SUMMARY

The present thesis deals with the investigations of kinetics and mechanism of decomposition of oxalates and their mixtures in different mole ratio. The chapter first and second includes the general introduction with literature survey and different experimental techniques used in the present studies respectively. The third chapter deals with the thermal decomposition study of ferrous (II) oxalate, barium (II) oxalate and copper (II) oxalate, while the decomposition of binary mixtures is explored in chapter four. The chapter five covers the effect of gamma radiation on the decomposition of ferrous (II) oxalate and barium (II) oxalate, while chapter six includes thermal decomposition study of tertiary mixtures of above mentioned oxalates in 1:1:2 and 1:2:3 mole ratios.

Chapter one begins with the general introduction of the subject with a review on the developments in the thermal studies of oxalates. The theory of decomposition of solid is discussed in terms of various parameters affecting reaction. The effect of gamma radiation on the decomposition of solid is explained with basic interactions leading to excitation and ionization. The purpose and scope of present work have been presented at the end of this chapter.

Chapter two mainly includes the description of different experimental techniques such as TGA, DTA and EGA which are used to carry out thermal study of oxalates. The details of $^{60}$Co source used for irradiation of the samples are presented in this chapter. The techniques Gouy balance, IR and DSC, XRD and SEM imaging used for examining the nature of defects are described briefly. The X-ray pattern of tertiary phase was recorded by using 'bruker axs D8 advance X-ray diffractometer'.

The results of the non-isothermal and isothermal (TGA, DTA and EGA) study of ferrous (II), barium (II) and copper (II) oxalates were described in chapter three. The DTA study provided dehydration and decomposition temperatures, as well as phase transition temperatures occurring during decomposition of individual oxalates. The onset of decomposition temperatures of ferrous (II) and copper (II) oxalates are found to be 150 °C and 260 °C as against the reported values of 160 °C and 255 °C respectively; while barium (II) oxalate begins to dehydrate at 150 °C as against the reported values of 150 °C. The experimental data obtained was processed to evaluate the kinetic parameters like order of the reaction, rate constants, energy of activation and the mechanism of
decomposition. The energy of activation obtained from non-isothermal study turns out to be 176.33, 36.80 and 140.46 KJ/mole from TGA; 90.80, 39.21 and 158.82 KJ/mole by EGA study for ferrous (II), barium (II) and copper (II) oxalates respectively by using Coats-Redfern equation. The isothermal TGA study of ferrous (II) oxalate reveals that the decomposition takes place by \(D_2 (\alpha)\) up to \(\alpha = 0.5\) and thereafter follows \(D_4 (\alpha)\) mechanism with activation energy of 136.07 and 138.09 KJ/mole respectively. While in EGA the decomposition takes place by \(D_2 (\alpha)\) up to \(\alpha = 0.5\) and thereafter follows \(D_4 (\alpha)\) mechanism with activation energy of 93.89 and 106.04 KJ/mole respectively. The isothermal TGA study of barium (II) oxalate undergoes decomposition by \(D_3 (\alpha)\) up to \(\alpha = 0.6\) and thereafter follows \(R_2 (\alpha)\) mechanism with activation energy of 34.09 and 48.85 KJ/mole respectively. While in EGA the decomposition takes place by \(D_4 (\alpha)\) up to \(\alpha = 0.68\) and thereafter follows \(A_2 (\alpha)\) mechanism with activation energy of 20.00 and 34.24 KJ/mole. But in case of copper (II) oxalate the decomposition in the entire alpha range occur by \(A_2 (\alpha)\) mechanism in TGA, while in EGA by \(A_3 (\alpha)\) with activation energies 172.40 and 144.31 KJ/mole respectively. The EGA being closed system, higher activation energies in barium (II) and copper (II) oxalate compared to that found by using TGA is obtained. The present work contributes significantly to the understanding of kinetics and mechanism of decomposition of oxalates.

Chapter 4 deals with the binary mixtures of ferrous (II), barium (II) and copper (II) oxalates at different mole ratio are presented. The non-isothermal TGA studies of the decomposition of the binary mixtures of ferrous (II) and barium (II) oxalates in 1:1 and 1:2 mole ratio showed the conversion of 100% barium carbonate to its oxide in the below 1000 °C, which is lower than the decomposition temperature of pure barium carbonate (1385 °C). The decrease in the decomposition temperature is thought to be due to the catalytic effect of Fe₂O₃. The energy of activation obtained from non-isothermal study turns out to be 15.07 and 21.19 KJ/mole from TGA; 16.57 and 38.26 KJ/mole by EGA respectively by using Coats-Redfern equation. The thermal decomposition by using TGA in 1:1 mixture takes place by \(D_3 (\alpha)\) up to \(\alpha = 0.58\) and thereafter follows \(A_2 (\alpha)\) mechanism with activation energy of 15.36 and 13.48 KJ/mole respectively. While in EGA the decomposition takes place by \(D_2 (\alpha)\) up to \(\alpha = 0.30\) and thereafter follows \(A_2 (\alpha)\) mechanism with activation energy of 16.91 and 18.48 KJ/mole respectively. The thermal
decomposition in 1:2 mixture takes place by $D_2 (\alpha)$ up to $\alpha = 0.26$ and thereafter follows $D_4 (\alpha)$ mechanism with activation energy of 25.03 and 25.79 KJ/mole respectively. While in EGA the decomposition takes place by $R_2 (\alpha)$ up to $\alpha = 0.49$ and thereafter follows $R_3 (\alpha)$ mechanism with activation energy of 32.83 and 33.61 KJ/mole respectively.

The barium (II) and copper (II) oxalates in 1:2 and 2:3 mole ratio showed 88.88% and 90% barium carbonate to its oxide in the temperature range of 780 °C to 1000 °C and 760 °C to 1000 °C respectively, which is lower than the decomposition temperature of pure barium carbonate to barium oxide (1385 °C). The decrease in the decomposition temperature is thought to be due to the catalytic effect of CuO. The energy of activation obtained from non-isothermal study turns out to be 33.50 and 21.55 KJ/mole from TGA; 23.72 and 53.86 KJ/mole by EGA respectively by using Coats-Redfem equation. The thermal decomposition by using TGA in 1:2 mixture takes place by $D_2 (\alpha)$ up to $\alpha = 0.62$ and thereafter follows $D_4 (\alpha) a =$ mechanism with activation energy of 28.29 and 31.41 KJ/mole respectively. While in EGA the decomposition takes place by $D_2 (\alpha)$ up to $\alpha = 0.30$ and thereafter follows $D_4 (\alpha)$ mechanism with activation energy of 24.25 and 28.26 KJ/mole respectively. The thermal decomposition by using TGA in 2:3 mixture takes place by $D_2 (\alpha)$ up to $\alpha = 0.50$ and thereafter follows $D_4 (\alpha)$ mechanism with activation energy of 27.55 and 28.25 KJ/mole respectively. While in EGA the decomposition takes place by $D_1 (\alpha)$ up to 0.20 and thereafter follows $D_4 (\alpha)$ mechanism with activation energy of 45.89 and 48.60 KJ/mole respectively.

The ferrous (II) and copper (II) oxalates in 1:2 and 1:3 mole ratio showed 100% oxide formation in the temperature range of 160 °C to 260 °C and 160 °C to 300 °C respectively, which is lower than the decomposition temperature of pure ferrous (II) and copper (II) oxalate in case of 1:2 mixture. The decrease in the decomposition temperature is thought to be due to the catalytic effect of ferric oxide, which starts formation at 220 °C as seen from the X-ray study. The energy of activation obtained from non-isothermal study turns out to be 144.5 and 94.30 KJ/mole from TGA; 124.81 and 129.29 KJ/mole by EGA respectively by using Coats-Redfem equation. The thermal decomposition by using TGA in 1:2 mixture takes place by $D_4 (\alpha)$ up to $\alpha = 0.74$ and thereafter follows $F_1 (\alpha)$ mechanism with activation energy of 141.51 and 177.29 KJ/mole respectively. While in EGA the decomposition takes place by $D_4 (\alpha)$ up to $\alpha = 0.80$ and thereafter follows $F_1 (\alpha)$
mechanism with activation energy of 95.17 and 129.41 KJ/mole respectively. The thermal decomposition by using TGA in 1:3 mixture takes place by D₄(α) up to α = 0.76 and thereafter follows F₁(α) mechanism with activation energy of 143.82 and 104.87 KJ/mole respectively. While in EGA the decomposition takes place by D₂(α) up to α = 0.60 and thereafter follows D₄(α) mechanism with activation energy of 61.05 and 61.72 KJ/mole respectively.

The SEM micrographs of ferrous (II) oxalate and copper (II) oxalate (1:2) mole ratio mixture heated dynamically at 220 °C, 230 °C, 240 °C and 260 °C in air showing the changes in texture and morphology. The result shows that the particle shape and size change throughout the decomposition process. Micrograph of the mixture is non-isothermally heated at 220 °C shows two types of crystals. The first type is due to the decomposition of copper oxalate and breaking into fine granules. The second type shows relatively large crystals of different size and shape, assigned to ferrous oxalate. Micrograph of the mixture is non-isothermally heated at 240 °C and 260 ° shows grain growth, re-texturing and aggregates of cubic large crystals of different sizes.

Chapter 5 deals with the thermal decomposition of ferrous (II) and barium (II) oxalates exposed to different doses for gamma radiation. The non-isothermal study of the irradiated salts showed a noticeable variation in decomposition route in relation to the one observed in the unirradiated salts. The decrease in the onset of decomposition temperature is noticed for the irradiated salts. The non-isothermal TGA study of ferrous (II) oxalate reveals that the maximum weight loss of 65.22% is observed in unirradiated sample as against the weight loss value of 54.62% at all doses of irradiated salt. The non-isothermal TGA study of barium (II) oxalate reveals that similar decomposition in high amount of BaO formation but decrease in onset temperature is observed in case of irradiated salt than unirradiated salt. An attempt has been made to explain these observations with the help of IR, DSC, Magnetic susceptibility measurement and XRD studies of these salts. The DSC studies of both ferrous (II) and barium (II) oxalate showed that there is decrease in the area of ‘endo’ peak in the case of former while increase in the area of ‘exo’ peak is observed in the latter. The variation in the results are undoubtly due to formation of defects/imperfections which is quantitatively estimated using DSC, in terms of energy stored in the lattice up on irradiation. The magnetic
behaviour of irradiated ferrous (II) and barium (II) oxalate are supported by magnetic susceptibility study. The decomposition end products are supplemented by IR and XRD studies. The experimental data obtained from non-isothermal study of pre-irradiated salts at various doses were analyzed by Coats-Redfern, Freeman-Carroll and Horowitz-Metzger expressions. At low doses of irradiation, the activation energy is found to be decreased, then increases to maximum at critical dose and again decreases with increasing dose due to cage effect, while barium (II) oxalate shows general trend that energy of activation decrease by increasing dose. After the saturation dose the energy is found to remain constant. The decomposition mechanism of irradiated ferrous (II) and barium (II) oxalate remains same as unirradiated salts. One of the important results brought about in the present work is in regards to the obeyance of isokinetic effect in the irradiated salts. The plots obtained from non-isothermal and isothermal data of both the salts satisfy all the conditions as stated by Agrawal and Gorbachev. The compensation parameters such as isokinetic temperatures, isokinetic rate constant and other constants are evaluated for both the systems studied.

Chapter 6 deals with the kinetics and mechanism study of tertiary mixtures of ferrous (II), barium (II) and copper (II) oxalates in the ratio 1:1:2 and 1:2:3 using non-isothermal and isothermal TGA, DTA and EGA are presented in chapter 6. The non-isothermal TGA study of 1:1:2 and 1:2:3 phases reveals that the decompositions occur by multistage processes and the final product existed in the single uniform homogeneous oxide mixture. This is supported by the XRD pattern of the residue formed at 940 °C and 900 °C in 1:1:2 and 1:2:3 mixtures. The DTA study shows characteristic ‘endo’ peaks for dehydration; while ‘exo’ peaks are noticed at the decomposition temperature of the oxalates in the mixture. The formation of intermediates like BaFe2O4, BaO, BaCO3, Fe2O3, Fe3O4, CuO and CuFe2O4 and in 1:1:2 and 1:2:3 mixtures are established by XRD studies respectively. The EGA studies of both 1:1:2 and 1:2:3 mixtures reveal the predominant formation of carbonate rather than oxide. The kinetic parameters of non-isothermal TGA and EGA were obtained by using Coats-Redfern equation.

The XRD pattern of the residue of 1:1:2 and 1:2:3 phases showed peaks at 2θ values of 24°, 36 °, 45 ° and 56.2°. Other relatively lower intensity peaks were observed at 2θ values of 29.5°, 34.8°, 44.2°, 47.9°, 51.2° are indicative of the formation of
pyrovskite structure in 1:2:3 mixture at 900 °C the uniform homogeneous single Fe$_2$Ba$_2$Cu$_3$O$_9$. It is to be noted that we were the first to report the formation of (FBCO) in the decomposition of tertiary mixture of oxalates. Another important result brought about in the present work is in regard to use of trivalent ions, such as Fe$^{3+}$ instead of divalent ions in the likely formation of superconducting phase.

The XRD pattern of above mentioned 1:1:2 and 1:2:3 phases have been found to be identical to a perovskite phase as reported by Cava et. al [14]. The perovskite structure is the characteristics of superconducting families. Therefore, the phase mentioned above may exhibit superconductivity.

The 1:1:2 and 1:2:3 mixtures heated dynamically to 940 °C and 900 °C and these products formed were quenched then SEM images taken. The SEM imaging analysis shows a large quantity of nano scale rod-like structures. The diameter of the nanorods is observed is not to be relatively uniform and their lengths of several micrometers. The nano rods are not aligned and have a scattered distribution. In the present work as proven by the SEM images (Fig 6.9) complete nano rods were formed. These nano rods are formed due to the decomposition of ferrous (II) oxalate and copper (II) oxalate which is decomposed completely at 300 °C and produce small fine granules of Fe$_2$O$_3$ and CuO in agreement with the XRD results. The fine granules rapidly shows the breaking Ba-O bond into small crystallites and re-texturing [41] of the fine grained particles of Fe$_2$O$_3$ and CuO into an aggregate of crystallites with roughening of the crystal surface takes place. The crystallites coalesced to form large homogeneous phases with nano rods in both 1:1:2 and 1:2:3 phases. The results obtained from SEM micrographs are consistent with XRD analysis results.

The free standing arrays of nano rods were formed. The vertical rods however they appear to have been snapped off. Due to the brittle nature of and the unidirectional position of the majority of rods within the sample it is likely that the rods were sheared from the base. It also seems observable that the homogeneous phase layer is the base. The production of uncontrolled nano rods arrays has proved to be relatively successful in regards to the formation of regular nano rods. However there have been difficulties in maintaining nano rods mechanical stable and vertical alignment.
The XRD analysis shows that the 1:1:2 and 1:2:3 mixture when heated dynamically at 940 °C and 900 °C showed formation of uniform homogeneous single Fe$_3$BaCu$_2$O$_6$ and Fe$_3$Ba$_2$Cu$_3$O$_9$ respectively, which may be conducting. This two end products Fe$_3$BaCu$_2$O$_6$ and Fe$_3$Ba$_2$Cu$_3$O$_9$ may be used applications in photovoltaics, photocatalysis, field emission devices, electronics, optoelectronics, and chemical gas sensing.

The isothermal TGA and EGA study of 1:1:2 mixture was carried out. The α-time data of isothermal TGA show that the decomposition of α up to 0.31 takes place by two dimensional diffusion controlled process, then α up to 0.60 the decomposition of mixture follows three dimensional diffusion controlled process and finally it proceeds at α up to 1.00 by first order decay law then with activation energy of 23.29, 27.18 and 21.56 KJ/mole respectively. The isothermal EGA decomposition α up to 0.30 occurs by two dimensional phase boundary reaction, then α up to 0.60 the decomposition of mixture follows three dimensional diffusion process and finally it proceeds at α up to 1.00 by first order decay law with activation energy of 42.12, 37.97 and 47.66 KJ/mole respectively.

The isothermal TGA and EGA study of 1:2:3 mixture was carried out. The α-time data of isothermal TGA show that the decomposition α up to 0.20 takes place by three dimensional phase boundary reaction, then α up to 0.45 the decomposition of mixture follows one dimensional diffusion process and finally it proceeds at α up to 0.98 by first order decay law with activation energy of 20.47, 28.90 and 20.47 KJ/mole respectively. The isothermal EGA decomposition α up to 0.33 takes place by two dimensional phase boundary reaction, then α up to 0.45 the decomposition of mixture follows three dimensional diffusion process and finally it proceeds at α up to 0.96 by first order decay law with activation energy of 40.03, 38.05 and 48.85 KJ/mole respectively.