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RESEARCH ARTICLE

Growth, Structural and Optical Studies on Pure and Doped Magnesium Sulphate Heptahydrate Single Crystals

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Abstract: Single crystals of pure and doped (Cd^{2+}, Hg^{2+} and histidine) magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) crystals were grown by slow evaporation method. The entry of the dopants into the crystal lattice was confirmed by energy dispersive x-ray (EDX) analysis. The infrared spectra recorded for histidine doped magnesium sulphate crystals showed the presence of amino group in the grown crystal. The powder x-ray data was indexed and there was no significant lattice distortion was observed due to the addition of dopants. The thermograms recorded for the grown crystals showed that these crystals were thermally unstable and decompose through many stages. UV-Vis spectral studies showed that the crystals were transparent in the visible region.

Keywords: Magnesium sulphate heptahydrate, Crystal growth, Optical studies

Introduction

Crystallization of metal sulphate heptahydrate (MSO_4 $7H_2O$) such as magnesium sulphate heptahydrate (MSHH), nickel sulphate heptahydrate (NSHH) and zinc sulphate heptahydrate (ZSHH) has become an important field of research for both academic interest and industrial applications in various areas like medical, agriculture and chemical industry[1-3]. These crystals are isomorphous to each other and they all belong to the orthorhombic system with space group $P2_1P2_1P2_1$. They have tetra molecular unit cell and are important due to the availability of several hydrogen bonds.

The pure magnesium sulphate heptahydrate (MSHH) crystals have been grown at low temperature from aqueous solutions[4-6]. The presence of foreign particles in the growth media has long been recognized in changing the growth habits of crystals[7-8]. Jibbouri *et al.,*[7] presented the influence of difference additives (KCl, K_2SO_4, NaCl and $MgCl_2$) on the crystallization kinetics of magnesium sulphate heptahydrate. They found that the impurities exert influence on the saturation and super-saturation limit. Ferdous *et al.,*[9] reported that the addition of KCl is found to increase the quality of the crystals. In the present study, we have attempted to grow pure and doped magnesium sulphate heptahydrate crystals by slow evaporation technique. The grown crystals are characterized by energy dispersive x-ray analysis, fourier transform infrared spectroscopy, powder x-ray diffraction, thermal studies (TG/DTA), UV-Vis spectroscopy. The results obtained are reported and discussed herein.

Experimental

Recrystallized samples of analytical reagent grade $MgSO_4.7H_2O$ and doubly distilled water were used in the present work for the growth of single crystals from aqueous solution by slow evaporation method. The pure crystals were grown by preparing a saturated solution of MSHH with water as solvent. The saturated concentration was kept same as reported by us earlier[10]. The solution is filtered and kept in a constant temperature bath (Sub-Zero make (acc. = ±0.01 °C)) at a predetermined temperature. Good quality and transparent crystals of MSHH were obtained in about 2-3 weeks time. The grown crystals were harvested and used for characterization studies. For the growth of doped crystals, 0.005 M concentration of cadmium chloride, mercury chloride and histidine was added to the saturated pure solution of MSHH.

The entry of dopants into the crystal lattice was confirmed by energy dispersive x-ray (JEOL Model JED - 2300) analysis. The infrared spectrum of histidine doped MSHH was recorded using FT-IR spectrometer (JASCO with ATR facility). X-ray diffraction studies were carried out using powder x-ray diffractometer (PANalytical make, ModelX'per PRO). The thermal stability of the grown crystals was studied using TGA and DTA (Perkin-Elmer thermogravimetric analyser) analysis. The experiment was done with a heating rate was 10 °C/min in nitrogen environment. The optical studies of the grown crystals were carried out by UV Vis spectroscopy. The UV Vis spectra of the grown crystals were recorded using Shimadzu (Model UV – 1800) in the wavelength range 200 – 1200 nm

Result and Discussion

Energy dispersive spectral analysis

The EDX spectra obtained for the Cd^{2+} and Hg^{2+} doped crystals are presented in Figures 1 and 2. From the spectra it is confirmed that the dopant has entered into the crystal lattice of MSHH. The characteristic peaks of cadmium (3.133keV) and mercury (2.195keV) are noted in the recorded EDAX spectrum.

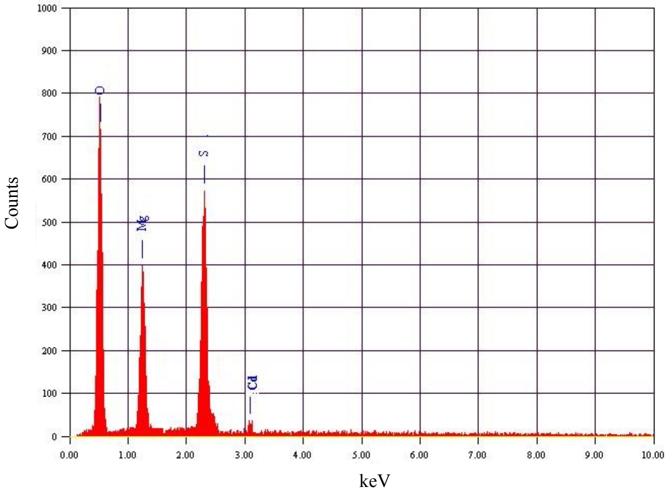


Figure 1. EDS spectrum of Cd doped MSHH

The ionic radius of Mg^{2+} (0.72Å) is smaller than the ionic radius of both the dopants considered in the present study (0.97Å for Cd^{2+} and 1.02Å for Hg^{2+}). Therefore it is expected the dopants may have entered into the crystal lattice as interstitials without affecting the overall charge neutrality of the crystal.

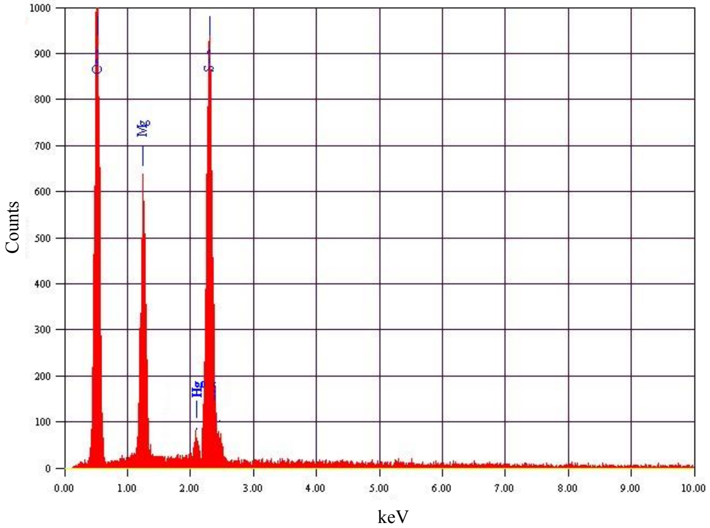


Figure 2. EDS spectrum of Hg doped MSHH

Fourier transform infra red spectral analysis

The FT-IR spectra obtained for the 0.005M histidine doped MSHH crystals are shown in Figure 3. The observed absorption bands and their respective assignments are reported in Table 1.

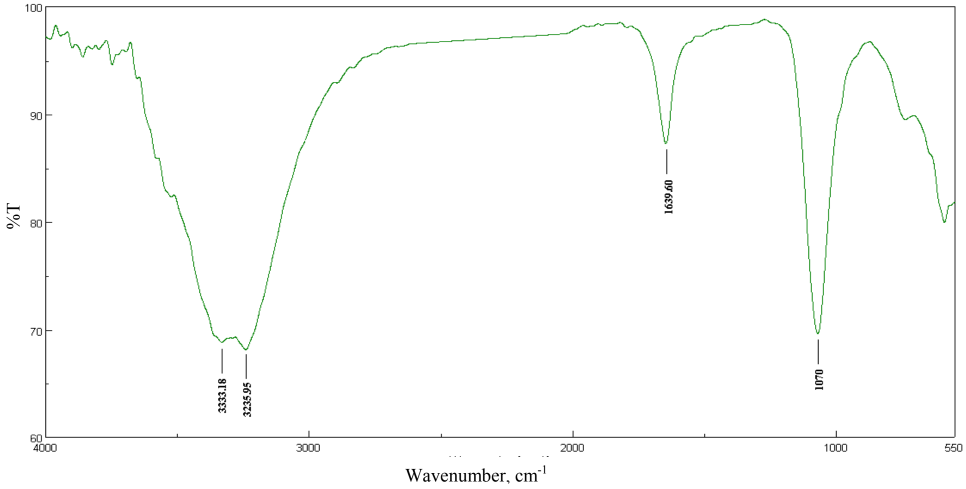


Figure 3. FTIR spectra of 0.005 M histidine doped MSHH crystals

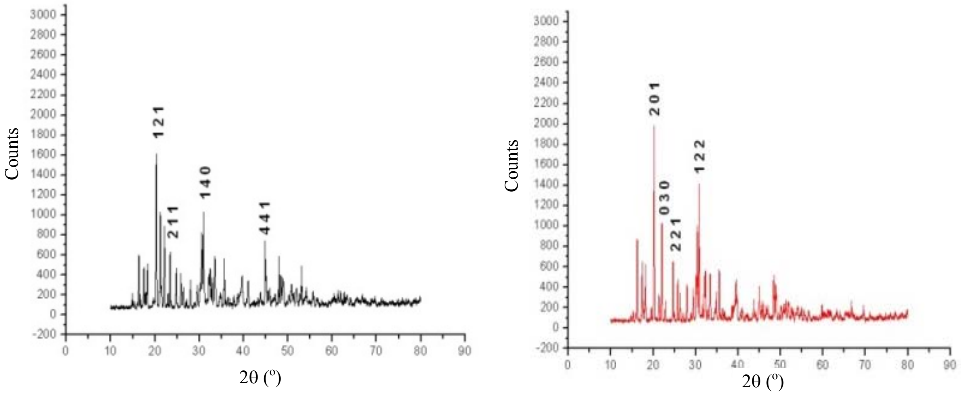
In the FT-IR spectrum of histidine doped magnesium sulphate heptahydrate single crystals, the broad band absorptions between 2779.99 cm^{-1} and 3652.26 cm^{-1} are due to OH stretching mode and water. The absorptions at 3333.18 cm^{-1} and 3235.95 cm^{-1} are due to NH stretching mode of primary amino group. The band at 1639.60 cm^{-1} is attributed to the C=O stretch. The peak at 1070 cm^{-1} is due to C-N stretch. The presence of amino group confirms the entry of histidine into the crystal lattice of MSHH.

Table 1. FTIR band assignment for histidine doped MSHH

Absorption Bands, in cm^{-1}	Band Assignment
3333.18	N-H stretch
3235.95	N-H symmetric stretches
1639.6	C = O stretch
1070	C-N stretch

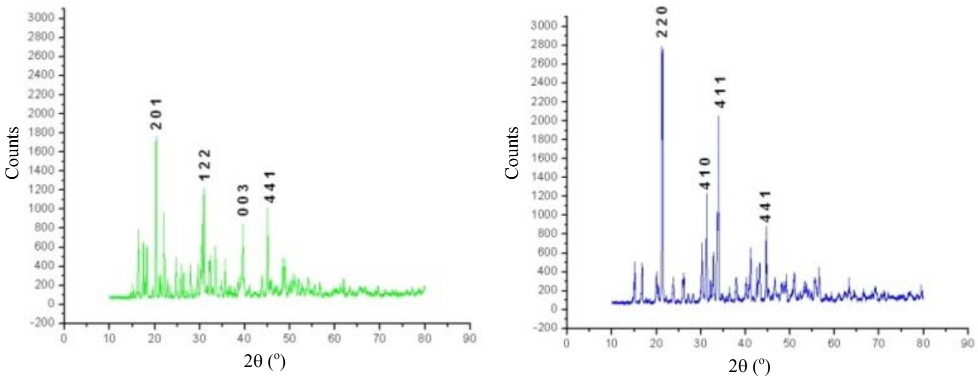
X-ray diffraction analysis

The x-ray diffraction pattern for the pure and doped MSHH crystals are presented in Figure 4. The x-ray diffraction agrees very well with the JCPDS data for pure MSHH [file No. 36 0419]. The indexed data of pure and doped crystals are tabulated in the Table 2. The x-ray diffraction pattern of the pure and doped MSHH single crystals differed in their relative intensities and the lattice spacing of the crystals. The reflection peaks are indexed with the help of powder X software[11] and are tabulated.



Pure MSHH

0.005 Cd doped MSHH



0.005 Hg doped MSHH

0.005 His doped MSHH

Figure 4. X-ray diffraction pattern of pure and doped MSHH

Table 2. Indexed powder diffraction data for pure doped MSHH

Samples	Calculated			Experimental			Δ2θ(°)
	2θ(°)	d(Å)	(hkl)	2 θ(°)	d(Å)	I/I_0%	
MSHH	21.084	4.2134	1 2 1	20.3688	4.3601	100	0.7152
	21.165	4.1974	2 1 1	21.2401	4.1832	67.58	-0.0751
	22.274	3.9910	0 3 0	22.1287	4.0171	61.82	0.1453
	30.161	2.9630	4 0 0	30.4821	2.9302	55.62	-0.3211
	30.809	2.9021	1 4 0	30.5734	2.9289	46.19	0.2356
	31.009	2.8838	1 2 2	30.9397	2.8879	71.78	0.0693
	45.038	2.0128	4 4 1	44.8387	2.0198	50.45	0.1993
Cd doped MSHH	16.590	5.3435	1 2 0	16.2915	5.4410	41.93	0.2985
	16.692	5.3110	2 1 0	17.4177	5.0916	31.97	-0.7257
	19.808	4.4819	2 0 1	20.2270	4.3903	100	-0.4190
	22.274	3.9910	0 3 0	22.0229	4.0362	52.62	0.2511
	24.815	3.5878	2 2 1	24.6812	3.6072	30.93	0.1338
	30.161	2.9630	4 0 0	30.4083	2.9396	51.46	-0.2473
	31.009	2.8838	1 2 2	30.8240	2.9009	73.61	0.1850
Hg doped MSHH	16.590	5.3435	1 2 0	16.3770	5.4127	42.63	0.2130
	19.808	4.4819	2 0 1	20.3247	4.3695	100	-0.5167
	22.274	3.9910	0 3 0	22.1220	4.0184	52.99	0.1520
	30.809	2.9021	1 4 0	30.5256	2.9286	43.9	0.2834
	31.009	2.8838	1 2 2	30.9035	2.8936	67.72	0.1055
	39.457	2.2836	0 0 3	39.5321	2.2797	43.96	-0.0751
	45.038	2.0128	4 4 1	45.0192	2.0137	55.77	0.0188
Histidine doped MSHH	21.094	4.2115	2 2 0	21.1787	4.1951	100	-0.0847
	21.165	4.1974	2 1 1	21.3957	4.1531	99.33	-0.2307
	31.093	2.8762	4 1 0	31.2497	2.8624	43.05	-0.1567
	33.726	2.6574	2 2 2	33.6637	2.6624	35.66	0.0623
	33.798	2.6520	4 1 1	33.9187	2.6408	74.06	-0.1207
	34.504	2.5993	0 3 2	34.0159	2.6400	37.07	0.4881
	45.038	2.0128	4 4 1	44.6365	2.0284	30.4	0.4015

The difference in experimental (2θ) and calculated (2θ) values suggest that the structures are slightly distorted in comparison to the pure crystal. This may be due to the strain caused on the lattice of MSHH by the entry of dopants. For pure crystals, the deviation in 2θ values may be due to the presence of natural impurities in the solutions. Similar observations were reported in the literature[9].

Thermal analysis

The thermograms recorded for all the grown crystals and are presented in the Figures 5-8. The thermal stability of pure MSHH was not affected due to the addition of dopants. Two stages of decomposition are found while heating the crystals from ambient to 250 °C. In both the stages of decomposition, water molecules are liberated. MSHH loses six water molecules at 176.42 °C whereas Cd, Hg and histidine doped crystals loses six water molecules around 213.12 °C, 192.21 °C and 163.58 °C respectively. All the stages of decomposition are supported by the corresponding exothermic and endothermic dips observed in the DTA thermograms. The expected loss of molecules in each stages of decomposition and corresponding percentage weight loss are tabulated in Table 3. There is a very good agreement between calculated and experimental weight loses.

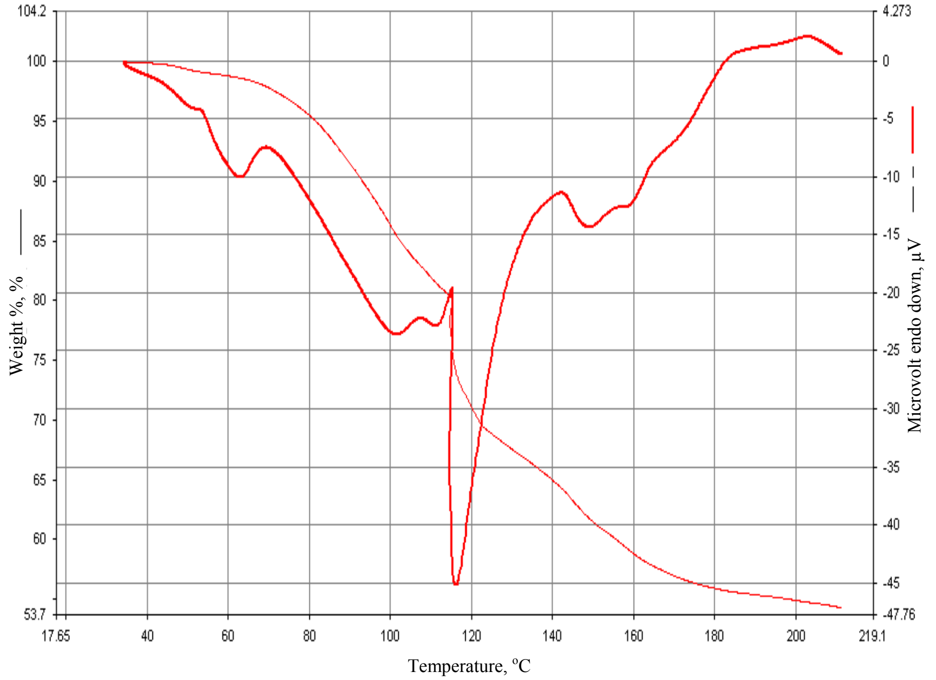


Figure 5. Thermogram of pure MSHH

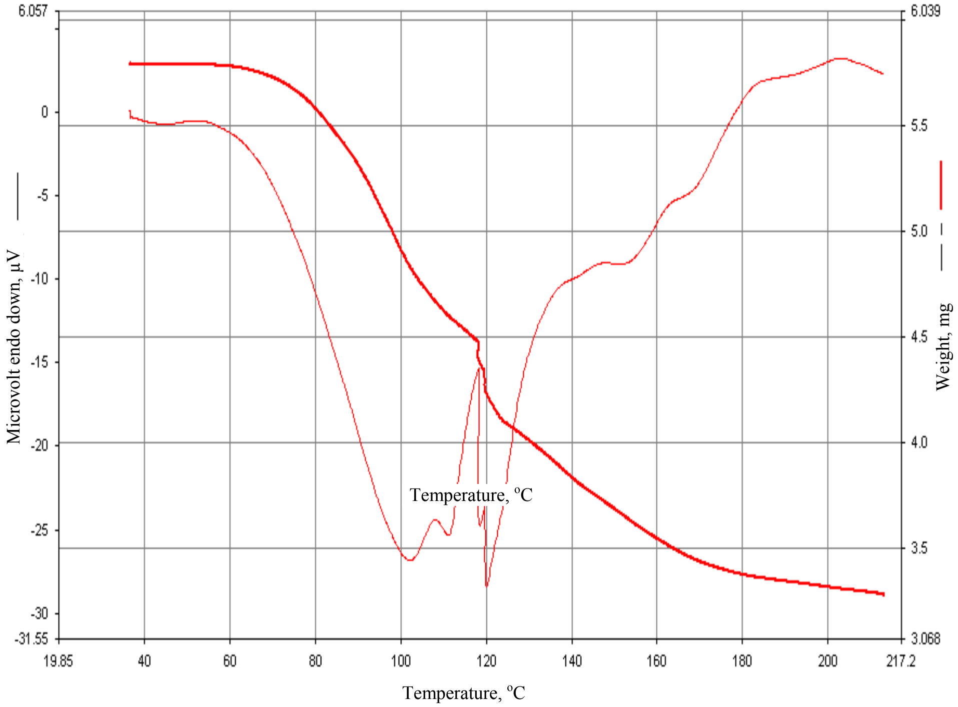


Figure 6. Thermogram of Cd doped MSHH

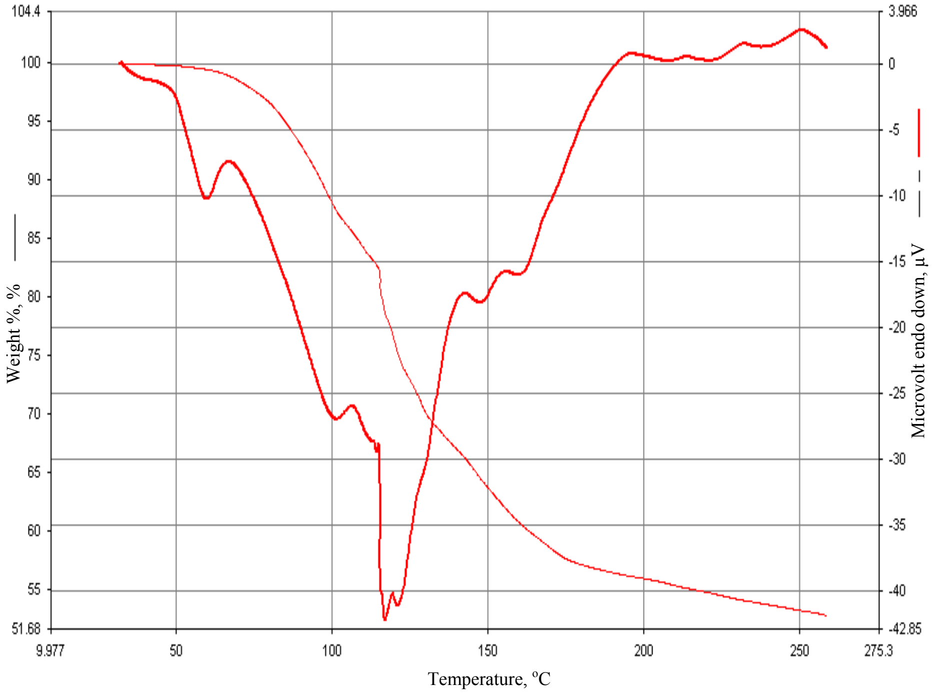


Figure 7. Thermogram of Hg doped MSHH

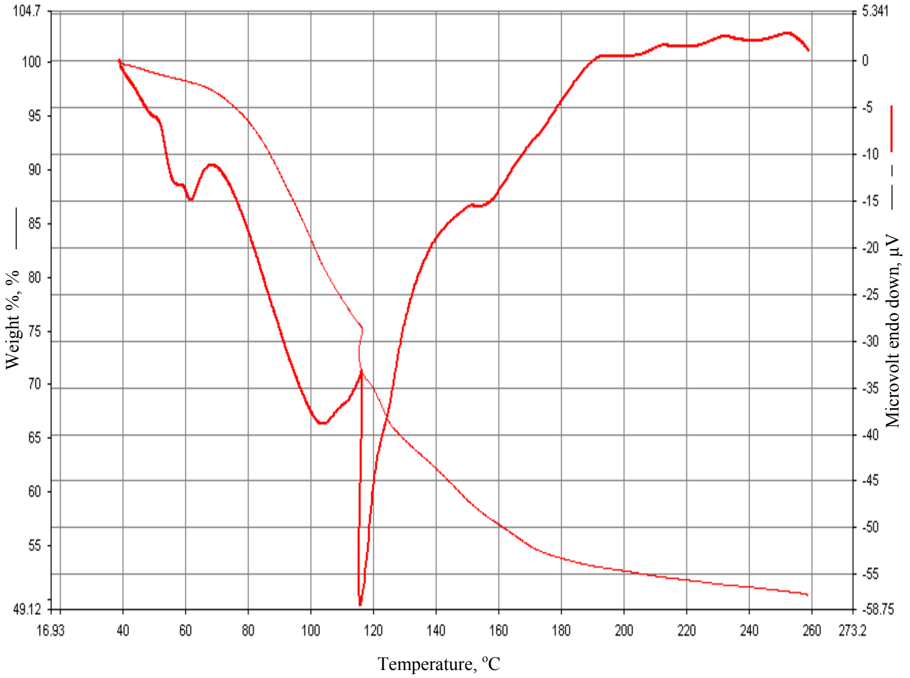


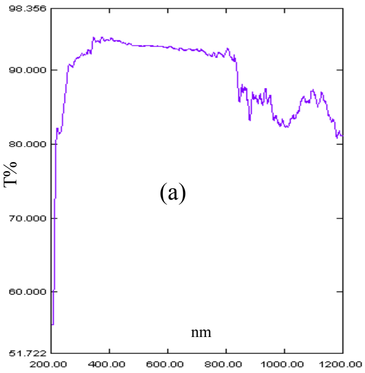
Figure 8. Thermogram of His doped MSHH

UV-Vis-NIR spectral analysis

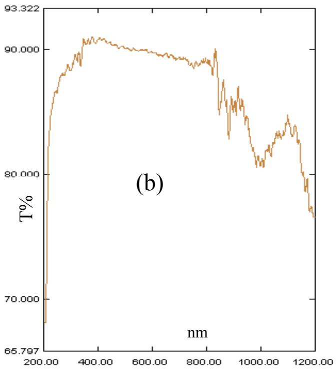
Single crystals are mainly used in optical applications and hence optical transmittance window and the transparency lower cut off (200-400 nm) is very important. This transparent nature in the visible region is a desirous property for the material used for NLO applications. The transmission spectra of pure and doped MSHH was recorded in the wavelength range between 200 and 1200 nm. The UV-Vis spectra were presented in Figures 9-12. The pure and doped crystals have maximum transmission in the entire visible region. The lower cut off wavelength of pure, 0.005 M Cd, 0.005 M Hg and 0.005 M histidine doped MSHH is 217.31 nm, 220.80 nm, 221.68 nm and 245.19 nm respectively. The wide optical transmission window of the grown crystals shows that these crystals are potential candidates for optical applications.

Table 3. Percentage of weight loss in the different stages of decomposition of pure and doped MSHH

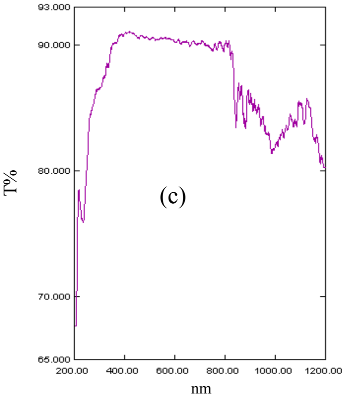
Grown crystals	Decomposition temperature, °C	Percentage of weight loss		Expected loss of molecules
		observed	calculated	
MSHH	114.72	21.98	21.92	$3H_2O$
	176.42	43.79	43.8	$3H_2O$
Cd doped MSHH	115.24	21.83	21.86	$3H_2O$
	213.12	43.41	43.72	$3H_2O$
Hg doped MSHH	117.77	21.91	21.83	$3H_2O$
	192.21	43.64	43.65	$3H_2O$
Histidine doped MSHH	109.44	21.82	21.84	$3H_2O$
	163.58	43.69	43.69	$3H_2O$



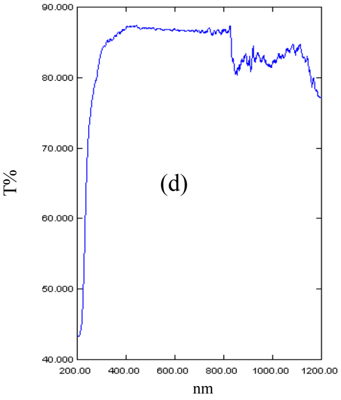
(a)→Figure 9. Transmission spectrum of Pure MSHH



(b) →Figure 10. Transmission spectrum of Cd doped MSHH



(c) →Figure 11. Transmission spectrum of Hg doped MSHH



(d) →Figure 12. Transmission spectrum of histidine doped MSHH

Conclusion

Pure and 0.005 M doped (Cd^{2+}, Hg^{2+}, histidine) magnesium sulphate heptahydrate single crystals were grown by slow evaporation method. Energy dispersive x-ray spectroscopy and fourier transform infrared spectroscopy confirmed the presence of Cd, Hg and histidine in the grown crystals. X-ray study reveals that the structures are slightly distorted due to the entry of dopants in to the crystal lattice. Enhancement of thermal stability was observed for the doped crystals. The crystals were found to decompose through two stages of decomposition. All the crystals possess a good transparency for the visible region which is essential for photonic devices.

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