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Crystal growth and characterization of $(NH_4)_3BaCl_5.2H_2O$

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Abstract : $(NH_4)_3BaCl_5.2H_2O$ single crystals were grown from aqueous solutions. The crystals obtained were subjected to a systematic morphological, X-ray and thermal analyses. The cell parameters are monoclinic, space group, $P2_1/n$, $a = 7.075$ (7), $b = 10.828$ (8), $c = 6.668$ (6) Å, $\beta = 91.20°$, $Z = 2$, $V = 492.6$ Å^3.

Keywords : Crystal growth, morphology, X-ray powder diffraction, thermal analysis

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1. Introduction

A_2BX_4 (where A = K, NH_4, Rb, Cs, Na, $N(CH_3)_4$; B = Cu, Cd, Co, Zn; X = Cl, Br, I) compounds represent the largest known group of insulating crystals with structurally incommensurate phases [1,2]. Similarly, $A_3BX_5.2H_2O$ (where A = Na, NH_4; B = Ba; X = Cl, Br) crystals exhibit very unusual physical properties and are closely related to the A_2BX_4 group [3–5]. These systems have attracted a great deal of attention owing to the occurrence of varying stoichiometries in them. Although no detailed X-ray single crystal data is available for these crystals, some structural data for the prototype compound $BaCl_2.2H_2O$ is available [4]. Also some data is available on the $Na_3BaCl_5.2H_2O$ [5]. However, $(NH_4)_3BaCl_5.2H_2O$ has not been studied in the literature. Here, the authors report the growth of single crystals of $(NH_4)_3BaCl_5.2H_2O$ for the first time and carried out their characterization through the morphological studies, XRD, TGA and DSC.

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2. Crystal growth

$(NH_4)_3BaCl_5.2H_2O$ (ABC) crystals were obtained through slow evaporation of a saturated aqueous solution. The starting components included 3 moles of NH_4Cl and 1 mole of $BaCl_2$ and the crystallization reaction occurred as follows :

$$3NH_4Cl + BaCl + 2H_2O \qquad (NH_4)_3BaCl_5.2H_2O.$$

Saturated solutions of analytical grade ammonium chloride and barium chloride (3 : 1 molar ratio) were prepared separately using triple distilled water. The two solutions were mixed thoroughly and filtered. The solution was then poured into a crystallizer shown in Figure 1a. The crystallizer was covered by a watch glass and placed on a beaker containing

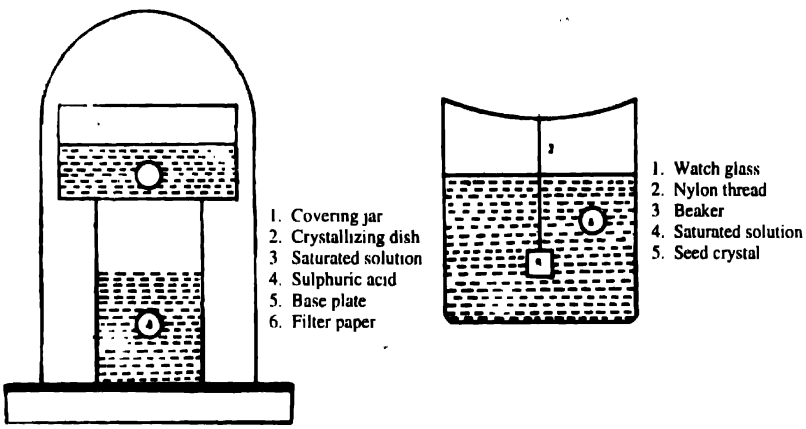

Figure 1. Experimental set up for the growth of $Na_3BaCl_5.2H_2O$ single crystals

about 200 ml of concentrated sulphuric acid. The whole assembly was covered by a large glass dome in order to protect it from dust and also to provide minimum thermal oscillations. The crystal growth experiments were carried out with minimum mechanical shocks. Under such conditions crystallization though slow, yielded transparent, colourless seed crystals which exhibit platelet habits. Crystallization took place for seven to ten days either in a neutral medium or acid medium using hydrochloric acid. In the acid medium, the crystallization process is fast due to common ion effect. The average size of the grown crystals are of the order $7 \times 4 \times 2$ mm^3. In some experiments, the crystals were as big as $20 \times 6 \times 3$ mm^3.

The crystallization was carried out essentially through spontaneous nucleation. The spontaneously grown large crystals of $(NH_4)_3BaCl_5.2H_2O$ were used as the seed crystals for the growth of large size single crystals as shown in Figure 1b. As the size of the crystals increased due to increased growth rate, the quality of the crystals slowly decreased.

The authors have made an attempt to grow the $(NH_4)_3BaCl_5.2H_2O$ crystals by gel method and the results were not encouraging. Therefore, the authors paid more attention to

the solution growth. The crystal growth experiments from solutions in general were carried out at two different temperatures (27°C and 32°C) and in both cases the experiments produced crystals of different size, habit and quality. This has been discussed in more detail under morphology.

The solubility study on $(NH_4)_3BaCl_5.2H_2O$ crystals was carried out with varying temperatures. The Figure 2 shows the solubility curve as a function of temperature for $(NH_4)_3BaCl_5.2H_2O$ crystals in grams per 100 ml of triple distilled water. As is evident from

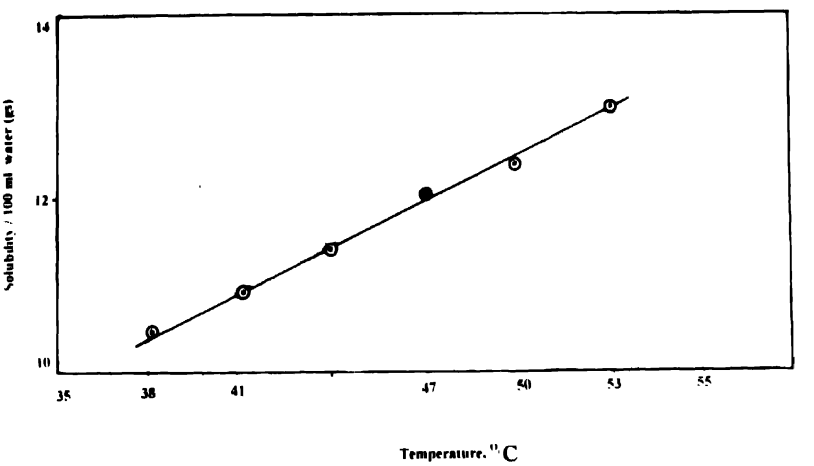

Figure 2. Solubility curve of $(NH_4)_3BaCl_5.2H_2O$.

Figure 2, the solubility increases with increasing temperature. Higher the temperature, bigger will be the solubility, and in turn the growth rate increases which reduces the crystal quality.

3. Morphology

The habit of a crystal is determined by the slowest growing faces having the lowest surface energy, but it is also apparent that a crystal habit is governed by kinetics rather than equilibrium considerations [6]. A number of factors, such as degree of supersaturation, type of solvent, pH of the mineralizer, *etc.* effect the habit of a crystal. Kern [7] has shown that many ionic crystals change their habits when suprsaturation exceeds a certain critical value. Wells [8] observed that a change in solvent results in a change in crystal habit. Sometimes the pH of the media has a considerable influence on the growth rate of crystals, which ultimately changes the growth habit [9]. Habit modifications are also observed when significant changes in the growth temperature and occurrence of impurities, because an increase in temperature increases the growth rates [10]. The most common cause of habit change is the presence of impurities in the crystallizing solution. It is observed that even very small traces (0.01%) are enough to produce significant changes. Therefore, many

observed crystal habits may be caused by unsuspected impurity effects. This is true with reference to the $(NH_4)_3BaCl_5.2H_2O$ crystals, which show a wide range of morphological variations not only due to the changes in the growth parameters, but also due to the deliberate or accidental entry of impurities. The changes in the growth parameters have been attributed to the slight temperature fluctuations and growth media.

The morphology of $(NH_4)_3BaCl_5.2H_2O$ crystals is very interesting and it was studied using a phase contrast microscope (Leitz-Laborlux, Germany). Since the experiments have been carried out at two different temperatures (27°C and 32°C), and also in different growth media (acid and neutral media), the crystal morphology varies significantly. The crystals are usually tabular, plate like, rectangular, long thick needles and so on. The most common faces observed in these crystals are (100), (010), (001), (011), (111), (101) and so on. The overall morphology of the crystals obtained is a typical monoclinic centrosymmetric. The faces are very well developed and so also the edges and solid angles. The overall morphology of these crystals is given in Table 1.

Table 1. Morphology of $(NH_4)_3BaCl_5.2H_2O$ crystals

Growth temp. (°C)	Common faces	Growth rate	Prominent face	Crystal morphology	Surface morphology
27	(100), (001), (111), (110), (010),	γ (010) > γ (001) or γ (011) or γ (111)	(010)	Long rectangular platelet [Fig. 3(c)]	surface is more or less smooth
32	(100), (001), (110), (111), (010),	γ (100) > γ (101) > γ (001) > γ (010) > γ (111)	(100)	Broad monoclinic platelets [Figs 3(b) and 3(d)]	spirals, octagonal interrupted spirals, dissected dissolution features

The morphology of the crystals obtained at 27°C show long rectangular habit with the most common faces like (010), (011), (111), (001) and so on. The size of the crystals vary from 20 × 6 × 3 mm^3 and even longer. The crystals are highly transparent, vitreous with very smooth surfaces and well developed faces, edges and solid angles. The growth along the c-axis is unusually high compared to the *a*- or *b*-crystallographic axes. The Figures 3(a–d) shows the characteristic photographs of the $(NH_4)_3BaCl_5.2H_2O$ crystals obtained at both 27°C (long rectangular and transparent) and 32°C (broad and semi-transparent platelets). The crystals obtained at 32°C are fairly bigger, in the sense more broader and also equi-dimensional in most of the cases. The crystals are slightly buff white in colour in some places and colourless in the remaining portions. However, both the crystals (obtained at 27°C and 32°C) show well developed monoclinic symmetry. The schematic diagrams of $(NH_4)_3BaCl_5.2H_2O$ crystals are shown in Figure 4. The crystal drawings were done using the CAMERA-LUCIDA set up, and the actual observed central distances were used in crystal drawings. As is evident from the Figure 4, the growth temperature clearly controls the crystal morphology and the growth rate.

Plate I

Figure 3(a).

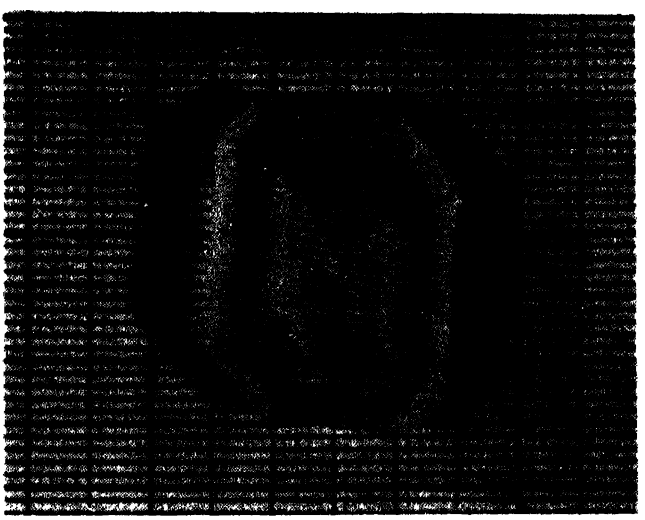

Figure 3(b).

Plate 1 (Cont'd.)

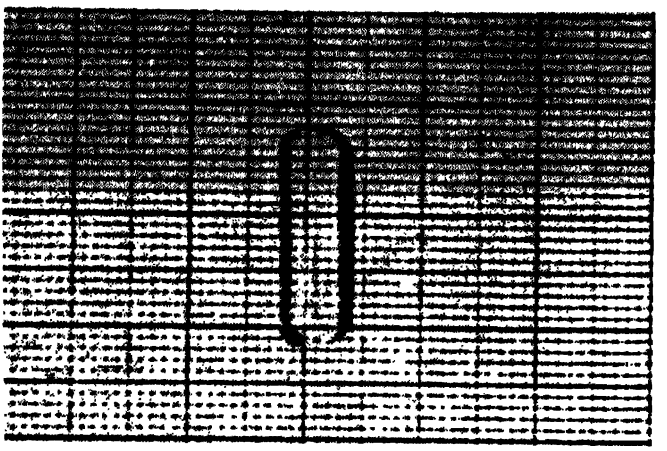

Figure 3(c).

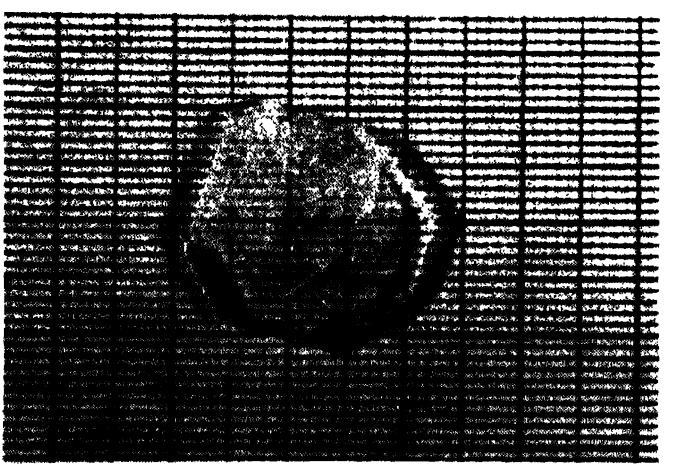

Figure 3(d).

Figure 3(a–d). Characteristic photographs of $(NH_4)_3BaCl_5.2H_2O$ crystals.

The authors have also studied the surface morphology of these $(NH_4)_3BaCl_5.2H_2O$ crystals in order to understand the growth defects and to find out the optimum growth conditions. The crystals obtained at 27°C show more or less smooth and shining surfaces without any major morphological features. Whereas, the crystals obtained at 32°C show

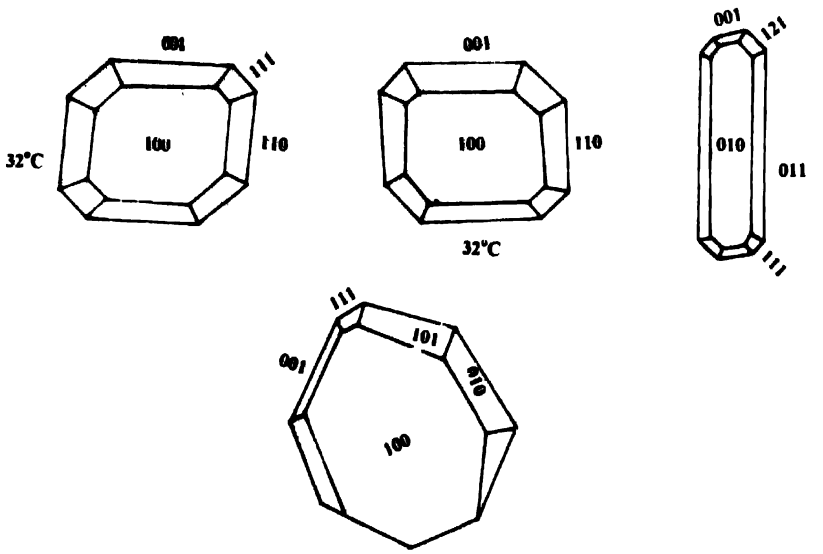

Figure 4. Schematic diagrams of $(NH_4)_3BaCl_5.2H_2O$ crystals.

very interesting surface morphological features like interrupted growth spirals, growth layers, dissolution features. The Figures 5(a–g) shows the characteristic surface morphological features observed in $(NH_4)_3BaCl_5.2H_2O$ crystals obtained at 32°C. The Figure 5a represents uniform growth bands in the middle of the crystal on (100) face. The Figure 5b shows the dissolution features along the growth steps under high magnification. The step height is relatively moderate. The Figure 5c shows a portion of the growth spiral and dissolution feature all along the spirals which is shown under high magnification (Figure 5d). This is also probably the region of impurity concentration. The Figure 5e shows the presence of small growth hillocks aligned along the (100) face. The Figure 5f shows the bottom portion of the crystal which is not really smooth, but growth spiral is seen from the bottom. The nucleus is well in the middle of the crystal and it is clearly seen in this picture. The Figure 5g shows most probably an edge dislocation on (010) face. All these surface morphological features observed in $(NH_4)_3BaCl_5.2H_2O$ crystals are actually seen not in the middle portion of the crystals except for the polygonal shaped growth spiral more or less in agreement with the symmetry of the face. The slight eccentricity is due to the anisotropy in the growth environment such as a supersaturation gradient. The morphological studies on $(NH_4)_3BaCl_5.2H_2O$ crystals show that the ideal temperature for the growth of these crystals is around 30°C.

4. Characterization

The $(NH_4)_3BaCl_5.2H_2O$ crystals obtained were characterized using XRD (both powder X-ray diffraction and single crystals methods were used) and TGA/DSC techniques.

4.1. X-ray diffraction:

The X-ray powder diffraction patterns for $(NH_4)_3BaCl_5.2H_2O$ crystals were recorded using Rich Seifert Unit, Germany, X-ray diffractometer with a monochromatic radiation of CuK_α (Lambda = 1.5406 Å). X-ray powder diffraction studies showed that the resultant product is a single phase and also a new phase. The powder XRD data is given in Table 2.

Table 2. XRD data for $(NH_4)_3BaCl_5.2H_2O$.

				Direct	Lattice	Parameters		
	7.78857			9.86151	6.41617	90.00008	91.71703	90.00008
	00656			01104	.00440	.00000	.06192	00000
				Volume = 492.6 *abc* = 492.8				
N	h	k	l	Refl Exp Phase No. 1	Refl. Fit	Differ	DK	chi-squ
1	0	1	1	5.3731	5.3764	−.0033	5.3764	.4
2	1	0	1	4.8601	4.8788	−.0187	4 8788	13.9
3	1	1	1	4.3779	4.3729	0050	4 3729	1.0
4	−2	1	0	3 6252	3 6207	0045	3.6207	.8
5	−2	0	1	3.3597	3.3727	−0130	3.3727	6 8
6	−2	1	1	3 1838	3.1912	−.0074	3 1912	2.2
7	−1	1	2	2 8831	2.8673	0158	2.8673	10 0
8	0	2	2	2 6914	2.6882	.0032	2.6882	4
9	1	2	2	2 5287	2.5215	0072	2 5215	3 2
10	3	0	1	2.3953	2.3809	.0144	2.3809	13 0
11	2	3	1	2.3270	2.3233	.0037	2.3233	8
12	−2	2	2	2.2402	2.2384	.0018	2 2384	.2
13	1	4	1	2 1962	2.2004	-.0042	2 2004	2.0
14	0	0	3	2.1387	2 1378	0009	2.1378	.1
15	−1	0	3	2.0764	2.0774	−.0010	2 0774	.1
16	3	0	2	1 9887	1.9883	.0004	1.9883	.0
17	2	5	1	1.6888	1.6908	−0020	1.6908	.2
18	−3	1	3	1.6536	1 6512	0024	1.6512	.2
19	−4	2	2	1.5976	1.5956	.0020	1.5956	.2
20	−2	5	2	1.5527	1.5513	.0014	1.5513	.1
21	−2	6	0	1.5134	1 5141	−.0007	1.5141	.0
22	−4	4	1	1.4953	1.4940	.0013	1.4940	1
23	0	5	3	1.4501	1.4496	.0005	1 4496	.0
24	−4	5	0	1.3850	1.3853	−.0003	1 3853	.0
25	−2	6	2	1.3748	1.3754	−.0006	1.3754	.0
26	4	3	3	1.3025	1.3022	.0003	1.3022	.0
27	−4	6	1	1.2377	1.2368	.0009	1 2368	.0
28	5	2	3	1.2014	1.2035	−.0021	1.2035	.3
29	5	6	1	1.1097	1.1091	0006	1 1091	.0

Refl. Exp. – *refers to the interplanar spacing values 'd' obtained using Bragg's angles.*

Refl. Fit. – *refers to 'd' spacings calculated after having corrected for the intensity of the lines (eliminating the noise and applying a least squares fit).*

DK – *refers to the interplanar spacing for various reflections after applying corrections for the lines.*

Plate II

Figure 5(a).

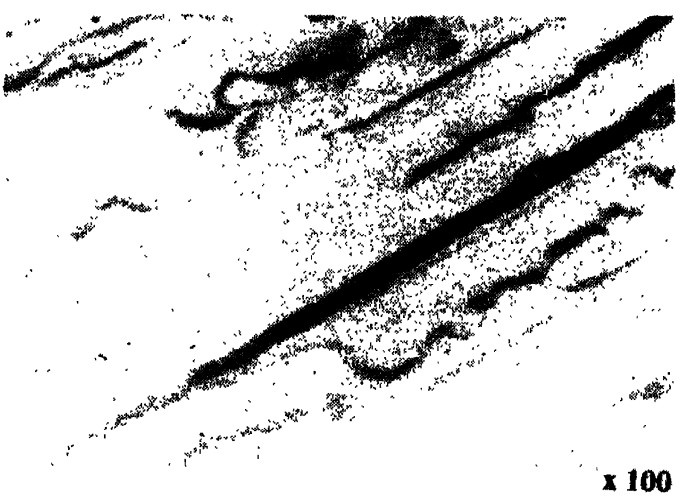

Figure 5(b).

Plate II (Cont'd.)

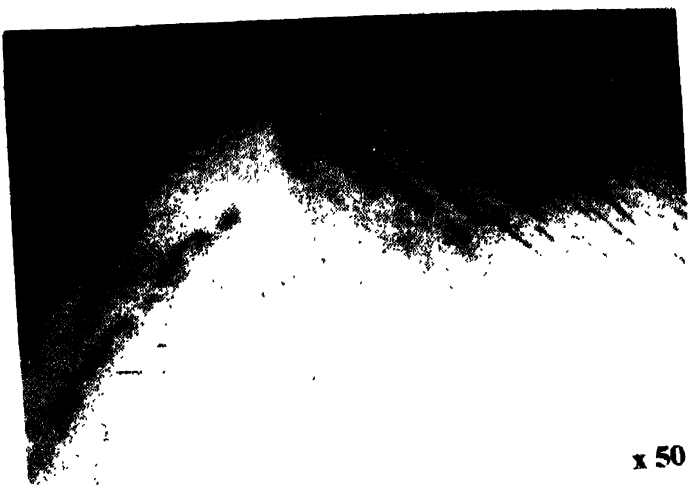

Figure 5(c).

Figure 5(d).

Plate II (Cont'd.)

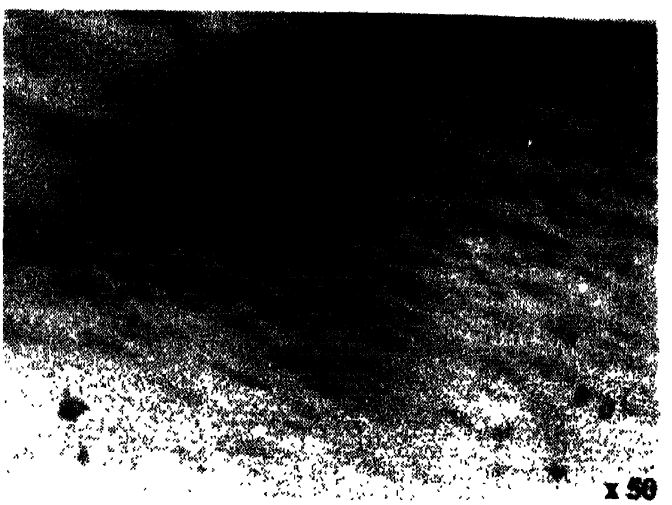

Figure 5(e).

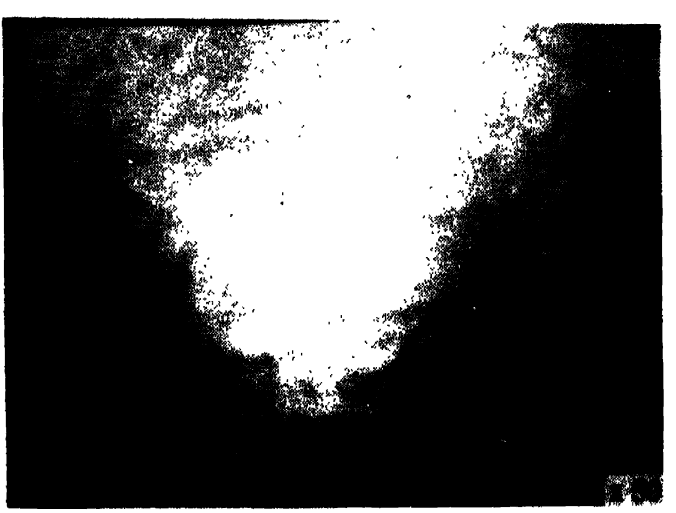

Figure 5(f).

Plate II (Cont'd.

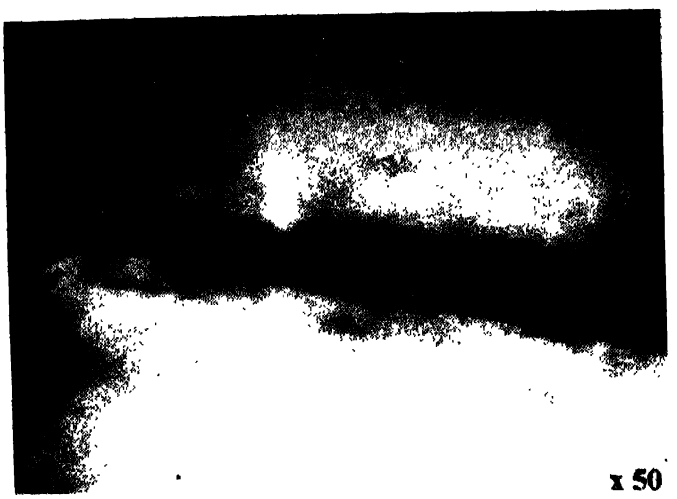

Figure 5(g).

Figure 5(a–g). Characteristic surface morphological features observed in $(NH_4)_3BaCl_5.2H_2O$ crystals obtained at 32°C : (a) uniform growth bands in the middle part of the crystal on (100) face; (b) dissolution features along the growth steps under high magnification, (c) a portion of the growth spiral; (d) dissolution feature all along the spirals which is shown under high magnification; (e) presence of small growth hillocks aligned along the (100) face; (f) bottom portion of the crystal which is not really smooth, but growth spiral is seen from the bottom and (g) an edge dislocation on (010) face

Therefore, the single crystal X-ray diffraction studies were carried out using Enraf Nonius CAD-4 X-ray diffractometer. The unit cell parameters were found to be a = 7.075 (7) Å, b = 10.828 (8) Å, c = 6.668 (6) Å and β = 91.20 (7) from the accurate centered 25 reflections in the θ range 20 to 30. The space group was found to be $P2_1/n$. The number of molecules in the unit cell was found to be two. A detailed structural refinement work is under progress for publication elsewhere.

4.2. Thermogravimetric analysis (TGA) :

The TGA curves for the $(NH_4)_3BaCl_5.2H_2O$ crystals were recorded using Mettler TA 3000, and the characteristic curves are shown in Figure 6. It is observed from Figure 6, that there

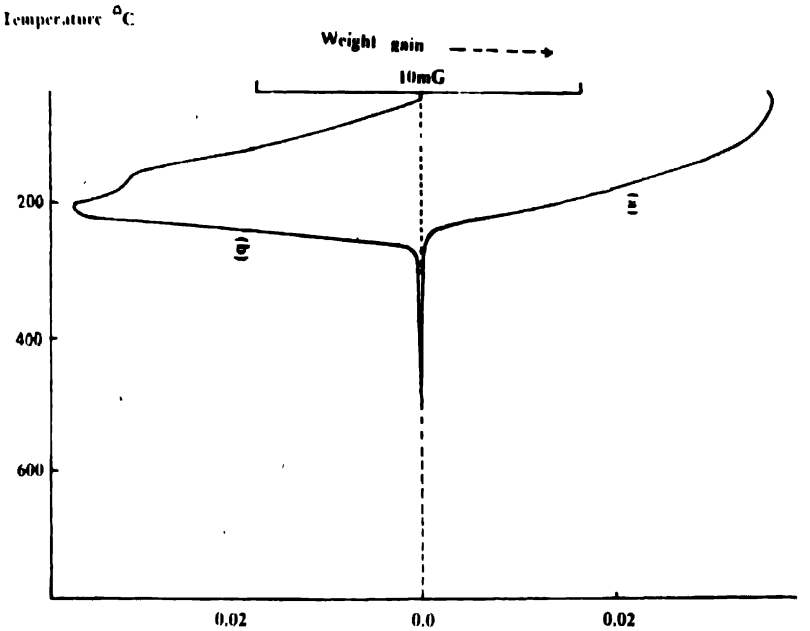

Figure 6. (a) TG and (b) TGA curves of $(NH_4)_3BaCl_5.2H_2O$.

was a percentage weight loss of 14.888 when the sample was heated from 47.5°C to 377.5°C. The peak temperature was observed at 212.5°C. The molecular weight of $(NH_4)_3BaCl_5.2H_2O$ crystals is 404.8. If the crystal is a dihydrate then the percentage weight loss should be 8.893 (36 × 100/404.8). Since the actual percentage weight loss is 14.888 and the percentage weight loss due to water of crystallization is 8.893, the remaining 5.995 percent weight loss has to be accounted for. The TGA was carried out by static weight loss method. A known weight of $(NH_4)_3BaCl_5.2H_2O$ crystals was taken in a previously weighed container. Then the substance was heated around 200°C for half an hour. The weight of the dehydrated substance was then taken immediately. This procedure was repeated thrice to get a constant weight of the anhydrous substance. The difference in weight between the

hydrated substance and the dehydrated anhydrous substance gave the amount of water present in the crystal. After heating, the transparent crystals became white without losing its shape and size. The following calculation shows that the percentage weight loss of water is 14.783 which closely resembles that obtained from TGA (14.888). It is observed that in these crystals there can be only loss of water at about 200°C, by analogy the difference between the initial and final weights of the $(NH_4)_3BaCl_5.2H_2O$ crystals is due to the dehydration process and not due to the decomposition of the $(NH_4)_3BaCl_5$ part and this remains intact during heating around 200°C. The remaining 5.995 percent weight loss can be accounted for the occluded and adsorbed water present in the crystals. Thus the thermogram predicts the decomposition of water of crystallization as follows :

$$(NH_4)_3BaCl_5.2H_2O \qquad (NH_4)_3BaCl_5 + 2H_2O.$$

4.3. Differential scanning calorimetry (DSC) :

DSC curves for $(NH_4)_3BaCl_5.2H_2O$ crystals were recorded both at low and high temperatures using Perkin-Elmer differential scanning calorimeter-2, USA. The sensitiveness used were between 10 and 5 m cal/sec. In case of low temperature DSC, the heating rates employed were 10 K/min. Subambient scans were recorded using liquid nitrogen as coolant. The instrument was calibrated for low temperature operation using the standards *viz* tetrachloride and cyclohexane. Thermal anomaly was found at 275 K in the heating run. The heat innut to the specimen as a function of temperature is shown in Figure 7, for the low temperature DSC studies. The thermal anamoly observed at 275 K is indicative of a phase transition.

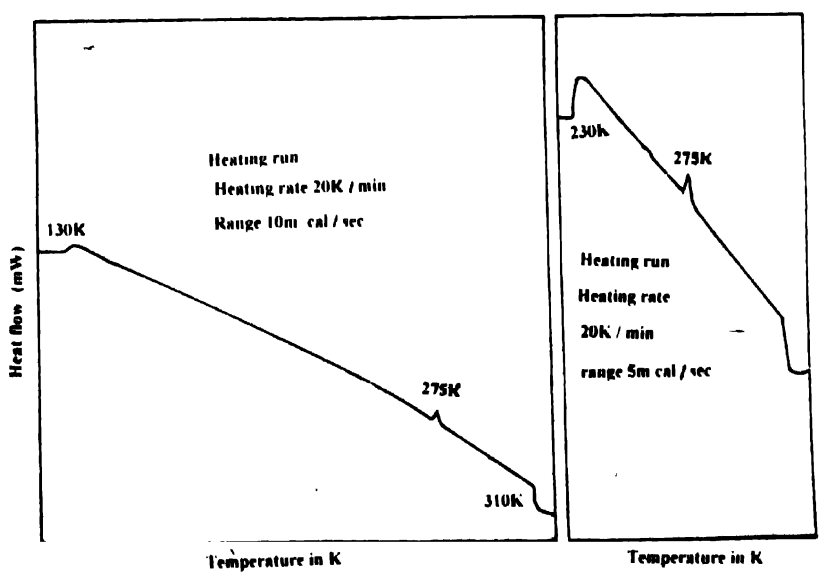

Figure 7. Heat input as a function of temperature

The high temperature DSC study was carried out between 323 K and 873 K. The sample was analysed with a heat flow rate of 20 K/min. The DSC curve above room temperature (Figure 8) shows four peaks at 340.2 K, 407.2 K, 460.9 K and 535.1 K.

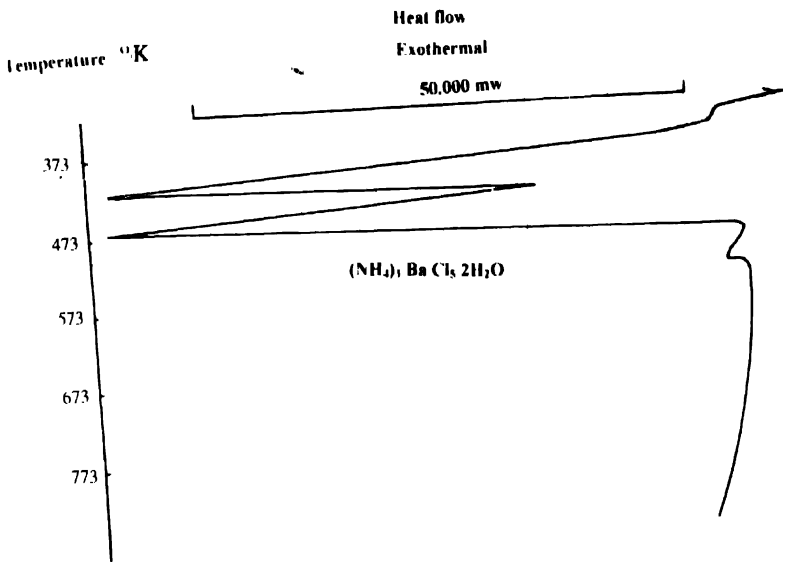

Figure 8. High temperature DSC of $(NH_4)_3BaCl_5.2H_2O$

The less pronounced first peak at 340.2 K indicates the loss of occluded and adsorbed water in the crystals. The peak at 407.2 K suggests that one molecule of water of crystallization is lost by breaking the hydrogen bonding and leaving the lattice at this temperature and the crystal goes from the dihydrate form to the monohydrate form. This involves a phase transition of the following type :

$$(NH_4)_3BaCl_5.2H_2O \xrightarrow{460.9\ K} (NH_4)_3BaCl_5.H_2O + H_2O.$$

The fourth less pronounced peak at 535.1 K suggests that the anhydrous $(NH_4)_3BaCl_5$ compound is stable at least up to this temperature without any decomposition (NH_4Cl sublimes at 613 K and boils at 793 K).

Both the TGA and DSC studies conclude that the $(NH_4)_3BaCl_5.2H_2O$ crystals contain two molecules of water and undergoes multiple structural phase transitions.

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