[1] **Title**

Kinetic and thermal Parameter of Fe doped Potassium Oxalate Monohydrate crystals grown by Slow evaporation technique.

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[2] Abstract

Thermal analysis of pure potassium oxalate monohydrate $K_2C_2O_4.H_2O$ (POM) and its doped varieties with 5%,10%,15%,20% Ferrous concentration investigated . Pure and Fe-doped POM crystals were grown by slow evaporation technique at ambient temperature. X-ray diffraction (XRD) and Thermogravimetric analysis (TGA) has been used to characterize the crystal material. The results inform that the doping concentration had a significant impact on the structural and thermal properties of the material. From XRD data analysis of the crystal suggest that this material forming $K_3Fe(C_2O_4)_3.3H_2O$ compound and is belong to $P2_{1/c}$ space group with the monoclinic structure and make a three-dimensional chain form. The decomposition of materials recorded in nitrogen gas medium at ambient temperature to 800˚c. K_2CO_3 and Fe are final product in TGA analysis in N_2. Thermogram of the sample have mainly four consecutive decomposition stage. The kinetic parameters (activation energy E_g) and also thermodynamic parameters (enthalpy changes ΔH, Gibbs energy changes ΔG). We calculated for the different steps occurring during the curse of dehydration and decomposition reaction. This Fe doped POM materials is mostly investigated for its wide application in photochemical studies, actinometry, sensors, magnetic materials, etc. We prefer various model to calculate kinetic parameters.

Keywords: Potassium oxalate monohydrate (POM), Fe-doping, XRD, TGA

[3] Introduction

In the theoretical concept of solid state decomposition, metal oxalates thermal decomposition is more considerable [1]. Number of research were concerned with the rate of decomposition in thermogravimetric analysis in air is higher than in nitrogen and hydrogen. And major products are K_2CO_3 and Fe_2O_3 in air for TGA [2]. The thermal decomposition of $K_2Fe(C_2O_4)_2.2H_2O$ in nitrogrn have been studied using Mossbauer spectroscopy by J.Ladriere[3]. Potassium oxalate monohydrate, $K_2C_2O_4.H_2O$ (POM) crystal belongs to the space group P2/c with monoclinic symmetry[4]. M.A.Mohamad, S.A.Halawy and M.A.Salem conducted some isothermal and non-isothermal studies of these crystal salt [5,6,7,8]. The first step in the decomposition of all oxalates is the cleavage of the C-C bond in the anion $C_2O_4^{2-}$. The residual solid product may be the metal oxide or the metal depending on the electro-positivity of the cation [9]. Fe-doped POM complexes is used as a chemical actinometer. It is an important substance in photochemistry and allows for the determination of the incident photon rate for a specific system of defined spectral domain [10,11]. This material was most studied to its more applications in photo-chemical studies, sensors, magnetic materials [12,13]. EPR and optical absorption studies of vanadium doped POM crystals were studied by Ram Kripal, Manju Maurya, Hargovind [14]. $Mn^{2+}$and VO^{2+} in $K_2C_2O_4.H_2O$ single crystal EPR investigated by V.K.Jain [15]. Navin Pant, A L Verma, S D Pandey studied the relative intensities of factor group split in Raman bands of vanadyl doped potassium oxalate monohydrate and suggest that the relative intensities changes arises from looking of adjacent doping in lattice of POM through the formation of a complex $VO(C_2O_4)_2 .H_2O$ and intensity changes saw that the decrease in water content at regular site in the VO^{2+} doped POM [16]. The

present study is undertaken to calculate the kinetic and thermodynamic parameter of pure POM and Fe-doped POM of various concentration of the decomposition of this salt.

[4] Material And Method

Fe-doped and undoped POM were crystalised using simple solution growth method. Ferrous sulfate heptahydrate ($FeSO_4 .7H_2O$), 0%, 5%, 10%, 15%, 20% V% were used as doping precursors. Single crystal of Fe-doped and undoped POM were grown by slow evaporation of a mixture of solutions obtained from adding potassium oxalate monohydrate ($K_2C_2O4.H_2O$) and ferrous sulfate heptahydrate ($FeSO_4 .7H_2O$) in 100 ml distilled water in prescribe ratio with constant starring for three hour[17]. This solution was boiled for 10 min and filtered at cold condition to remove any unreacted residue. After filtration the green color solution was kept for slow evaporation at room temperature for crystallization. After 15 days the green crystals were grown. All chemical materials were use are analytical grade. Thermogravimetric testing were performed in N_2. The parent salt first cruse gently to avoid the effect of variation of particle size on decomposition characteristics. Sample powder weight were about 10 to 15 mg used in the testing. The heating rate was 10 K/min. the instrument used for characterization is Perkin Elmer STA6000.
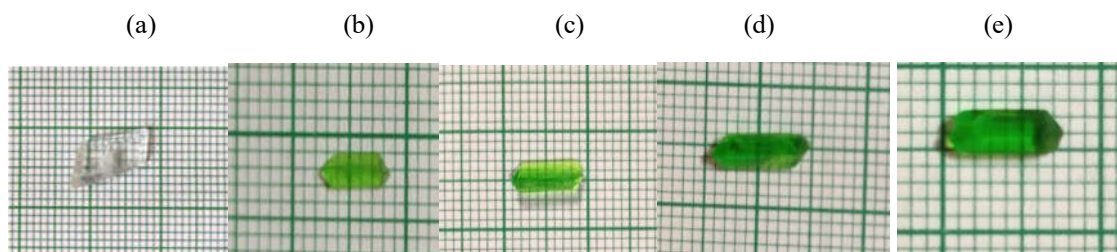
[5] Result and Discussion

(a) (b) (c) (d) (e)

Fig.1 Photographic image of (a) POM (b) POM:Fe(5%) (c) POM:Fe(10%) (d) POM:Fe(15%)(e) POM:Fe(20%) crystals
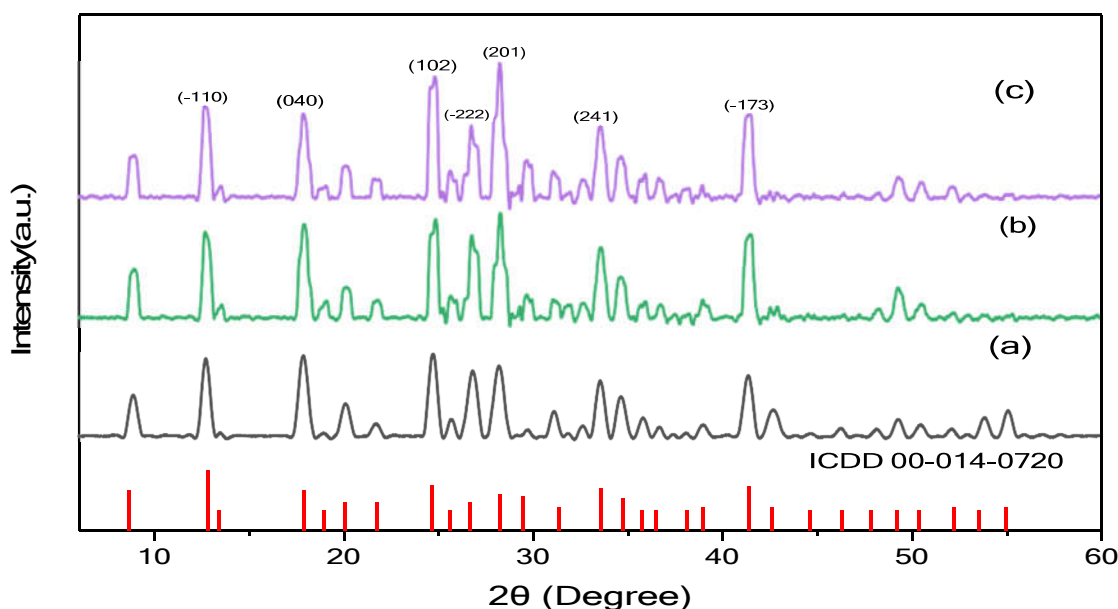

Fig.2 Powder XRD Pattern of Fe-doped POM crystal (a) POM:Fe(20%) (b) POM:Fe(15%) (c) POM:Fe(10%)

Pure and Fe-doped crystals photographic images shows in the fig.1. In the fig.2 (a,b,c,) are the xrd-pattern for 20%, 15% and 10% Fe-doped POM crystal. This xrd-pattern are match with the ICDD Card

No. 00-014-0720. X-ray analysis of the crystal revels that this compound forming $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ and is belong to the monoclinic structure with $P2_{1/c}$ space group and make a three-dimensional chain form.
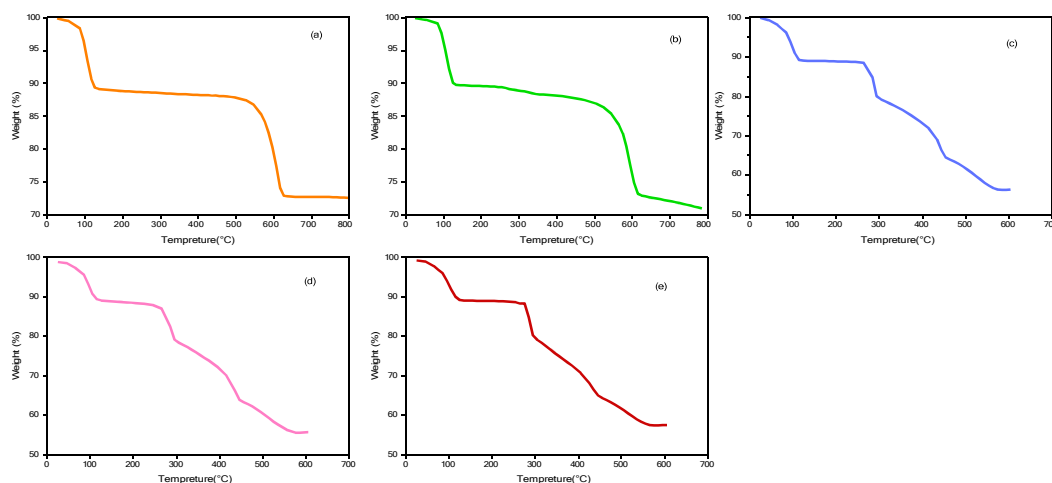

Fig.3 TGA thermogram of POM:Fe sample with various amount of Fe doping.(a) POM (b) POM:Fe(5%) (c) POM:Fe(10%) (d)POM:Fe(15%) (e)POM:Fe(20%)

	Stage	Ea (kJ/mol)	ΔH (kJ/K)	ΔG (kJ)
Pure POM	1	85.21	81.88	108.99
	2	238.27	230.79	256.36
5% Doped	1	87.04	83.73	108.86
	2	168.65	161.27	256.79
10% Doped	1	155.04	151.82	103.01
	2	376.1	371.38	153.91
	3	56.63	50.67	211.902
	4	148.17	141.2	240.78
15% Doped	1	131.68	128.45	104.14
	2	376.1	371.38	153.91
	3	52.85	46.89	211.59
	4	111.48	104.51	243.61
20% Doped	1	60.62	57.39	108.64
	2	436.55	431.82	152.66
	3	51.27	45.29	211.45
	4	122.121	115.14	241.77

Piloyan–Novikova model[18]:

$$\log \left(\frac{Y}{T^2}\right) = \log \left(\frac{AR}{E\beta}\right) - E/2.303 \; RT \tag{1}$$

$$\text{Activation Energy E (eV)} = \text{slope} * 2.303 * k/ \; 1.6 \times 10^{-19} \tag{2}$$

$$\text{and} \quad \text{Intercept} = \log (AR/ \beta E) \tag{3}$$

Thermogram of Pure and Fe-doped POM crystals shows in fig.3 .From Fig3(a,b,c,d,e) for Pure POM, 5% Fe doped POM, 10% Fe doped POM, 15% Fe doped POM, 20% Fe doped POM were associated with 26.46%, 26.45%, 40%, 40.142% and 38.446% decomposition. The Pure POM and 5% Fe-doped POM decompose in two consecutive step. The first step is dehydtration and next is decomposition. While in 10%,15% and 20% Fe-doped POM decompose in four consecutive step, first is dehydration and other three step are decomposition. The thermograph for fig3(a,b) are similar which indicate that for 5% doping not make more change crystal. While the fig3(c,d,e) shaws four stages which indicate that Fe doping in POM crystal.

In table.1 listed the value of the kinetic parameter (activation energy E_a) and the thermodynamic parameter (Enthalpy ΔH, Gibbs energy ΔG) of the dehydration and the decomposition steps from Piloyan–Novikova model. The activation energy E_a of the dehydration process is decrease as the doping concentration increase. And as doping concentration increase the activation E_a increase for the decomposition process. In the decomposition step third step for every doping concentration the activation energy E_a and enthalpy ΔH is comparatively low from other decomposition stage. For increasing in the doping concentration the the activation energy E_a and enthalpy ΔH and the gibbs energy ΔG increase.

[6] Conclusion

From the thermogram of pure POM and 5% Fe doped POM saws the two stage of decomposition. It implies that the 5% doping is not more affect in crystal structure. For further doping concentration in POM saws four stage, first is dehydration and then decomposition. In present using P-N model, finding the kinetic parameter (activation energy E_g) and the thermodynamic parameter (Enthalpy ΔH, Gibbs energy ΔG) of Fe doped POM crystal agree with a previous study[19].

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