


Fig. 5. Conductivity (σ) as a function of 1/T

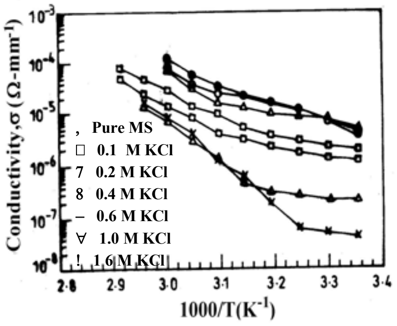


Fig. 6. Dielectric constant as a function of frequency for pure and doped crystals.

Dielectric constant and dielectric loss

The study of dielectric constant and dielectric losses as a function of frequency is performed to see the polarization mechanism in the samples. Dielectric studies on the grown epsomite crystal have been carried out for various frequencies at room temperature. The samples of dimension 8 mm x 6 mm x 2 mm were used for dielectric studies. The dielectric constant (ε') and dielectric loss (ε'') were calculated from $\varepsilon' = Cd/\varepsilon_0 A$ and $\varepsilon'' = \varepsilon' D$, where ε_0 is the permittivity of free space. The frequency Vs ε' and frequency Vs tanδ are shown in Figures 6 and 7. The dielectric constant is found almost constant up to the frequency 10^6 Hz and then increases non-linearly with the increase of frequency. It was also observed that dielectric constant decreases as the concentration of KCl increases. The dielectric constant is contributed due to space charge polarization. The dielectric loss factor for all the samples decreases as the frequency increases. At low frequencies, the dielectric loss was found to be large. This indicates that the frequency of the electric field is equal to that of natural frequency of bounded charge, which tends to oscillate the molecules with large energy. Due to the presence of damping forces of solids, dipole energy is quickly dissipated resulting in large radiation of electrical energy. Increase of dielectric loss is attributed to ionic polarization and oscillation of dipoles. At higher frequencies, the dielectric loss is relatively low due to the frequency of the electric wave which is not equal to that of natural frequency of the bounded charge and hence the radiation is very weak. The measure of low dielectric loss at various frequencies is also due to dipole rotations. At high frequencies, the orientation polarization ceases and hence the energy need not be spent to rotate dipoles. It is observed from the dielectric studies that the crystal possesses low dielectric constant and low dielectric loss, which is suitable for electro-optic applications.

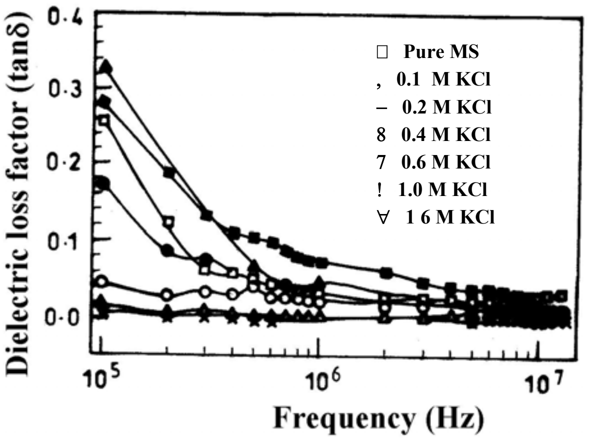


Fig. 7. Dielectric loss as a function of frequency for pure and doped crystals.

4. CONCLUSIONS

In this study, pure and KCl doped epsomite crystals were grown by slow cooling as well as by an isothermal evaporation method. Highly transparent and well faceted large size epsomite single crystals have been grown successfully. The addition of KCl is found to increase the quality of the crystals. The increasing in the quality of the epsomite crystal in presence of KCl is due the complexion of trace metal ion by Cl^- ion. Lattice parameters for pure crystal are found more or less same and are in good agreement with the ASTM standard data. X-ray study reveals that structures are slightly distorted and adoption of impurities into the crystal lattice. DC conductivity increases in the temperature range of 25-70 ^oC and also with the KCl concentration. Dielectric constant is found almost independent of frequency but decreases with the increase in KCl concentration. The dielectric studies showed that KCl doped epsomite possesses low dielectric constant and low dielectric loss, which could be suitable for electro–optic applications.

REFERENCES

1. M. Ikeya, M. G. Hassan, H. Sasaoka, Y. Kinoshita, S. Takaki, C. Yamanaka, Strategy for finding new materials for ESR dosimeters, Appl. Radiat. Isot. **52**, 1209, 2000.
2. S. Deminkaya, O. Vural, Z. Gökail, Z. Odabashi, F. Ozdag, E. Erolu and M. Yardim, Norol Bil D, Vol. 15, No. 3, 131-136, 1998.
3. M. Ema, A. Gebrewold, B. T. Altura and B. M. Altura, Report, Department of Physiology, State University of New York, Health Science Centre, Brooklyn, 1998.
4. E. S. Dana, W. E Ford, Crystallography and Physical mineralogy, Wiley Eastern Limited, p 760, 1985.
5. H. Cano, N. Gabas, J.P. Canselier, Experimental study on the ibuprofen crystal growth morphology in solution., J. Crystal Growth, **224**, 335, 2001.

6. S. Ramalingom, J. Podder, S. N. Kalkura, Crystallization and characterization of orthorhombic MgSO4.7H2O, Cryst. Res. Technol. **36,** 12, 1357-1364, 2001.

7. I. A. Kasatkin, Interferometric study of MgSO4. 7H2O single crystal growth kinetics from solution,.Cryst. Res. Technol. **37**, 2-3, 193-205, 2002.

8. G. Sgualdino, G. Vaccari, D. Aquilano and M. Rubbo, Growth kinetics of epsomite ($MgSO_4$. $7H_2O$), J. of Crystal Growth, **83**, No. 4, 523-527, 1987.

9. S. A. Jibbouri, C. Strege and J. Ulrich, Crystallization kinetics of epsomite influenced by pH value and impurities, J. of Crystal Growth, **236**, No. 1-3, 400-406, 2002.

10. M. Rubbo, D. Aquilano, and M. F. Angela, Growth morphology of epsomite ($MgSO_4$. $7H_2O$), J. of Crystal Growth, **71**, No. 3, 470-482, 1985.

11. S. Ramalingom, J. Podder, S. N. Kalkura and G. Bocelli, Habit modification of epsomite in presence of urea, J. of Crystal Growth, **247**, 523-529, 2003.

12. N. Kubota and J. Fukazawa, H. Yashiro, J. W. Mullin, Impurity effect of chromium (III) on the growth and dissolution rates of potassium sulfate crystals, J of Growth, **149**, 113, 1995.

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