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Research Paper - Physics

Thermal study of zinc iodate crystals

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1. Introduction

A variety of crystals required for the purpose of research and application can be grown in silica gels. The gel medium prevents turbulence and being chemically inert, it provides a three-dimensional crucible which permits the reagents to diffuse at a desirable controlled rate. Its softness and uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth (1-2).

The growth of single crystals in gel at an ambient temperature, which are sparingly soluble in water, is a fascinating alternative to the techniques involving high temperature and expensive equipments (3). During the last few years, successful application of gel growth technique has been demonstrated by the preparation of single crystals of alkaline earth metal iodate (4). The gel growth technique appeared quite attractive for growing crystals of such compounds on account of its unique advantages in terms of crystals produced and the simplicity of process (5-6).

In the present work, crystals of zinc iodate were grown by gel technique using diffusion method. Optimum growth conditions for crystals were determined. Optimum conditions were established by varying various parameters such as pH of gel, gel reactants, concentration programming, effect of neutral gel etc.

2. Experimental

The silica gel was used as a growth media and test tubes were used as crystallizing vessels. Gel was prepared by using glacial acetic acid and sodium meta silicate having different pH values. The chemicals used for growth of of zinc iodate crystals were CH3COOH, Na2SiO3.5H2O, KIO3, ZnCl2. All chemicals were of AR grade.

The chemical reaction inside the gel can be expressed as

ZnCl2 + 2KIO3 ? Zn(IO3)2 + 2KCl

3. Results and discussions

The various optimum conditions for growing crystals were established and are given in table 1.

Table 1.

Conditions	Zinc iodate
Density of sodium meta silicate solution	1.04 g/cm^3
Amount of 2N acetic acid	5 ml
pH of the gel	4.4
Temperature	Room temperature
Concentration of KIO_3	0.4 M
Concentration of $ZnCl_2$	1.0 M
Gel setting time	12 days
Gel aging time	120 hours
Period of growth	3 weeks

Different parameters such as concentration of reactants, pH of gel, gel setting time, gel aging time etc have considerable effect on growth rate. In the steady state of concentration gradient, growth rate also becomes steady which favours growth of well developed crystals. However, very slow growth rate along one direction results in the whisker growth.

4. Observations

The different growth stages of zinc iodate crystals inside the test tubes were observed

Figure1(a) shows crystals of zinc iodate inside the test tube and Figure1(b) shows few crystals of zinc iodate with their scaling on a graph paper.

5. Charactarization

Zinc iodate crystals grown were thermally characterized by TGA, DTA, DTG and DSC. Thermal study of zinc iodate crystals was carried out at NCL, Pune.

5.1 Thermo Gravimetric Analysis (TGA) :

The thermal decomposition of zinc iodate passes through an intermediate Zn5(IO6)2 ,which is unstable and immediately decomposes to ZnO. It has a one stage course until ZnO is obtained, an intermediate orthoperiodate Zn5(IO6)2 is obtained in this process, analogously as in the thermal decomposition of the alkaline earth iodates. However, unlike Zn5(IO6)2 , immediately after it is obtained begins to decompose to ZnO (7).

Anhydrous zinc iodate decompose at high temperature according to reaction

5Zn(IO3)2 Zn5(IO6)2 (3.5 O2 ?) + (9O2 ? + 3 I2 ?) + (2 I2 ?) + 5ZnO

TGA data of zinc iodate crystals is as shown in the Table-2.

Stage	Temperature range (°C)	Observed weight loss (%)	Calculated weight loss (%)	Probable loss of molecule
I	113.25 °C to 333.63 °C	05.199	05.395	3.5 O_2
II	344.34°C to 635.12 °C	50.147	50.553	9 O_2 and 3 I_2
III	647.36 °C to 974.87 °C	28.994	24.453	2 I_2
Stable residual weight (ZnO)		15.660	19.599	----------

The T.G.A. curve for zinc iodate gel grown crystals is as shown in the figure 2(a) by continuous line. TGA curve of zinc iodate showed clearly three stages of decomposition. T.G curve did not show an appreciable weight change in the temperature range 30°C to 113°C indicating that the crystals of zinc iodate are thermally stable in this range. The crystals become thermally unstable beyond 113°C. The first stage of decomposition occurs in the temperature range 113.25°C to 333.63°C in which weight loss of 5.199 % agrees with the calculated weight loss of 5.395 %. This weight loss is attributed to loss of 3.5 O2. There is no further weight loss up to 344°C showing thermal stability of anhydrous zinc iodate crystals in the temperature range of 334°C - 344°C. The second stage of decomposition occurs in the temperature range 344.34°C to 635.12°C in which weight loss of 50.147 % is due to loss of 9 O2 and 3 I2 is observed. This is in agreement with the calculated weight loss of 50.553 %. In the third stage of decomposition in the temperature range of 647.36°C to 974.87°C, the weight loss of 28.994 % is observed which is due the loss of 2 I2. This is in agreement with the calculated weight loss of 24.453 %. The remaining product finally turns in to zinc oxide at 975°C which is confirmed by the

observed residual weight of 15.660 % up to the end of analysis. This is in agreement with the calculated residual weight 19.599 %. This confirms the presence of zinc in the grown crystals.

5.2 Differential Thermo Gravimetry (DTG) :

D.T.G. data of zinc iodate crystals is as shown in the table-3.

Table-3.

Peak	Onset	Inflection point
242.11 °C	230.39 °C	239.94 °C
539.77 °C	496.11 °C	513.19 °C
930.32 °C	823.40 °C	929.17 °C

The D.T.G. curve for zinc iodate gel grown crystals is as shown in the figure 2(a) by dotted line.

1) The endothermic peak at 242.11°C is due to the decomposition of zinc iodate loosing 3.5 oxygen molecules. In the first stage of decomposition, peak at 242.11°C is attributed to the loss of 3.5 O2 molecules. This endothermic peak observed in the DTG curve indicates that the reaction starts at 230.39 °C and inflection occurs at 239.94 °C. The peak observed in the DTG curve corresponds to the weight loss in the TG curve.
2) The endothermic peak at 539.77 °C is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of 9 O2 and 3 I2. This endothermic peak observed in the DTG curve indicates that the reaction starts at 496.11 °C and inflection occurs at 513.19 °C. The peak observed in the DTG curve corresponds to the weight loss in the TG curve.
3) The endothermic peak at 930.32 °C is due to the decomposition of compound and this peak in the third stage of decomposition is attributed to the loss of 2 I2. This endothermic peak observed in the DTG curve indicates that the reaction starts at 823.40 °C and inflection occurs at 929.17 °C. The peak observed in the DTG curve corresponds to the weight loss in the TG curve.

Beyond the temperature 930°C, the reaction proceeds and finally stable residue ZnO remains up to the end of analysis.

5.3 Differential Thermal Analysis (DTA) :

The D.T.A. curve for zinc iodate gel grown crystals is as shown in the figure 2(b).

The DTA data collected from this curve is tabulated in the table 4.

Table-4.

eaks recorded	Nature	Peak height	Onset	Area (mJ)	?H (J/gm)
242.11 °C	Endothermic	-31.707	229.45 °C	3311.899	119.374
539.77 °C	Endothermic	-52.157	425.52 °C	13821.686	498.186
676.03 °C	Endothermic	-6.662	671.56 °C	-1.982	-0.071
930.32 °C	Endothermic	-6.889	866.03 °C	607.569	21.899

In DTA curve we can observe three endothermic peaks at 189.20°C, 654.77°C and 950.85°C while one exothermic peak at 340.46°C.

1) The endothermic peak at 242.11°C is due to the decomposition of zinc iodate loosing 3.5 oxygen molecules. In the first stage of decomposition, peak at 242.11°C is attributed to the loss of 3.5 O2 molecules. This endothermic peak observed in the

DTA curve corresponds to the weight loss of 3.5 O2 molecules in the TG curve.

2) The endothermic peak at 539.77 °C is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of 9 O2 and 3 I2. This endothermic peak observed in the DTA curve corresponds to the weight loss of 9 oxygen and 3 iodine molecules in the TG curve.

3) The endothermic peaks at 676.03 °C and 930.32 °C are due to the decomposition of compound and these peaks in the third stage of decomposition may be attributed to the loss of remaining part of the iodine. These endothermic peaks observed in the DTA curve corresponds to the weight loss of 2 iodine molecules in the TG curve.

5.4 Differential Scanning Calorimetry (DSC) :

The DSC curve of zinc iodate crystals is as shown in the fig. 2(c).

The DSC data collected from this curve is listed in the table 5.

Table 5.

Sample	Weight of the sample	Change in the enthalpy (? H)	Transition temperature (Tr)
Zinc iodate	0.0100gm	0.1482 KJ/mole	242.23 °C
		0.0008 KJ/mole	336.05 °C

In the DSC study of zinc iodate crystals, the two endothermic stages are obtained but an exothermic phase transition process was not noticed. The results of DSC measurements are presented in the table 5.

The two stages of DSC curve under study are as follows

Stage (I)

1. The initiation temperature is 182 °C and equilibrium temperature is 264 °C. At 182 °C (initiation temperature), initiation of phase change starts and is completed at peak endo-down temperature of 242.23 °C (transition temperature). The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 264 °C.
2. Area under under the curve is 1482.168 mJ and
3. Heat of transition, ?H i.e. enthalpy change of transition is 148.2168 J/g which is 0.1482 KJ/mole. Since molecular weight is 1 g/mole, ?Htr = ?Hf i.e. heat of phase transformation is also 0.1482 KJ/mole, where ?Hf is enthalpy change of new phase formation or it is called heat of phase formation.

Stage (II)

1. The initiation temperature is 330 °C and equilibrium temperature is 342 °C. At 330 °C (initiation temperature), initiation of phase change starts and is completed at peak endo-down temperature of 336.05 °C (transition temperature). The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 342 °C.
2. Area under under the curve is 7.737 mJ and
3. Heat of transition, ?H i.e. enthalpy change of transition is 0.7737 J/g which is 0.0008 KJ/mole. Since molecular weight is 1 g/mole, ?Htr = ?Hf i.e. heat of phase

transformation is also 0.0008 KJ/mole, where ?Hf is enthalpy change of new phase formation or it is called heat of phase formation.

6. Conclusions

From the above studies we observe that

(I) Gel growth technique is suitable for growing crystals of zinc iodate.

(II) Crystals are shining and quite transparent, hence are of reasonably good quality

(III) Thermal stability of the grown crystals is observed and is found to be nearly matched with the reported one.

(IV) The residual zinc oxide (ZnO) identified from T.G.A.,D.T.G. and D.T.A. analysis confirms the presence of zinc (Zn) in the grown crystals.

(V) Water of crystallization is absent in grown crystals confirmed by TGA and DTA analysis.

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References

1) Shitole S J and Saraf K B , Bulletin of Material Science 5 461 (2001)

2) Garud S L and Saraf K B , Bulletin of Material Science 4 639 (2008)

3) Sangwal K and Patel A R , J. Crystal growth 23 282 (1974)

4) Joshi M S and Trivedi S G , Indian J. pure & App. Phys. 21 435 (1983)

5) Ranadive D, Blank Z, Brenner W and Okamoto Y , Nature 223 829 (1969)

6) Kurtz S K and Perry T T , J. Appl. Phys. 39 3798 (1968)

7) M. Maneva and V. Koleva, Journal of thermal analysis, vol. 42, (1994)