Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2011, 2(6):318-324

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Kinetic behaiour of X-doped (X = Al, Zn and Cu) and undoped Lead Iodide single crystals

D. S. Bhavsar

Research Laboratory, Department of Electronics, Pratap College, Amalner India

---

ABSTRACT

In the present paper X-doped (X = Al, Zn and Cu) and undoped Lead Iodide crystals have been synthesized by gel technique. Then, these crystals were characterized by XRD and Thermal study. XRD shows that the grown crystals were of high quality and lattice parameters almost matching with the ASTM data for Lead Iodide. Thermal studies carried out especially in kinetic behaviour of X – doped (X = Al, Zn and Cu) Lead Iodide crystals.

Keyword: Gel method; XRD; Thermal analysis (kinetic behaviour)

INTRODUCTION

Lead Iodide, PbI2 is one of a large number of compounds which have the same crystal structure as CdI2. The atomic arrangement is in form of layers of Lead and Iodine atoms oriented perpendicularly to the c-axis. The sequence of layers is repeated in units of I-Pb-I held together by van der Wall's forces. Lot of work has been done on Lead Iodide single crystals. Mostly important properties have been studied by no.of researchers, but less attention was provided towards the thermal behaviour of Lead Iodided crystals. Hence, it has been decided to work on thermal behaviour of Lead Iodide especially in kinetic parameters.

MATERIALS AND METHODS

Single diffusion technique were used to grow the crystals of X - doped (X = Al, Zn and Cu) and undoped Lead Iodide crystals. Crystals were grown at constant temperature of 30^0 in constant temperature bath. For this Lead Acetate and Sodium metasilicate has been used. Kottasium Iodide (1N) and X-Chloride, (X = Al, Zn and Cu, different concentration) is incorporated in the gel, after setting the gel, Lead Acetate (1N) poured slowly over the set gel. After 10/12 days, growth of the crystals has been observed. After completion of growth of Lead Iodide, crystals

has been withdrawn from the test tube, washed and crushed into small size for the characterization and kept in light for whole night. The X-ray diffraction patterns (XRD) were obtained by a diffractometer (Philips PW-1730) using CuKα radiation with Ni filter (1.5418Å) at 30 KV and 15 mA at North Maharashtra University, Jalgaon. The thermal analysis (TGA and DTA) of gel grown, X-doped and undoped Lead Iodide crystals have been carried out at CMET, Pune and Pratap College, Amalner.

RESULTS AND DISCUSSION

XRD

The result of the XRD are already explained elsewhere (1).

Kinetic parameters

TGA and DTA curve of doped and undoped Lead Iodide crystals were recorded as function of temperature and % weight loss of substance [Not shown in the present paper]. Table 1 and Table 2 represents kinetic data and kinetic parameters [α and f(α)] for doped and undoped Lead Iodide crystals respectively. Fig. 1, 2, 3 and 4 depicts plots of α Vs temperature for undoped and X – doped (X = Al, Zn and Cu) respectively. While fig. 5, 6, 7 and 8 shows plots of f(α) Vs. temp. (^{0}C) for undoped and X – doped (X = Al, Zn and Cu) respectively.

Table 1 Kinetic parameters for doped and undoped Lead Iodide crystals

Compound	Kinetic equation	Ea (KJ mole^{-1})	Log (A) (S^{-1})	r
Undoped PbI_2	MKN	120	2.93	0.99597
	C-R	123	3.07	0.99597
Al-doped PbI_2	MKN	147	4.73	0.99141
	C-R	146.76	4.67	0.99141
Zn-doped PbI_2	MKN	119	2.92	0.97090
	C-R	118.61	2.85	0.97064
Cu-doped PbI_2	MKN	129.93	3.50	0.99469
	C-R	129.91	3.43	0.99468

MKN (Madhusudhanan Krishnan Ninan), C-R (Coats-Redfern)

Table 2 Kinetic data for doped and undoped Lead Iodide crystals

For undoped PbI_2			For Al-doped PbI_2			For Zn-doped PbI_2			For Cu-doped PbI_2		
Temp.^{0}C	α	f(α)	Temp.^{0}C	α	f(α)	Temp.^{0}C	α	f(α)	Temp.^{0}C	α	f(α)
465.09	0.0345	0.1874	465.04	0.266	01611	465.92	0.0488	0.192	476.12	0.0362	0.2237
471.07	0.0388	0.1989	474.04	0.0324	0.1815	471.90	0.0538	0.2059	482.11	0.4150	0.2352
477.07	0.0439	0.2119	483.00	0.0411	0.2049	477.89	0.0595	0.2213	488.09	0.0478	0.2477
483.04	0.0500	0.2265	491.97	0.0525	0.2322	483.88	0.0663	0.2385	494.07	0.0553	0.2619
489.02	0.0571	0.2425	497.95	0.0618	0.2526	489.85	0.0742	0.2572	500.07	0.0640	0.2777
495.01	0.0656	0.2605	503.91	0.0728	0.2570	495.84	0.0829	0.2779	506.04	0.0743	0.2942
501.00	0.0756	0.2804	509.88	0.0858	0.3265	501.83	0.0928	0.3006	512.01	0.0864	0.3121
506.98	0.0873	0.3023	515.84	0.1011	0.3265	507.82	0.1041	0.3255	517.98	0.1005	0.3316
512.97	0.1011	0.3265	524.82	0.1293	0.3721	513.79	0.1173	0.3528	523.95	0.1170	0.3533
518.95	0.1171	0.3529	530.80	0.1523	0.4065	519.78	0.1327	0.3764	528.75	0.1321	0.3774
524.94	0.1358	0.3821	536.79	0.1792	0.4444	525.77	0.1506	0.3827	529.93	0.1362	0.4040
530.92	0.1573	0.4137	542.74	0.2106	0.4863	531.74	0.1714	0.4085	534.72	0.1537	0.4336

536.91	0.1822	0.4485	548.74	0.2471	0.5328	537.73	0.1954	0.4436	540.70	0.1786	0.4663
542.87	0.2108	0.4866	554.69	0.2892	0.5843	543.69	0.2232	0.4823	546.67	0.2075	0.5026
548.80	0.2435	0.5283	560.68	0.3378	0.6421	549.63	0.2552	0.5247	552.61	0.2406	0.5429
554.83	0.2804	0.5737	566.67	0.3936	0.7073	555.66	0.2920	0.5715	558.58	0.2786	0.5877
560.80	0.3217	0.6231	572.65	0.4574	0.7821	561.63	0.3343	0.6237	564.55	0.3222	0.6380
566.80	0.3679	0.6773	578.64	0.5297	0.8686	567.60	0.3828	0.6818	570.52	0.3717	0.6947
572.77	0.4193	0.7373	584.62	0.6111	0.9719	573.58	0.4382	0.7476	576.49	0.4281	0.7594
578.75	0.4761	0.8041	590.60	0.7013	1.0993	579.56	0.5012	0.8227	582.47	0.4917	0.8341
584.74	0.5376	0.8783	596.61	0.7988	1.2664	584.55	0.5721	0.8675	584.64	0.5288	0.9214
590.75	0.6019	0.9595	602.64	0.8996	1.5162	594.63	0.6935	0.9629	591.62	0.6043	1.0875
596.79	0.6673	1.0491	605.73	0.9460	1.7086	600.56	0.7829	1.0776	597.62	0.6868	1.2360
602.80	0.7290	1.1427	608.90	0.9682	1.8571	606.68	0.8667	1.2053	603.71	0.7660	1.4197
608.87	0.7764	1.2240	618.11	0.9743	1.9136	612.87	0.9144	1.3139	609.82	0.8220	1.5680
614.95	0.8000	1.2688	630.18	0.9754	1.9250	619.01	0.9272	1.3594	612.90	0.8424	1.6118
620.98	0.8087	1.2862	636.16	0.9757	1.9282	643.15	0.9339	1.3972	615.93	0.8580	1.6884
626.99	0.8125	1.2939	642.18	0.9759	1.9303	646.15	0.9343	1.4234	618.98	0.8681	1.6502
632.99	0.8140	1.2970				679.22	0.9372	1.4548	631.12	0.8795	1.6638
						703.29	0.9386	1.4640	643.18	0.8823	1.6706

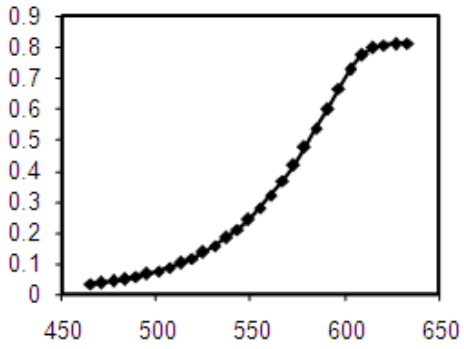

Fig. 3 Plot of α Vs. temp. ^{0}C for undoped PbI_2

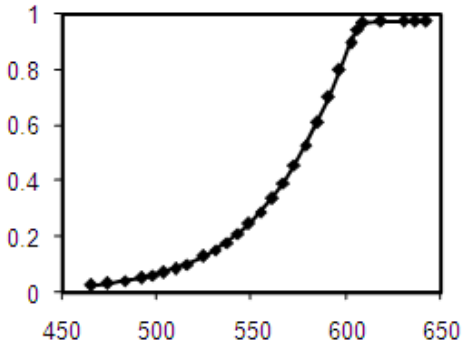

Fig. 4 Plot of α Vs. temp. ^{0}C for Al-doped PbI_2

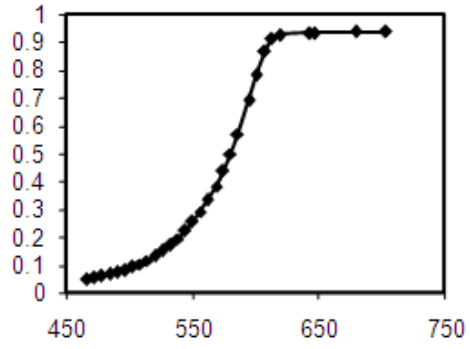

Fig. 5 Plot of α Vs. temp. for Zn-doped PbI_2

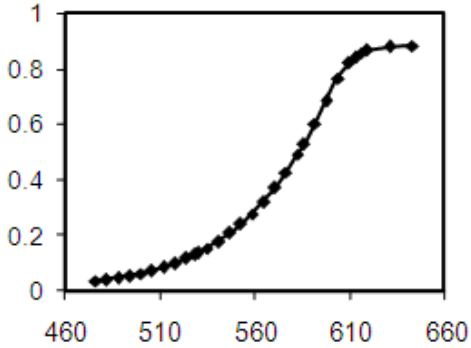

Fig. 6 Plot of α Vs. temp. for Cu- PbI_2

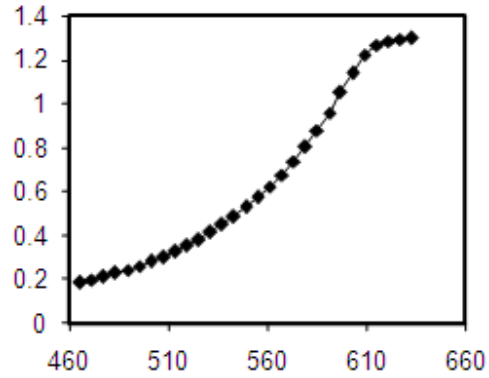

Fig. 7 Plot of f (α) Vs. temp. For undoped doped PbI_2

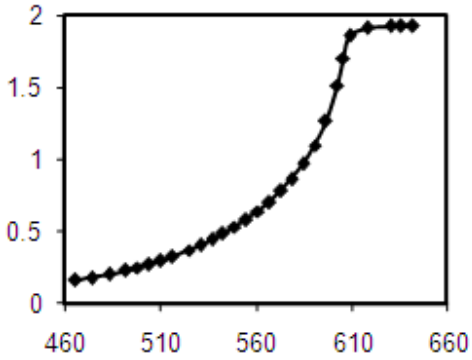

Fig. 8 Plot of f(α) Vs. temp. For Al- PbI_2

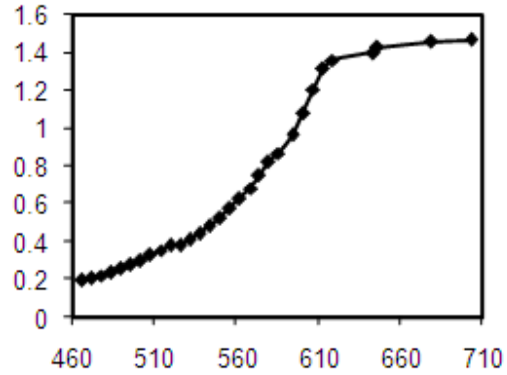

Fig. 9 Plot of f (α) Vs. temp. for Zn-doped doped PbI_2

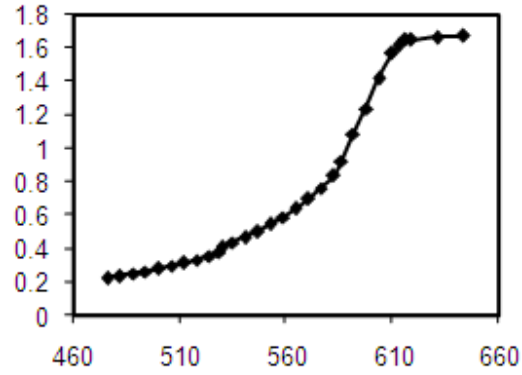

Fig. 10 Plot of f(α) Vs. temp. for Cu- PbI_2

Both TGA and DTA are widely used in chemical analysis, and for obtaining thermodynamic and kinetic data. There are many good reviews, worked on application of thermoanalytical methods [2, 3, 4, 5, 6, 7]. The parameters such as rate constant 'K', activation energy 'Ea', order of reaction 'n' and frequency factor 'A' are derived from these methods. Kinetic parameters from dynamic TGA curves were calculated using computer programs. The programs are based on the well kinetic expressions developed by [8, 9, 10] This instrument is fabricated in the Physics Department, Pratap College, Amalner. Also, this characterization was carried out at I.I.T., Mumbai and C-MET, Pune.

Standardization of TGA

The instrument was standardized as follows:

The air buoyancy effect of furnace on sample cup was determined using a clean empty sample cup in the temperature range ambient to 800^0C, at a heating rate of 4^0C per min. It was found that there was negligible weight change in this range of temperature The temperature of weight losses and the nature of the loss curve for the above compounds were in excellent agreement with those reported in the literature [11].

Kinetic parameters

Kinetic parameters from TGA curves were calculated using the computer programmes developed in the author's laboratory, Department of Physics, Pratap College, Amalner. The programs are based on the well-known kinetic expressions was developed [8, 9, 10].

The kinetics of a solid-state decomposition reaction follows from a simple formal expression,

$$\frac{d\alpha}{dt} = k\alpha^n$$

where, α = the fraction of a sample undergoing
n = the order of reaction, and
K= the specific rate constant

Based on the formation of germ nuclei and the nucleus growth models, different authors have proposed a number of relations assuming the validity of Arrhenius law to the solid-state decompositions. Important of these relations applied in the present work are given below:

1) Freeman and Carroll relation

The order of reaction and activation energy could be calculated from,

$$\frac{\left(\frac{Ea}{2.303xR}\right)\Delta(1/T)}{\Delta \log Wr} = \frac{-n + \Delta \log dw/dt}{\Delta \log Wr}$$

Where, Wr = Ws-W
Ws, is the mass loss and
W, is the total loss in mass upto time t,
T, is the temperature in degree K and
R, is the gas constant in J mole-1 $^oK^{-1}$

A graph of,

$$\frac{\Delta \log(dw/dt)}{\Delta \log Wr} \text{ Vs } \frac{\Delta(1/T)}{\Delta \log Wr}$$

should give a straight line. The intercept gives the order of the reaction (n) and the slope yields an activation energy (Ea).

2) Coats and Redfern relation

For the reaction in which the order is unknown, Coats and Redfern derived the following expression:

$$\left[\text{Ln}\ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln(\theta R/aEa)1-2RT/Ea\ -Ea/RT$$

Where, Ea, R and T have the usual meaning as before, and 'a' is the heating rate, n is the order of reaction and θ preexponential factor.

A plot of, $\text{Ln}\ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}$ Vs 1/T

should result in a straight line, where the slope gives the activation energy for the correct value of the order of reaction. In the calculation coefficient is obtained close to =1 for the given set of data.

3) Horowitz and Metzer relation

$\ln[\ln(W_0\text{-}W/W\text{-}W_t)] = Ea\theta/RT_s^2$

Where,

W_0 = the initial sample weight
Wt = weight remaining at any specified temperature
W = final weight of sample

T_s = a specified temperature other than T usually a temperature where dα/dt is maximum, and θ=T-Ts, other symbols have usual meaning.

A plot of $\ln[\ln(W_0\text{-}W/W\text{-}W_t)]$ Vs θ should give a straight line, where the slope is Ea/RT_s^2

Standardization of DTA

The following specifications of the samples were used for DTA.

Sample size	150 mg
Particle size	150 mesh
Rate of heating	4^0C/min.
Temperature range	ambient to 800^0C
Thermocouple	Chromel-Alumel
Atmosphere	Static air

The base line for differential thermocouple with furnace temperature was decided from a mean quadruplicate in the temperature range 800^0C.

1. DTA of empty clean sample and reference cup of quartz.
2. DTA of freshly prepared magnesium oxide in reference cup (which was obtained by heating magnesium carbonate at about 800^0C for two hours).
3. DTA with both the cups containing MgO. The plots of ΔT Vs temperature were prepared for standard base line correction.

If Ts –Tr = positive the reaction is considered as exothermic,
If Ts – Tr = negative the reaction is considered as endothermic.

4. The DTA plots for standard compound were studied,

CONCLUSION

1. Lattice constant ‘a’ and ‘c’ (particularly ‘c’) and the unit cell volume are sensitively affected by the dopant concentrations.
2. The addition of impurities into Lead Iodide crystals is considered to enhance the atomic rearrangement of Lead vacancies.
3. The ratio of lattice parameters ‘c/a’ tends to increase, indicating that there is no dilation of the unit cell along the ‘a’ direction rather ‘c’ direction.
4. Doping concentrations tends to increase unit cell volume.
5. Good crystals could be grown around 30^0C. Temperatures below 30^0C do not yield good crystals.
6. Growth rate of doped and undoepd Lead Iodide crystals are nearly same and are around 12/15 days.
7. In terms of transparency of crystals, Al-doped crystals are most transparent than Cu-doped, Zn-doped and undoped Lead Iodide crystals. Undoped Lead Iodide crystals are least transparent compared to X-doped (X=Al^{+1}, Zn^{+2} and Cu^{+2}).
8. The size of the doped Lead Iodide crystals are smaller than undoped Lead Iodide crystals. Various types of kinetic parameters have been calculated and well matching with the earlier work.

REFERENCES

[1] D.S.Bhavsar, *Archives of Physics Research*, **2011**, 2 (1): 99-106
[2] Duval, C., (**1963**), Inorganic Thermogravimetric Analysis, 2nd Ed. Elsevier London.
[3] Garn D.D., (**1964**), Thermo analytical methods of investigation, Academic Press, New York.
[4] Keattch, C.J., (**1969**), An introduction to thermogravimetric Hegdon, London
[5] Mackenzie, R.C., (**1970**), Differential thermal analysis, Vol.1, Academic Press, London.
[6] Redfern, J.P., (**1964**), *Thermal Analysis Reviews* Vol. 1-6
[7] Wendlandt, W.W., (**1974**), Thermal methods of analysis, John Wiley, London.
[8] Freeman, E.S. and Carroll, B., (**1966**), *J.Phys.Chem*. 62, 394.
[9] Horowitz, H.H., and Metzer, G.K (**1963**), *Analytical chem.*, 35, 1464
[10] Coats, A.W. and Redfern, J.P., (**1964**), *Nature* 201, 68
[11] Blazek, A., (**1972**), Thermal Analysis, Van Nortrand, London.