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Growth ,Thermal, Mechanical, Structural Properties and Surface Morphology of Manganese Chloride Diammonium Phosphate Mixed Crystal

R.G.Vidhya[1,*], R.Ramasamy[2] and L.Vijayalakshmi[3]

[1]Department of Physics, Shrimati Indira Gandhi College,Tiruchirapalli,TamilNadu ,India.

[2]Department of Physics, National College, Thiruchirapalli, Tamil Nadu, India.

[3]Auxilium College of Arts and science for Women, Pudukottai, Tamil Nadu, India.

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ABSTRACT

The inorganic compounds often consist of relatively small number of broad bands compared with the spectra of organic compounds. The metal halogen absorption band is dependent on the strength of the bond, the mass of the metal atom and the valence state of the metal atom. A number of crystalline ammonium compounds undergo characteristic phase transitions, resulting in dramatic changes in a variety of physical properties as their temperature is changed. In the report on Mn doping on barium tartrate identifies few extra peaks and the intensity of the prominent peak is found to be decreased . In this paper we report the thermal,mechanical, structural properties and surface morphology of manganese chloride diammonium hydrogen phosphate mixed crystal .

1. Introduction

Diammonium Hydrogen Phosphate (DAHP) is one of the series of water soluble ammonium phosphate salts that can be used as a corrosion inhibitor and fertilizer. It increases soil pH. It lowers combustion temperature of material, decreases maximum weight loss rates. This is also used in the manufacturing of important materials, such as fire-proofing textiles, paperwood, and vegetable fibres. The applications of diammonium hydrogen phosphate crystals are discussed in many literature**[1-7]**.There is no literature reporting the change in the physical and chemical properties of DAHP crystals by the addition of manganese chloride. In this article the change in mechanical, thermal and structural properties of DAHP due to addition of manganese chloride is discussed.

2 Growth Procedure

The commercially available AR grade sample of DAHP and manganese chloride were the parent materials. 1M DAHP solution was prepared by constant stirring. IM $MnCl_2$ solution was also prepared. Both the solutions were mixed and stirred for 10 hours using magnetic stirrer. Super saturated conditions were confirmed by the formation of precipitate. The solution was filtered and kept undisturbed. Single crystals of manganese chloride diammonium hydrogen phosphate mixed crystals[MCDAHP] were grown by solution method after a period of 30 days. The crystals of high quality can be obtained by purification of starting material. The grown crystals are shown in the Figure 1.

3 Results and Discussions

3.1Thermo gravimetry analysis (TGA)

TGA was carried cut in the nitrogen atmosphere at 20ml/min using Perkin-Elmer make at the rate of 30 deg/min between the temperature range 35ºC-900ºC.

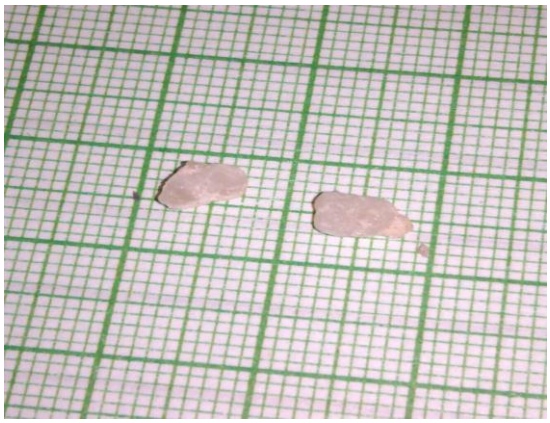

Figure 1. MCDAHP Crystals.

The trace is shown in the Figure2. Pure DAHP decomposes in a complex manner.The mass loss is due to sublimation of P_2O_5 with maximum rate at 625°C. This is confirmed from crystal transition of diammonium hydrogen phosphate reported **[8,9]**. It was reported that strontium doped Barium hydrogen Phosphate crystal has more thermal stability than pure Barium Hydrogen Phosphate (BHP) crystal and it may be due to increase in bond energy caused by the incorporation of Sr^{2+} ions in the lattice of the doped BHP Crystals**[10]**. Similarly the manganese chloride mixed diammonium hydrogen phosphate crystal has higher thermal stability than DAHP. From the thermal study of a variety of phosphate crystals, it was concluded that the thermal decomposition is a complex process with the release of ammonia gas and yields pyrophosphate**[11]**.

In the present study the maximum weight loss of about 95% occurs in the range 200°C - 350°C which is due to the decomposition of the sample.

Tele:

E-mail address: vidsigc@gmail.com

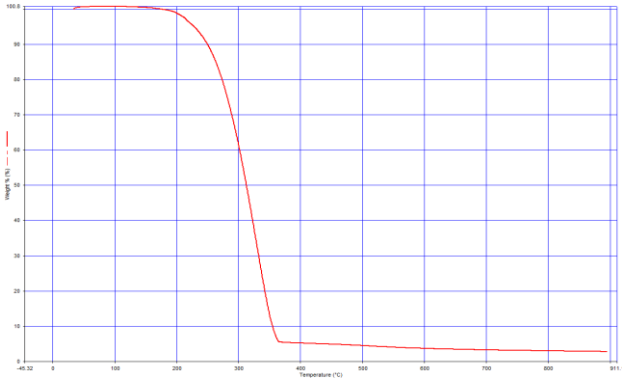

Figure 2. TGA of MCDAHP.

3.2. Differential Thermal Analysis

The DTA curve of MCDAHP is given in the Figure 3. It shows a sharp endothermic peak at 326.32°C. This value can be attributed to the decomposition or melting point of the crystal. From the DTA result it may be interpreted that MCDAHP crystal has more thermal stability than DAHP crystal.The absence of endothermic peak around 100°C shows that there is no inclusion of water molecules in the same.

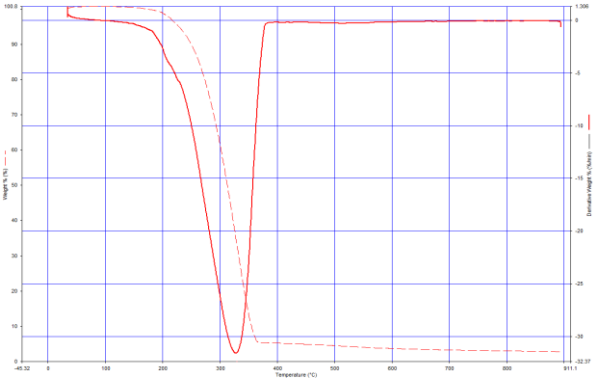

Figure 3. DTA of MCDAHP.

3.3 Differential Scanning Calorimetry (DSC)

DSC was carried cut in the nitrogen atmosphere at 20ml/ml using Perkin-Elmer make at the rate of 30 deg/min between the temperature range 35ºC-400ºC.The DSC curve of MCDAHP is shown in the Fig 4.It has two endothermic peaks. The peak around 340ºC is due to decomposition of MCDAHP.The DSC curve has similar profiles, verifying the endothermic and exothermic transitions, in agreement with the DTA and TGA results.

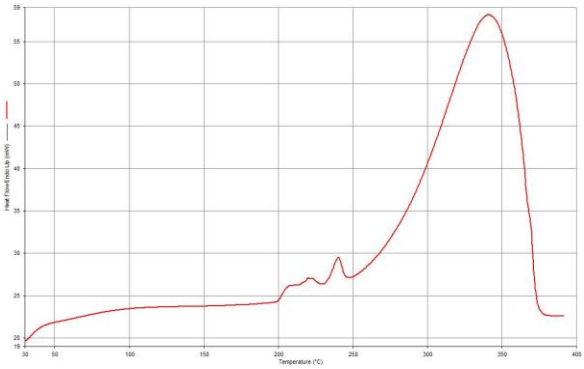

Figure4. DSC of MCDAHP.

3.4. Vicker's Microhardness Test

The mechanical strength of the grown crystal is studied using Shimadzu model HMV-2T. The hardness of the material is a measure of its resistance to applied load. The response for low loads is observed. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed.

The variations of micro hardness number with load applied is given in the Figure 5. The Hardness number H_v increases with applied load. The hardening coefficient is calculated from the plot [Figure 6] between log d and log p. The crystals come under soft material category. The stiffness constant C_{11} is also measured from the formula.

$$C_{11} = H_v^{7/4} \text{ and}$$

C_{11} gives the idea of toughness of bonding between neighbouring atoms. Table -1 gives the C_{11} corresponding to H_v values.

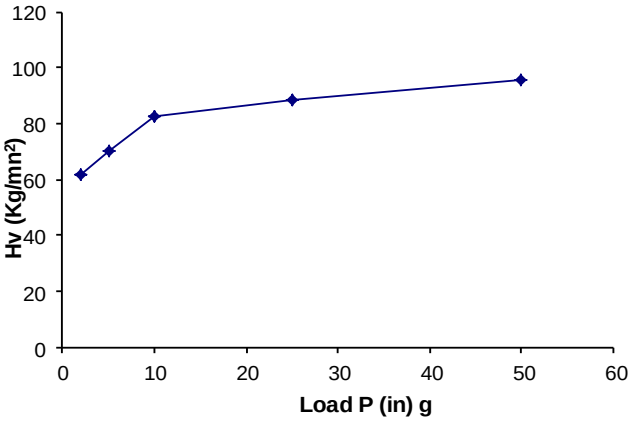

Figure 5.Variation of Vicker's micro hardness number Hv with load.

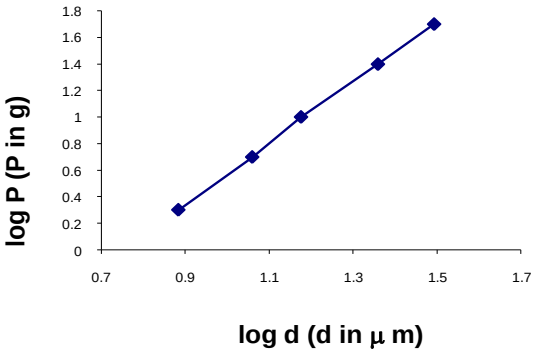

Figure 6. log P vs log d.

Table 1. Stiffness Constant for Various Load

Load 10^{-3} Kg	H_vKg/mm^2	$C_{11}10^{14}$Pa
2	62	13.7
5	70.3	17.06
10	82.6	22.63
25	88.4	25.48
50	95.7	29.28

3.5 Structural Analysis

3.5.1 Single Crystal X-ray Diffraction Analysis

The Single Crystal X-ray diffraction has been carried out using Bruker Kappa APEX II diffractometer with Mo K_α(0.71073Aº) radiation as the source. The crystallographic parameters of the grown crystal is given in Table 2.The crystal belongs to tetrogonal system. The unit cell parameters,crystal system and hence the volume of unit cell of MCDAHP differ from pure DAHP crystal.

Table 2. Crystallographic Parameters.

Parameters	MCDAHP
a Å	7.528
bÅ	7.528
cÅ	7.586
Crystal system	tetrogonal
Space group	P4
Volume($Å^3$)	429.8

3.5.2 Structural Analysis from Powder X-ray diffraction

To confirm the crystal structure of the grown crystals , powder XRD has been performed at room temperature using Rigaku Ultima 3 diffractometer. The diffraction pattern shows sharp peaks.The well defined peaks at specific 2θvalues prove the high crystallinity of the grown crystals.

The diffraction pattern is shown in Figure 7. The reflections of the PXRD pattern was analysed using chekcell and expo 2014 software**[12,13]**. The d spacing, FWHM and relative intensity corresponding to 2θ values are given in Table -3. The indices of the six major peaks are presented in Table -4. The grain size is calculated from the formula

$D = 0.9\lambda / \beta\cos\theta$ as7.266Å

The analysis of different diffraction peaks indicate the formation of tetrogonal system. The indices of the major peaks of MCDAHP are (022), (004), (332),(002) and (331) respectively in the decreasing order of intensities.

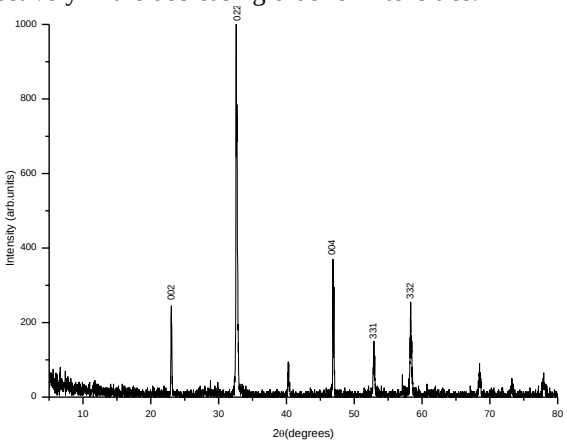

Figure 7. Powder XRD of MCDAHP.

Table 3. d spacing, FWHM and relative intensity corresponding to 2θ values.

S.No	2theta	d	FWHM	100. *I/I_{max}
1)	7.2886	12.118	0.2406	3.98
2)	7.5600	11.6841	0.2051	4.98
3)	7.7800	11.3542	0.4196	5.47
4)	8.2000	10.7735	0.2379	4.98
5)	8.9200	9.9055	0.3880	3.98
6)	9.3600	9.4408	0.2597	3.98
7)	10.1400	8.7163	0.3607	3.48
8)	10.8800	8.1250	0.2511	3.48
9)	11.0631	7.9910	0.1857	1.99
10)	11.7597	7.5191	0.3395	4.48
11)	12.3994	7.1326	0.3427	2.99
12)	12.6412	6.9967	0.4389	2.99
13)	12.6910	6.8248	0.2786	2.49
14)	14.5161	6.0969	0.7550	3.48
15)	17.6221	5.0287	0.1895	2.49
16)	17.9763	4.9304	0.2813	2.49
17)	18.5441	4.7807	0.1789	1.49
18)	19.5205	4.5437	0.1688	2.49
19)	21.6094	4.1090	0.1587	1.99
20)	21.9609	4.0440	0.1211	2.99
21)	22.2217	3.9971	0.2643	2.49
22)	23.0203	3.8602	0.1468	24.38
23)	27.9646	3.1879	0.3067	2.99
24)	32.5800	2.7461	0.1988	100.00
25)	33.1400	2.7010	0.3372	3.48
26)	33.6445	2.6616	0.1875	2.99
27)	34.2350	2.6170	0.1548	1.99
28)	34.2088	2.6190	0.1496	1.99
29)	36.4170	2.4651	0.1283	1.99
30)	40.2627	2.2381	0.2164	9.45
31)	46.8615	1.9371	0.1608	36.82
32)	51.6000	1.7698	0.1789	1.99
33)	52.1200	1.7534	0.2786	2.99
34)	52.9000	1.7293	0.2328	14.93
35)	53.5635	1.7095	0.1559	2.49
36)	55.6074	1.6514	0.1730	1.99
37)	56.3798	1.6306	0.2437	1.99
38)	56.5621	1.6258	0.1832	1.99
39)	57.1056	1.6116	0.2437	5.97
40)	57.4803	1.6020	0.1303	2.99
41)	58.3201	1.5809	0.2210	25.37
42)	67.0990	1.3938	0.1052	2.99
43)	68.4776	1.3690	0.1866	8.96
44)	68.6213	1.3665	0.1966	6.47
45)	69.6553	1.3487	0.1812	1.49
46)	70.5696	1.3335	0.1438	2.49
47)	71.2922	1.3217	0.2372	1.99
48)	73.2143	1.2917	0.2746	4.98
49)	73.4495	1.2882	0.2638	3.48
50)	77.1793	1.2349	0.1141	2.99
51)	77.6409	1.2287	0.1653	3.98
52)	77.9401	1.2248	0.2560	6.47

Table 4. hkl indexing.

S.No	2θ	Relative intensity	hkl index
1	32.58	100	022
2	46.8615	36.82	004
3	58.32	25.37	332
4	23.02	24.38	002
5	52.9	14.93	331

3.6 SEM Analysis

The SEM analysis was performed using Vega 3 instrument. The SEM micrographs are shown in Figure 4.10. SEM acceleration voltage was 5.0 kV. Sample was kept in highly vacuum state 18.16 nm work distance was maintained and monochromatic colour modes were employed. SEM shows homogeneous distribution of the material with plate, triangular, tetragonal and pentagonal structures.

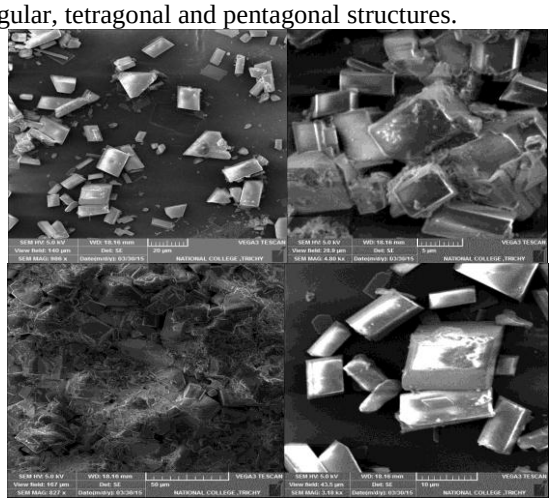

Figure 8. SEM Images of MCDAHP.

4. Conclusions

The title compound has been synthesized and the characterization studies are carried out to know the change in mechanical, thermal and structural properties .

The TGA Analysis confirms that there is no water molecules present in the grown crystal . Due to inclusion of manganese chloride in DAHP crystal, there is variation in melting point of MCDAHP which is observed from DSC curve .Vicker's hardness study shows that the crystal has a high hardness value .This reveals the reasonable mechanical strength of the material. The crystals belong to soft material category. The unit cell parameters of the mixed crystal varies from pure DAHP crystal. The MCDAHP crystal belong to tetragonal system whereas DAHP crystal belong to monoclinic system.

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