

Research Article

Thermal Decomposition Studies of Layered Metal Hydroxynitrates (Metal: Cu, Zn, Cu/Co, and Zn/Co)

Thimmasandra Narayan Ramesh and Theeta Lakshamaiah Madhu

Department of Studies and Research in Chemistry and Professor C N R Rao Centre for Advanced Materials, Tumkur University, Tumkur 572 103, India

Correspondence should be addressed to Thimmasandra Narayan Ramesh; adityaramesh77@yahoo.com

Received 30 September 2014; Revised 20 December 2014; Accepted 22 December 2014

Academic Editor: Alfonso Castiñeiras

Copyright © 2015 T. N. Ramesh and T. L. Madhu. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Layered metal hydroxynitrates and mixed metal hydroxynitrates (copper/cobalt hydroxynitrates and zinc/cobalt hydroxynitrates at different mole ratios) were synthesized by hydrolysis of urea and metal nitrates at 140°C. Layered metal hydroxyl nitrates derive their structure from brucite mineral and generally crystallize in hexagonal and monoclinic phases. Isothermal decomposition studies of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, $\text{Co}_2(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$, $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ samples were carried out at different intervals of temperature and the structural transformations during the process were monitored using powder X-ray diffractograms. Biphasic mixture of metal hydroxynitrate/metal oxide is observed in case of cobalt/zinc based layered hydroxynitrates, while copper hydroxynitrate or copper/cobalt metal hydroxynitrate decomposes in a single step. The decomposition temperatures of layered metal hydroxynitrates and mixed layered metal hydroxides depend on the method of preparation, their composition and the nature of metal ion, and their coordination.

1. Introduction

Layered metal hydroxysalts (LHS) are used in dye adsorption, catalysts in organic reactions such as catalyst supports, fire retardants, polymer composites, electrodes, magnetism, electrochromic devices, and photocatalysts [1–5]. The structure of layered metal hydroxysalt is comprised of a hydroxyl deficient positively charged compound and the composition $[\text{M}(\text{OH})_{1-x}]^{x+}$ where M denotes metal ion; $x = 0$ to 1 [6]. Anions (A^{n-}) will get intercalated to compensate its charge neutrality resulting in the formula $[\text{M}(\text{OH})_{2-x}(\text{A}^{n-})_{x/n}]$ [7, 8]. The value of “ x ” dictates the composition of the compound; that is, when $x = 0$, we get layered metal hydroxide- $[\text{M}(\text{OH})_2]$ and, at “ x ” = 2, metal nitrate MA_2 to obtain two end members. The structure of metal hydroxide is comprised of hexagonally close packed OH^- ions in which divalent metal ions occupy octahedral sites resulting in the formation of charge neutral layers. These charge neutral layers stack on top of each other having an interlamellar spacing of 4.6 Å. Intermediate values of “ x ” will dictate the composition of the layered metal

hydroxysalt. “ x ” = 0.5 results in the formation of $\text{M}(\text{OH})\cdot(\text{A}^{n-})$, and $\text{M}_2(\text{OH})_3\text{X}/\text{M}_3(\text{OH})_4(\text{NO}_3)_2/\text{M}_5(\text{OH})_8(\text{NO}_3)_2$ will be obtained at “ x ” = 0.67 where the above compounds crystallize in hexagonal or pseudo-hexagonal symmetry [9–13].

Several methods have been reported on the preparation of layered hydroxysalts [9–14]. Precipitation method involves addition of an alkali solution to metal nitrate solution to attain pH-6.8–7.0. Aging of metal oxide in aqueous solution of metal salt has also been adopted for the precipitation of layered hydroxysalts [3]. Hydrolysis of metal nitrates using urea/hexamine precipitates metal hydroxysalts [15, 16]. Thermodynamics and kinetic factors control the stoichiometry and composition product formation. The kinetics of the reaction can be controlled by adjusting the temperature, concentration of the reagents, pH, hydrolysis rate, and metal salt to hydrolyzing agent ratio.

Zinc, nickel, cobalt, and copper based layered hydroxysalts have been extensively studied. Cobalt and nickel based layered metal hydroxynitrates (CoHN/NiHN) crystallize in the hexagonal system and have been used as magnetic

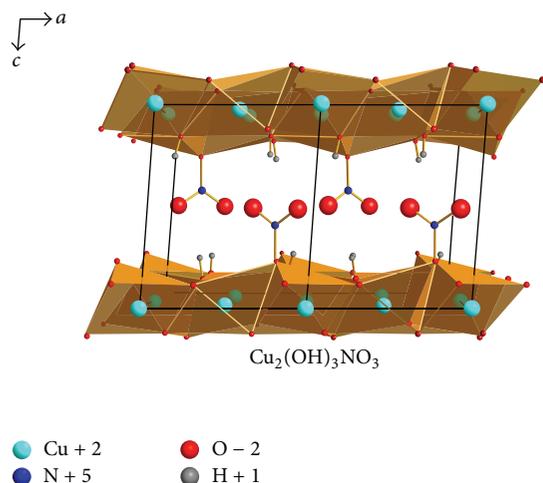


FIGURE 1: Crystal structure of copper hydroxynitrate- $\text{Cu}_2(\text{OH})_3\text{NO}_3$.

materials. While zinc hydroxynitrate is used as an anticorrosive agent and copper hydroxynitrate is used in vehicle air bags [17, 18]. Copper based hydroxynitrate (CuHN) with composition $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ crystallizes in orthorhombic and monoclinic crystal systems [19, 20]. The crystal structure of monoclinic copper hydroxynitrate [$\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ or $\text{Cu}(\text{OH})_{1.5}(\text{NO}_3)_{0.5}$] is comprised of copper hydroxide layers in which some of the hydroxyl ions ($x = 0.5$) are replaced by the nitrate ions and are directly coordinated to the sheets. Copper occupies two different distorted octahedral sites within the layer and the structure of copper hydroxynitrate- $\text{Cu}_2(\text{OH})_3\text{NO}_3$ is shown in Figure 1.

Divalent metal ions or cations occupy octahedral or tetrahedral sites in the sheets of layered hydroxynitrate. One of the classic examples is zinc hydroxynitrate (ZnHN) with the composition $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ which is comprised of hexagonal close packing of hydroxide ions in which three-fourths of the octahedral sites are occupied by divalent Zn^{2+} ions and one-fourth of the octahedral sites are vacant in the layer. Two tetrahedral sites, one above and one below the layer, will be available if one of the octahedral sites is vacant in the sheet of zinc hydroxynitrate. Zn^{2+} ion occupies tetrahedral coordination in the sheets of zinc hydroxynitrate which are coordinated by 3 OH^- ions on the layer and one of the OH^- group from the water molecule present in the interlayer region to form tetrahedron. Nitrate ions are present in the interlamellar region and do not have any bonding or coordination with the ions present in the lattice. The formula of zinc hydroxynitrate is $\text{Zn}_3(\text{octa})\text{Zn}_2(\text{tetra})(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ [21]. Figure 2 shows the crystal structure of zinc hydroxynitrate.

Extensive studies have been carried out on the decomposition of magnesium hydroxide, nickel hydroxide, and calcium hydroxide to obtain their respective metal oxides. There are also reports on the utilization of thermal energy storage density of magnesium hydroxide and calcium hydroxide during hydration-rehydration process [22, 23]. We had reported on the structural transformations during thermal

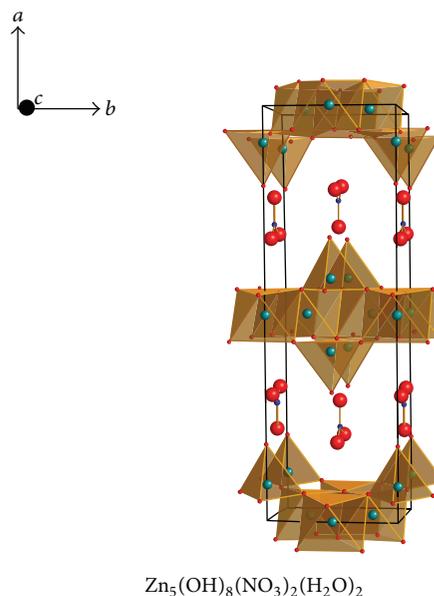


FIGURE 2: Crystal structure of zinc hydroxynitrate.

decomposition of nickel hydroxide to nickel oxide, depending on the conditions of synthesis and crystallinity [24, 25]. Metal oxides have been extensively investigated in the last two decades in view of their application as magnetic materials, electrochromic devices, gas sensors, high-temperature solar selective absorbers, and catalysts [1, 26–29]. The information about the decomposition studies of layered metal hydroxysalt is important to prepare high surface area solid for adsorption, catalytic supports, and catalysts. Decomposition of layered hydroxysalt also results in formation of metal oxide. We have reported the thermal decomposition studies of cobalt and nickel based layered hydroxynitrates and their mechanism of structural transformation to metal oxides. On continuing our investigations on layered hydroxysalts, the present work is concerned with the synthesis and characterization of layered metal hydroxynitrates, layered mixed metal hydroxynitrates, and their thermal evolution studies. To the best of our knowledge, there are no reports on what is mentioned above and in this paper, we have reported on the thermal decomposition of metal hydroxynitrates (metal: Cu, Co, Zn, Cu/Co, and Zn/Co) and their phase evolution using powder X-ray diffraction analyses.

This work describes the preparation and characterization of zinc/copper/cobalt hydroxynitrate samples. The term zinc/copper/cobalt used in this paper covers not only mixed metal salts, but also a single metal ion present in the lattice of the compound. Thermal decomposition studies of CoHN, CuHN, ZnHN, $\text{Cu}_{1-x}\text{-Co}_x\text{HN}$ ($x = 0.25, 0.33, 0.5$), and $\text{Zn}_{1-x}\text{-Co}_x\text{HN}$ ($x = 0.25, 0.33, 0.5$) and their structural transformation have been investigated.

1.1. Experimental Section

1.1.1. Reagents. Analytical grade $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea were procured from

Merck, India, and SD Fine Chemicals, India, and were used as received.

Stoichiometric quantities of the divalent transition metal nitrates, that is, $M(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (where $M = \text{Cu}/\text{Co}/\text{Zn}$), were mixed with 2 g of urea and 2 mL of distilled water in 100 mL beaker. The mixture was stirred well, and beaker was covered with watch glass and placed in hot air oven maintained at 140°C for 2 h. The above mixture was periodically stirred and after 2 h, it was cooled to room temperature (RT). The solid formed was washed with distilled water and dried at room temperature till constant weight is obtained. In separate experiments, mixed metal hydroxynitrates were prepared by following the procedure reported above by taking mixed metal nitrates [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in the mole ratios of $x = 0.25, 0.33, 0.5$. Solid solution series of layered mixed metal hydroxynitrate ($x = 0.25, 0.33, 0.5$) have been prepared and the details are given in Table 1.

1.1.2. Thermal Decomposition Studies. Thermal conversion of layered metal hydroxynitrates and layered mixed metal hydroxynitrate samples to their respective oxides has been carried out on the following samples: $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ (CuHN), $\text{Co}_2(\text{OH})_3(\text{NO}_3)$ (CoHN), $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$ [$\text{Cu}_{1.5}\text{Co}_{0.5}(\text{HN})$], $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$ [$\text{Cu}_{1.34}\text{Co}_{0.66}(\text{HN})$], $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ (ZnHN), $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ [$\text{Zn}_{3.75}\text{Co}_{1.25}(\text{HN})$], and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$.

In a typical procedure, approximately 100 mg of as-prepared layered metal hydroxynitrate/layered mixed metal hydroxynitrates was placed in an alumina boat and isothermally heated to different temperatures (100, 150, 200, 250, 300, 350, 400, and 500°C) for 2 h and cooled to room temperature. The details of the starting compounds are given in Table 1. The decomposed products were collected for structural characterization using powder X-ray diffraction.

2. Characterization

All the samples were characterized by powder X-ray diffraction (pXRD) using Bruker D8 advanced diffractometer ($\text{CuK}\alpha$ source = 1.5418 \AA ; 30 mA and 40 kV) in a 2θ range of 5° to 65° . Data was collected at a scan rate of 4° min^{-1} with 2θ steps of 0.05° . X-ray diffractogram of the following compounds: $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_3(\text{OH})_4(\text{NO}_3)_2(2\text{H}_2\text{O})_2$, $\text{Cu}_4(\text{OH})_6(\text{NO}_3)_2$, CoO (cubic), CoO (monoclinic), $\text{Co}_2(\text{OH})_3(\text{NO}_3)$, CoO (cubic), Co_3O_4 (cubic), CoCu_2O_3 , $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$, $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$, $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, ZnO (hexagonal), and $\text{Zn}_{0.85}\text{Co}_{0.15}\text{O}$ was obtained at different experimental conditions and their decomposed products were indexed using the powder diffraction data of from ICSD database.

3. Results and Discussion

3.1. Formation Mechanism of the Precursors. Precipitation of layered metal hydroxynitrates by mixing metal nitrates with alkali at appropriate pH range from 7 to 9 does not

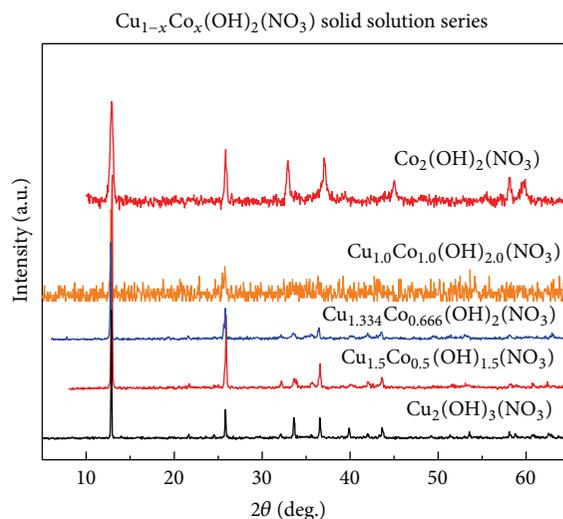
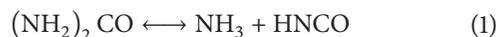
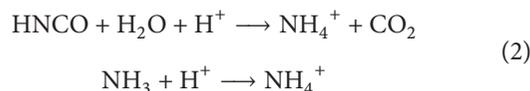


FIGURE 3: Powder X-ray diffraction patterns of copper hydroxynitrate- $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, cobalt substituted copper hydroxynitrate, and cobalt hydroxynitrate samples obtained by urea hydrolysis.

provide control over the crystal growth [30]. Hence urea, $(\text{NH}_2)_2\text{CO}$, is a nontoxic, cheap, stable, and water soluble hydrolyzing agent that was used to control the precipitation of layered metal hydroxysalts and the products obtained will be homogeneous in nature. Decomposition of urea decomposes at 70°C leading to the following reaction:



In acidic or neutral conditions, HNCO will be converted to carbon dioxide and ammonia/ammonium cation:



Consumption of H^+ ions results in an increase in the solution pH. The precipitation of layered metal hydroxynitrate involves reaction of hydroxyl ions with metal nitrate solution.

Figure 3 shows the powder X-ray diffraction patterns of copper hydroxynitrate, $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$, and $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$ samples obtained by urea hydrolyses.

In the pXRD patterns of the CuHN, successive reflections, up to at least the third order, indicate the lamellar structure and could be indexed to monoclinic crystal system space group- P_{21} using the JCPDS-ICDD 75-1779 file. The cell parameters of copper hydroxynitrate are as follows: $a = 5.79319(79) \text{ \AA}$, $b = 5.94419(66) \text{ \AA}$, $c = 10.9092(18) \text{ \AA}$, $\beta = 96.6288(95)^\circ$, and $V = 373.158(90) \text{ \AA}^3$ with an interlayer distance of 6.9 \AA . The powder X-ray diffraction patterns of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_3(\text{OH})_4(\text{NO}_3)_2(2\text{H}_2\text{O})_2$, and $\text{Cu}_4(\text{OH})_6(\text{NO}_3)_2$ samples were simulated using the single crystal data obtained from ICDD database. The simulated powder X-ray diffraction pattern of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ matches the observed X-ray diffraction pattern of copper hydroxynitrate (see Figure 4).

TABLE I: Weight of the reagents used to prepare layered metal hydroxynitrates.

Sample	Weight of zinc nitrate g	Weight of zinc nitrate moles	Weight of cobalt nitrate g	Weight of cobalt nitrate moles	Weight of copper nitrate g	Weight of copper nitrate moles	Weight of urea g	Weight of urea moles	Volume of water (cm ³) moles	Temperature (°C)	Duration (h)
Cu ₂ (OH) ₃ (NO ₃)	—	—	—	—	14.942	1.0	2.0	0.033	2.0	140	2
Cu _{1.5} Co _{0.5} (OH) ₃ (NO ₃)	—	—	4.5	0.25	11.206	0.75	2.0	0.033	2.0	140	2
Cu _{1.34} Co _{0.66} (OH) ₃ (NO ₃)	—	—	5.939	0.333	9.962	0.667	2.0	0.033	2.0	140	2
Zn ₅ (OH) ₈ (NO ₃) ₂ (H ₂ O) ₂	18.399	1.0	—	—	—	—	2.0	0.033	2.0	140	2
Zn _{3.75} Co _{1.25} (OH) ₈ (NO ₃) ₂ (H ₂ O) ₂	13.8	0.75	4.49	0.25	—	—	2.0	0.033	2.0	140	2
Zn _{3.35} Co _{1.65} (OH) ₈ (NO ₃) ₂ (H ₂ O) ₂	12.25	0.667	6	0.333	—	—	2.0	0.033	2.0	140	2
Co ₂ (OH) ₃ (NO ₃)	—	—	17.999	1.0	—	—	2.0	0.033	2.0	140	2

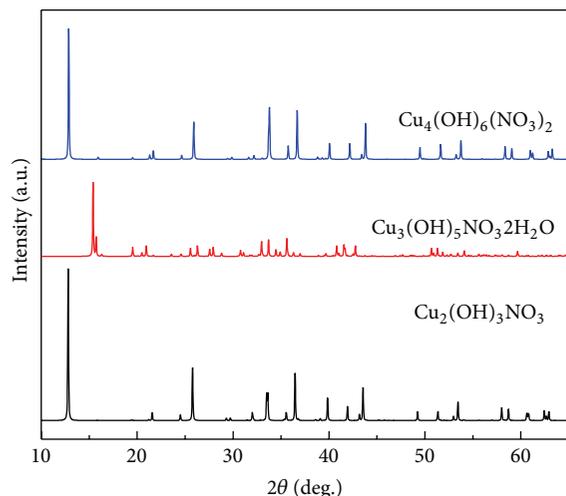
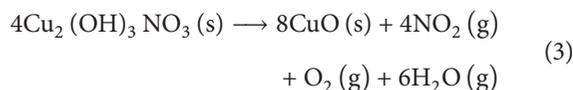


FIGURE 4: Simulated powder X-ray diffraction patterns of different polymorphic modifications of copper hydroxynitrate.

Thermal decomposition of layered hydroxynitrate follows dehydration, denitration, and disruption of layered framework under atmospheric conditions. The elimination of hydroxyl and nitrate groups from the precursors has great influence on the crystallinity of metal oxides, and new intermediate phase might also form during the disruption of the original structure. The copper hydroxynitrate undergoes decomposition in one step producing CuO according to the equation:



The theoretical weight loss for the reaction $\text{Cu}_2(\text{OH})_3(\text{NO}_3) \rightarrow 2\text{CuO}$ is 33.17%.

Powder XRD was very important in the identification of the phase formation and in Figure 5 the data of the copper hydroxynitrate heated to different temperatures is shown. The XRD results show that up to 200°C the samples do not show any structural changes. Thermal decomposition of copper hydroxynitrate occurs at single step in which dehydroxylation and decomposition of the nitrate in the interlayer space take place simultaneously leading to the destruction of the layered structure (250°C) (see Figure 5). The total weight loss on isothermal heating of the copper hydroxyl nitrate sample is 31%. Copper oxide can exist in monoclinic or cubic crystal system and in Table 2 the XRD data is shown. The decomposed product could be indexed to monoclinic phase of copper oxide. Figure 6 shows the crystal structure of copper oxide (monoclinic) formed on decomposition of copper hydroxynitrate.

3.2. $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$ and $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$ Series. In the structure of layered hydroxynitrate, divalent transition metal ions can be isomorphically substituted by the other divalent cations across the whole range of composition

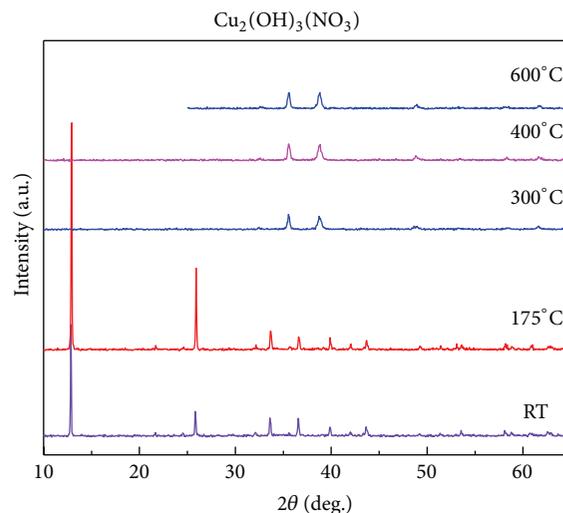


FIGURE 5: Copper hydroxynitrate- $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ heated to different intervals of temperature.

TABLE 2: XRD data of (ICSD-97597) $(\text{Zn}_{0.85}\text{Co}_{0.15})\text{O}$ (hexagonal).

2θ (°)	d -spacing (Å)	h	k	l
31.754	2.8179	0	1	0
34.465	2.6022	0	0	2
36.251	2.478	0	1	1
47.562	1.9117	0	1	2
56.568	1.6269	-1	2	0
62.911	1.4773	0	1	3

“ x ” which results in the formation of continuous solid solution series. Goldschmidt’s rule states that a continuous solid solution cannot be obtained if the difference in ionic radii is greater than 15% of the smallest cation. The ionic radii of Co^{2+} are 0.745 Å for high spin and 0.65 Å for low spin complexes. The ionic radius of Cu^{2+} is 0.73 Å when the coordination number is 6. Co^{2+} substitution in Cu^{2+} sites of layered metal hydroxynitrate is permitted as the difference in their ionic radii is <10% and hence the values are within the limits set by Goldschmidt, and solid solution series Cu/Co hydroxynitrates with the composition of $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$ and $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$ were prepared by using urea hydrolysis route and their powder X-ray diffraction patterns are shown in Figure 3. We observe structural similarities among $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$, and $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$ as the peak positions in their diffraction patterns appear at similar positions in 2θ . However, the Co^{2+} and Cu^{2+} have d^7 and d^9 electronic configurations, respectively. Cu^{2+} ion is prone to Jahn Teller distortion and results in the irregular octahedral coordination arrangement around it. On substitution of Co^{2+} into the lattice, we observed a decrease in its irregularity in the structure of cobalt substituted copper hydroxynitrate. The pXRD patterns of $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$ and $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$

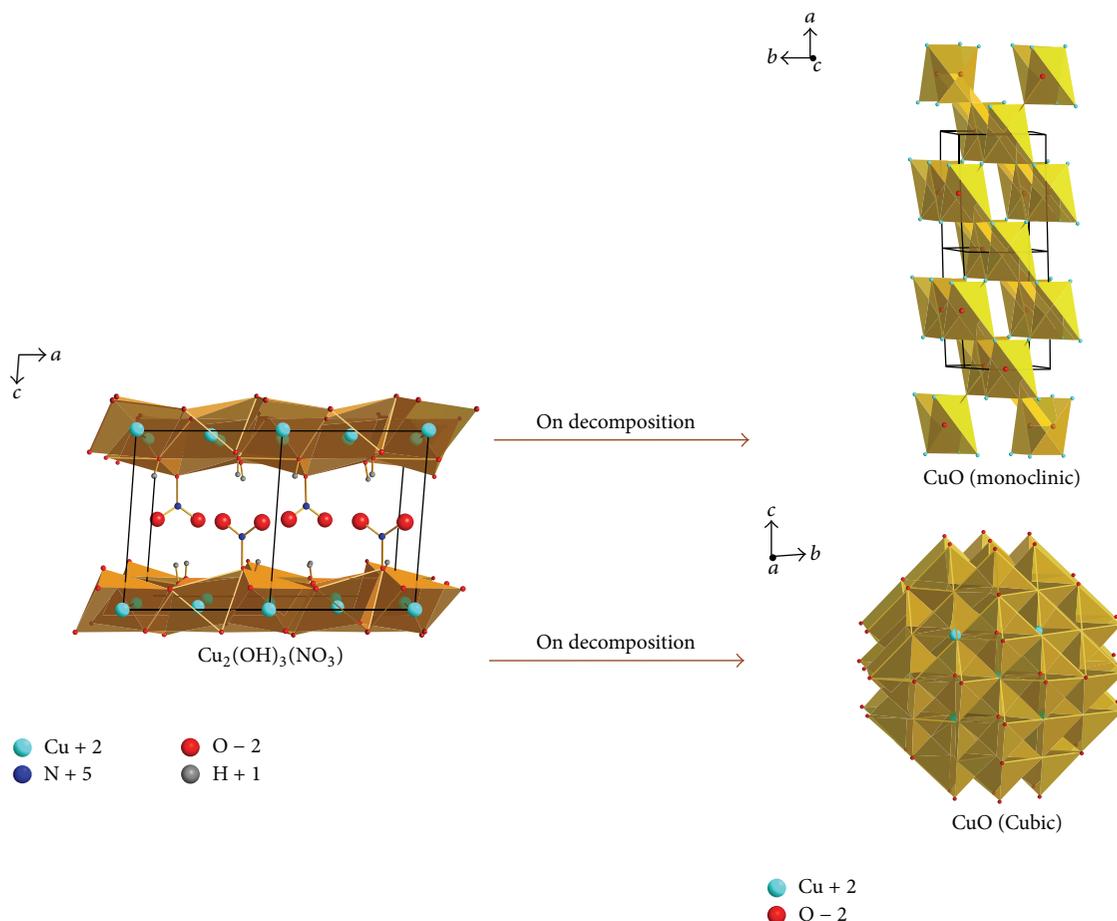


FIGURE 6: Schematic representation on the structural transformation of copper hydroxynitrate to copper oxide on isothermal heating (250°C).

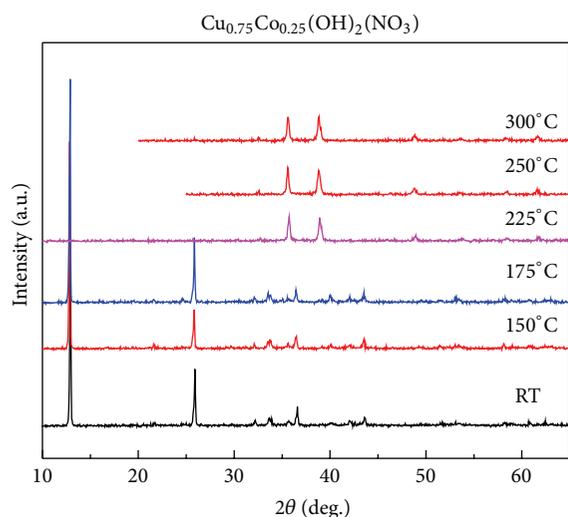


FIGURE 7: Powder X-ray diffraction patterns copper hydroxynitrate- $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$ heated to different intervals of temperature.

heated to different temperatures are shown in Figures 7 and 8, respectively. The mixed metal hydroxynitrates

$[\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)]$ and $[\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)]$ undergo dehydration and denitration at lower temperatures compared to pure zinc/copper/cobalt based hydroxynitrates. It was found that on substitution of cobalt into the structure of basic copper hydroxynitrate in mixed metal hydroxynitrates, the decomposition temperature is reduced by $\sim 50^\circ\text{C}$. The dramatic decrease in the decomposition temperature was due to decarboxylation reaction on substitution of cobalt for copper in the cobalt substitute copper hydroxynitrates.

In Figure 9, the structural transformations of $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)/\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)/\text{Cu}_{1.0}\text{Co}_{1.0}(\text{OH})_3(\text{NO}_3)$ to copper-cobalt oxide, respectively, are shown. The decomposed product, $\text{Co}_{0.333}\text{Cu}_{0.666}\text{O}$, could crystallize in cubic or monoclinic system. The powder X-ray diffraction patterns of $\text{Co}_{0.25}\text{Cu}_{0.75}\text{O}/\text{Co}_{0.333}\text{Cu}_{0.666}\text{O}/\text{Co}_{0.5}\text{Cu}_{0.5}\text{O}$ shown in Figures 9 and 10 could be indexed (at temperatures $>250^\circ\text{C}$) to monoclinic system.

Table 3 shows the decomposition temperatures of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$, and $\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$, respectively.

3.3. Zinc Hydroxynitrate. Figure 10 shows the powder X-ray diffraction pattern of zinc hydroxynitrate obtained by urea hydrolysis. Zinc hydroxynitrate can crystallize

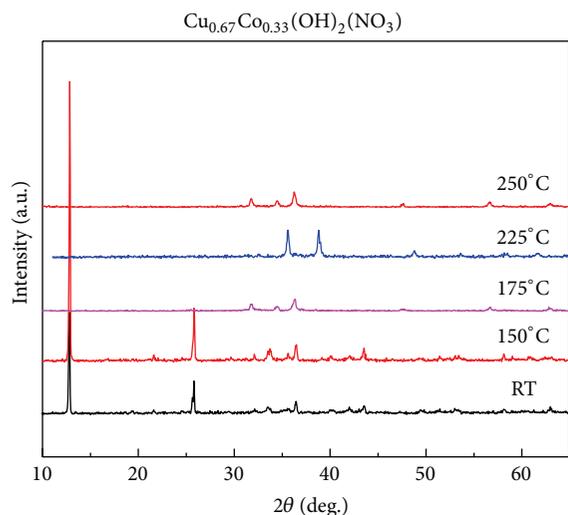


FIGURE 8: Powder X-ray diffraction patterns of copper hydroxynitrate- $\text{Cu}_{1.33}\text{Co}_{0.664}(\text{OH})_5(\text{NO}_3)$ heated to different intervals of temperature.

TABLE 3: Decomposition temperatures for layered metal hydroxynitrate and mixed metal hydroxynitrate samples.

Sample	Decomposition temperature ($^{\circ}\text{C}$)
$\text{Cu}_2(\text{OH})_3(\text{NO}_3)$	250
$\text{Cu}_{1.5}\text{Co}_{0.5}(\text{OH})_3(\text{NO}_3)$	225
$\text{Cu}_{1.34}\text{Co}_{0.66}(\text{OH})_3(\text{NO}_3)$	225
$\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$	175
$\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$	200
$\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$	200
$\text{Co}_2(\text{OH})_3(\text{NO}_3)$	225

in different crystal structures and depends on the composition, that is, $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$, $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$, and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$. Figure 11 shows the simulated powder X-ray diffraction patterns of $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$, $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$, and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, respectively. The experimentally observed pattern of zinc hydroxynitrate matches the simulated powder X-ray diffraction pattern of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$. On isothermal heating of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ the total weight loss observed was 50%, while theoretically the total weight loss expected was 40% indicating higher water content. Figure 12 shows the powder X-ray diffraction patterns of the $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ samples obtained on isothermal heating at different intervals of temperature.

The powder X-ray diffraction pattern of zinc hydroxynitrate heated to 100°C shows additional peaks indicating evolution of second phase of zinc hydroxynitrate with composition $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$. The formation of $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ could arise due to dehydration of a $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$. At 175°C , peaks due to $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ disappear and the zinc oxide peaks are prominently observed.

TABLE 4: XRD data of (ICSD-41488) ZnO (hexagonal).

2θ ($^{\circ}$)	d -spacing (\AA)	h	k	l
31.802	2.8137	0	1	0
34.447	2.6035	0	0	2
36.29	2.4754	0	1	1
47.583	1.911	0	1	2
56.66	1.6245	-1	2	0
62.914	1.4772	0	1	3

TABLE 5: XRD data of (ICSD-163383) ZnO (cubic).

2θ ($^{\circ}$)	d -spacing (\AA)	h	k	l
34.609	2.5917	1	1	1
40.176	2.2445	0	0	2
58.12	1.5871	0	2	2

Tables 4 and 5 show the XRD data of zinc oxide in hexagonal and cubic systems, respectively. The experimental data of the decomposed product obtained from $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ can be indexed to hexagonal phase of ZnO. The decomposition of layered metal hydroxynitrate results in the absorption of heat and the process is endothermic in nature. The decomposition reaction of this type yields metal oxide and water vapour and nitrates as by-products. Figure 13 shows the crystal structure of zinc oxide formed on decomposition of zinc hydroxynitrate- $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$.

3.4. $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$. Solid solution series of Co/Zn hydroxynitrates were prepared by urea hydrolysis route. The ionic radii of Co^{2+} are 0.745\AA for high spin and 0.65\AA for low spin complexes, respectively. Zn^{2+} with ionic radius of 0.74\AA indicates its coordination number to be 6. Co^{2+} substitution in Zn^{2+} sites is permitted as the difference in the ionic radii is $<10\%$ and hence the values are within the limits set by Goldschmidt. The powder X-ray diffraction patterns of $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ are shown in Figure 10. We observe structural similarities among $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, $\text{Cu}_1\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ as the peak positions appear at similar positions. Co^{2+} and Zn^{2+} have d^7 and d^{10} electronic configurations, respectively, and both Co^{2+} and Zn^{2+} do not induce any distortion of octahedral geometry. The pXRD patterns of $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ heated to different temperatures are shown in Figures 14 and 15, respectively. The mixed metal hydroxynitrates, $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, undergo dehydration and denitration at 150 to 200°C temperatures compared to pure zinc/copper/cobalt based hydroxynitrates. The decomposition temperatures of $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ are shown in Figure 16.

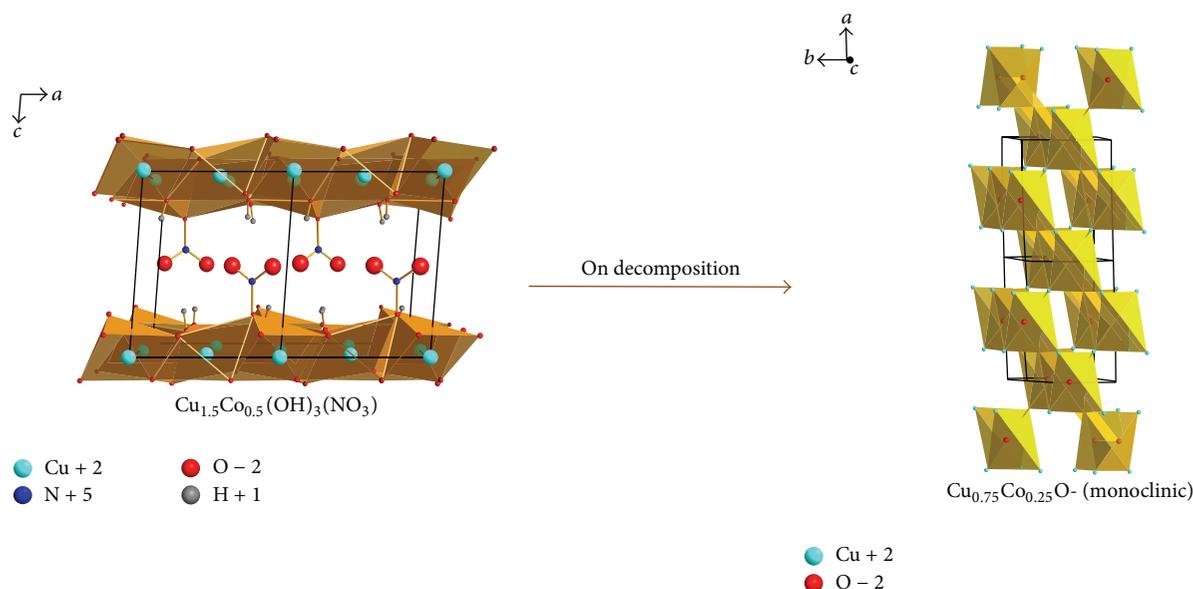


FIGURE 9: Schematic representation on the structural transformation of solid solution of copper-cobalt (25%) hydroxynitrate to $\text{Cu}_{0.75}\text{Co}_{0.25}\text{O}$ on isothermal heating (225°C).

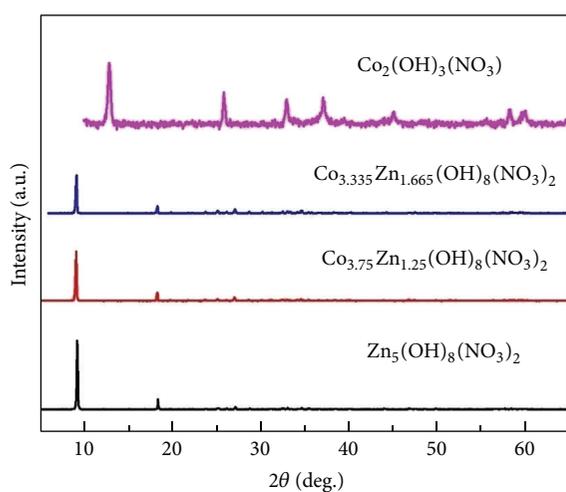


FIGURE 10: Powder X-ray diffraction pattern of zinc hydroxynitrate- $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2$ and cobalt substituted zinc hydroxynitrate samples obtained by urea hydrolysis.

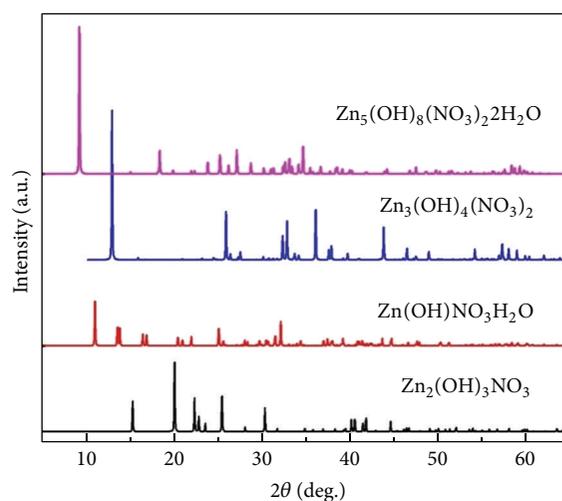


FIGURE 11: Simulated powder X-ray diffraction patterns of zinc hydroxynitrate- $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$, $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$, and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, respectively.

$(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ are shown in Table 3. The pXRD patterns of the decomposed products of $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ heated to 250°C could be indexed to hexagonal phase of zinc oxide. Figures 14 and 15 show the powder X-ray diffraction patterns of $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ on decomposition, respectively, to form $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$. Figure 16 shows the structural transformation of $\text{Zn}_{3.75}\text{Co}_{1.25}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ and $\text{Zn}_{3.35}\text{Co}_{1.65}(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ on decomposition, respectively, to form $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$.

Tables 6 and 7 shows the lattice parameters, expected, of different phases of layered metal hydroxynitrate and mixed metal hydroxynitrates and their respective decomposed products. Table 8 shows the percentage weight loss of the layered metal hydroxynitrate and mixed metal hydroxynitrates, respectively.

4. Conclusion

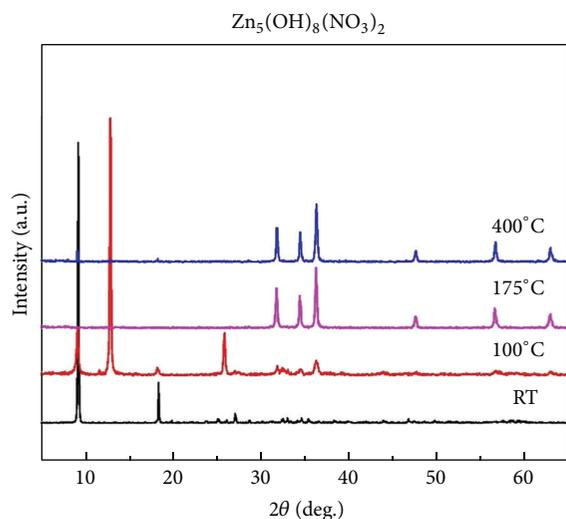
Simple preparative method has been adopted for the synthesis of layered hydroxynitrates/mixed metal hydroxynitrates by urea hydrolyses. Thermal decomposition studies

TABLE 6: Lattice parameters of decomposed products obtained from layered hydroxynitrate samples (expected).

Sample	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space group	Crystal system	Cell volume (Å ³)	z
CuO	4.6797	3.4314	5.1362	90	99.26	90	C 12/c1	Monoclinic	81.40	4
CuO	4.245(5)	4.245(5)	4.245(5)	90	90	90	F m-3m	Cubic	76.50	4
ZnO	3.2490	3.2490	5.2070	90	90	120	P 63mc	Hexagonal	47.60	2
ZnO	4.4890	4.4890	4.4890	90	90	90	F m-3m	Cubic	90.46	4
CoO	4.260	4.260	4.260	90	90	90	F m-3m	Cubic	77.31	4
Co ₃ O ₄	8.1893	8.1893	8.1893	90	90	90	F m-3m	Cubic	549.21	4
CoCu ₂ O ₃	9.4085	3.9801	3.1980	90	90	90	P m m n	Orthorhombic	119.75	2
(Zn _{0.85} Co _{0.15})O	3.2538	3.2538	5.2044	90	90	120	P 63mc	Hexagonal	47.72	2

TABLE 7: Lattice parameters of different polymorphic modifications of layered hydroxynitrate samples.

Sample	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space group	Crystal system	Cell volume (Å ³)	z
Cu ₂ (OH) ₃ (NO ₃)	5.605	6.087(4)	6.929(4)	90	94.48	90	P 1 211	Monoclinic	235.68	2
Cu ₃ (OH) ₅ (NO ₃)(H ₂ O) ₂	5.830(1)	6.775(1)	21.711	90	90	90	P cmn	Orthorhombic	857.55	4
Cu ₄ (NO ₃) ₂ (OH) ₆	5.576(2)	6.050(2)	6.896(3)	90	94.5	90	P121/m1	Monoclinic	231.92	1
Zn(OH)(NO ₃)(H ₂ O)	17.951	3.2600	14.272	90	114.91	90	P 121/c1	Monoclinic	757.50	8
Zn ₃ (OH) ₄ (NO ₃) ₂	7.038	9.658(2)	11.182(2)	90	100.96	90	P 121/c1	Monoclinic	746.21	4
Zn ₅ (OH) ₈ (NO ₃) ₂ (H ₂ O) ₂	19.480	6.238	5.517(1)	90	93.28	90	C 12/m1	Monoclinic	669.31	2
Co ₂ (OH) ₃ (NO ₃)	3.12	3.12	6.98	90	90	120	—	Hexagonal	—	—

FIGURE 12: Powder X-ray diffraction patterns of zinc hydroxynitrate-Zn₅(OH)₅(NO₃)₂(H₂O)₂ heated to different intervals of temperature.

of mixed metal hydroxynitrates (zinc/cobalt hydroxynitrates and copper/cobalt hydroxynitrates) were investigated. The mechanism of thermal decomposition of the layered metal/mixed metal hydroxynitrates was deduced and the effect of substituting other metal cations into the structure of layered hydroxynitrate was determined. The single metal hydroxynitrate will have higher decomposition temperature than cobalt substituted copper hydroxynitrates. It was found that the mixed metal hydroxynitrate decomposed at lower

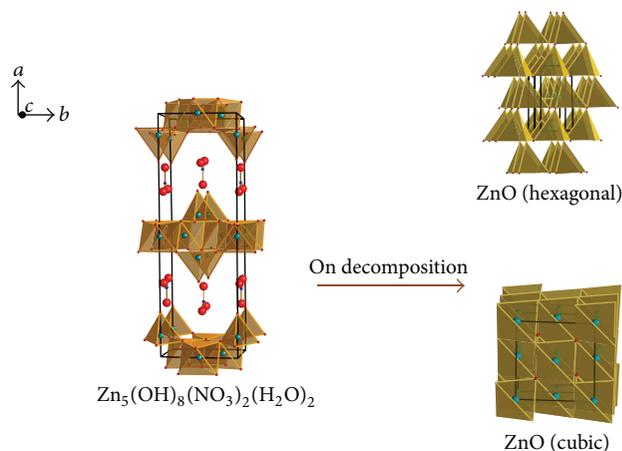


FIGURE 13: Schematic representation on the structural transformation of solid solution of zinc hydroxynitrate to ZnO on isothermal heating (175°C).

TABLE 8: Total weight loss observed for layered metal hydroxynitrate samples.

Sample	% Weight loss
Cu ₂ (OH) ₃ (NO ₃)	30
Cu _{1.5} Co _{0.5} (OH) ₃ (NO ₃)	50
Cu _{1.34} Co _{0.66} (OH) ₃ (NO ₃)	50
Zn ₅ (OH) ₈ (NO ₃) ₂ (H ₂ O) ₂	50
Zn _{3.75} Co _{1.25} (OH) ₈ (NO ₃) ₂ (H ₂ O) ₂	50
Zn _{3.35} Co _{1.65} (OH) ₈ (NO ₃) ₂ (H ₂ O) ₂	60
Co ₂ (OH) ₃ (NO ₃)	60

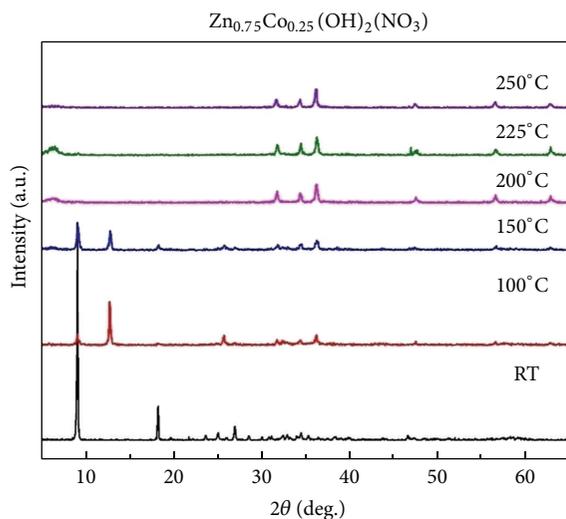


FIGURE 14: Powder X-ray diffraction patterns of zinc hydroxynitrate- $\text{Zn}_{0.75}\text{Co}_{0.25}(\text{OH})_2(\text{NO}_3)$ heated to different intervals of temperature.

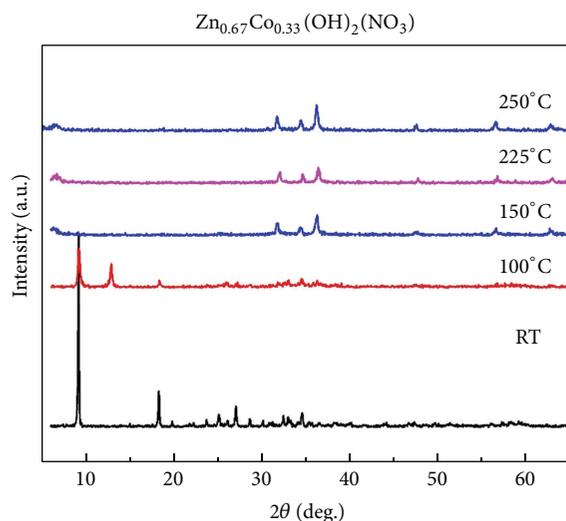


FIGURE 15: Powder X-ray diffraction patterns of zinc hydroxynitrate- $\text{Zn}_{3.35}\text{Co}_{1.667}(\text{OH})_5(\text{NO}_3)_2(\text{H}_2\text{O})_2$ heated to different intervals of temperature.

temperatures than the single metal hydroxynitrate studied. The work will be used as a basis for further studies of mixed metal hydroxynitrate for the preparation of novel catalyst precursors. The mechanism of decomposition provides insight into the nature of phases formed at different temperatures which can significantly affect the catalytic activity. These metal/mixed metal hydroxynitrates with high surface area may exhibit unusual and unexpected properties for device based applications.

Conflict of Interests

The authors declare that they have no competing financial interests.

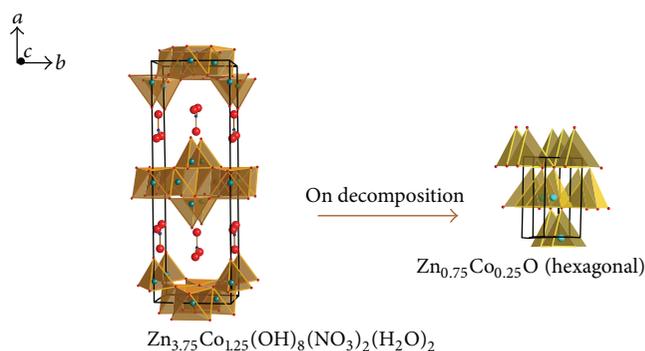


FIGURE 16: Schematic representation on the structural transformation of solid solution of zinc-cobalt (25%) hydroxynitrate to $\text{Zn}_{0.75}\text{Co}_{0.25}\text{O}$ on isothermal heating (175°C).

Acknowledgments

Ramesh Thimmasandra Narayan gratefully acknowledges the Council of Scientific and Industrial Research (CSIR) (project ref: 01/(2741)/13/EMR-II dated 18-04-2013), New Delhi, for the financial support. Ramesh Thimmasandra Narayan wishes to thank Professor P. Vishnu Kamath lab of Bangalore University for providing laboratory facilities. Authors gratefully thank Mr. Shivanna, Supreeth Nagendran, and Mr. Kiran of Bangalore University for their help in collection of powder-ray diffraction data. The author would like to thank Tumkur University for providing facilities.

References

- [1] P. B. Himelfarb, G. W. Simmons, K. Klier, and R. G. Herman, "Precursors of the copper-zinc oxide methanol synthesis catalysts," *Journal of Catalysis*, vol. 93, no. 2, pp. 442–450, 1985.
- [2] R. G. Herman, K. Klier, G. W. Simmons, B. P. Finn, J. B. Bulko, and T. P. Kobylinski, "Catalytic synthesis of methanol from CO and H_2 . I. Phase composition, electronic properties, and activities of the Cu/ZnO/ M_2O_3 catalysts," *Journal of Catalysis*, vol. 56, no. 3, pp. 407–429, 1979.
- [3] M. Meyn, K. Beneke, and G. Lagaly, "Anion-exchange reactions of hydroxy double salts," *Inorganic Chemistry*, vol. 32, no. 7, pp. 1209–1215, 1993.
- [4] C. Yuan, H. B. Wu, Y. Xie, and X. W. Lou, "Mixed transition-metal oxides: design, synthesis, and energy-related applications," *Angewandte Chemie International Edition*, vol. 53, no. 6, pp. 1488–1504, 2014.
- [5] G. Shen, P.-C. Chen, K. Ryu, and C. Zhou, "Polyol-mediated synthesis of zinc oxide nanorods and nanocomposites with poly(methyl methacrylate)," *Journal of Materials Chemistry*, vol. 19, pp. 828–839, 2009.
- [6] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, UK, 1979.
- [7] H. R. Oswald and R. Asper, "Bivalent metal hydroxides," in *Preparation and Crystal Growth of Materials with Layered Structures*, R. M. A. Lieth, Ed., vol. 1, pp. 71–140, Redial Publishing Company, Dordrecht, The Netherlands, 1997.
- [8] P. M. Louer and L. Grandjean, "Etude structurale des hydroxynitrates de nickel et de zinc, I. Classification structural," *Acta Crystallographica B*, vol. 29, pp. 1696–1703, 1973.

- [9] D. Louër, "Analyse des profils de raies de diffraction des rayons X d'un hydroxynitrate de nickel non stoechiométrique," *Journal of Solid State Chemistry*, vol. 13, no. 4, pp. 319–324, 1975.
- [10] P. Gallezot and M. Prettre, "Etude structural dnun nitrate basique de nickel non stoechiometrique," *Bulletin of Society Chimia France*, vol. 2, pp. 407–411, 1969.
- [11] M. Louër, D. Louër, D. Grandjean, and D. Weigel, "Etude structurale des hydroxynitrates de nickel et de zinc. III. Etude structurale des nitrates basiques $Zn(OH)_2 \cdot Zn(NO_3)_2 \cdot 2H_2O$ et $Ni(OH)_2 \cdot Ni(NO_3)_2 \cdot 2H_2O$," *Acta Crystallographica B: Structural Crystallography and Crystal Chemistry*, vol. 29, no. 8, pp. 1707–1710, 1973.
- [12] B. Bovio and S. Locchi, "Crystal structure of the orthorhombic basic copper nitrate, $Cu_2(OH)_3NO_3$," *Journal of Crystallographic and Spectroscopic Research*, vol. 12, no. 6, pp. 507–517, 1982.
- [13] H. Nishizawa and K. Yuasa, "Preparation of anion exchangeable layered mixed basic salt $Ni_{1-x}Zn_{2x}(OH)_2(OCOCH_3)_{2x}nH_2O$ thin film under hydrothermal conditions," *Journal of Solid State Chemistry*, vol. 141, pp. 229–234, 1998.
- [14] G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Academic Press, New York, NY, USA, 1965.
- [15] T. N. Ramesh, M. Rajamathi, and P. Vishnu Kamath, "Anion mediated polytype selectivity among the basic salts of Co(II)," *Journal of Solid State Chemistry*, vol. 179, no. 8, pp. 2386–2393, 2006.
- [16] M. Rajamathi and P. Vishnu Kamath, "Urea hydrolysis of cobalt(II) nitrate melts: synthesis of novel hydroxides and hydroxynitrates," *International Journal of Inorganic Materials*, vol. 3, no. 7, pp. 901–906, 2001.
- [17] Y. Guo, H. Zhang, Y. Wang, Z. L. Liao, G. D. Li, and J. S. Chen, "Controlled growth and photocatalytic properties of CdS nanocrystals implanted in layered metal hydroxide matrixes," *Journal of Physical Chemistry B*, vol. 109, no. 46, pp. 21602–21607, 2005.
- [18] M. J. Kang, S. W. Rhee, H. Moon, V. Neck, and T. Fanghänel, "Sorption of MO_4 ($M = Tc, Re$) on Mg/Al layered double hydroxide by anion exchange," *Radiochimica Acta*, vol. 75, no. 3, pp. 169–173, 1996.
- [19] B. Bovio and S. Locchi, "Crystal structure of the orthorhombic basic copper nitrate, $Cu_2(OH)_3NO_3$," *Journal of Crystallographic and Spectroscopic Research*, vol. 12, no. 6, pp. 507–517, 1982.
- [20] W. Stählin and H. R. Oswald, "The crystal structure of zinc hydroxide nitrate, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$," *Acta Crystallographica Section B*, vol. 26, no. 6, pp. 860–863, 1970.
- [21] S. Ghose, "The crystal structure of hydrozincite, $Zn_5(OH)_6(CO_3)_2$," *Acta Crystallographica*, vol. 17, no. 8, pp. 1051–1057, 1964.
- [22] J. Mu and D. D. Perlmutter, "Thermal decomposition of carbonates, carboxylates, oxalates, acetates, formates, and hydroxides," *Thermochimica Acta*, vol. 49, no. 2-3, pp. 207–218, 1981.
- [23] I. Fujii, K. Tsuchiya, Y. Shikakura, and M. S. Murthy, "Consideration on thermal decomposition of calcium hydroxide pellets for energy storage," *Journal of Solar Energy Engineering*, vol. 111, no. 3, pp. 245–250, 1989.
- [24] T. Sato, T. Nakamura, and F. Ozawa, "Thermal decomposition of nickel hydroxide," *Journal of Applied Chemistry*, vol. 25, no. 8, pp. 583–590, 1975.
- [25] T. N. Ramesh, "X-ray diffraction studies on the thermal decomposition mechanism of nickel hydroxide," *Journal of Physical Chemistry B*, vol. 113, no. 39, pp. 13014–13017, 2009.
- [26] M. Sui and L. She, "Review on research and application of mesoporous transitional metal oxides in water treatment," *Frontiers of Environmental Science & Engineering*, vol. 7, no. 6, pp. 795–802, 2013.
- [27] A. Umar and Y.-B. Hahn, Eds., *Metal Oxide Nanostructures and Their Applications*, American Scientific Publishers, 2010.
- [28] T. Gershon, "Metal oxide applications in organic-based photovoltaics," *Materials Science and Technology*, vol. 27, no. 9, pp. 1357–1371, 2011.
- [29] T. Zhai, X. Fang, M. Liao et al., "A comprehensive review of one-dimensional metal-oxide nanostructure photodetectors," *Sensors*, vol. 9, no. 8, pp. 6504–6529, 2009.
- [30] H. R. Oswald and R. Asper, "Bivalent metal hydroxides," in *Preparation and Crystal Growth of Materials with Layered Structures*, R. M. A. Lieth, Ed., vol. 1, pp. 71–140, Redial Publishing Company, Dordrecht, The Netherlands, 1997.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

