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Short Communication

Preparation and Characterization of Nickel Cobalt Phenylacetate Hydrazinate – A Precursor for Cobaltite Nanoparticles

Rakkiyasamy Manimekalai*, Kalimuthu Kalpanadevi and Rangasamy Sinduja
Department of Chemistry, Kongunadu Arts and Science College, Coimbatore, Tamilnadu–641 029 INDIA

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Abstract

A good precursor is foremost in the preparation of nanosized metal, metal oxide and mixed metal oxides. In the present study, a novel precursor nickel cobalt phenylacetate hydrazinate has been prepared which decomposes at 400˚C to give the corresponding nanosized mixed-metal oxide. The synthesized complex has been characterized by elemental analysis and spectroscopic techniques. The thermal behaviour of the complex has been studied by thermogravimetry and differential thermal analysis. The Infrared analysis of the residue shows two absorption bands in the region 660-665 and 555-562 cm^{-1} corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of cobaltites. Formation of cobaltite has been confirmed by thermogravimetry (TG) weight loss and X-ray diffraction. Combustion of the precursor in air yields fine powder of cobaltites with large surface area which has been confirmed by XRD patterns.

Keywords: Hydrazine, cobaltites, IR Spectra, thermogravimetry, differential thermal analysis, XRD.

Introduction

Among the binary cobaltites of transition metals with the general formula MCo_2O_4, where M is a divalent cation of a d element, Ni, Cu and Zn cobaltites are of definite interest due to their diverse applications as oxide electrode materials, magnetic materials, thermistors and catalysts[1-10]. Cobaltites have attracted much attention of the chemists due to their application as low cost fuel cell electrodes.

A wide option of preparative methods can be employed to obtain the desired novel products. Some of the methods applied are traditional ceramic preparation or better known as solid-state route and chemical techniques such as sol-gel, electrochemical, solvothermal, hydrothermal, combustion and co-precipitation. Thermal treatment of co-precipitated precursors is proven to be the most promising method in preparing cobaltite spinels[11,12]. Nickel cobaltite, $NiCo_2O_4$ is one of the promising metal oxides in the family of cobaltite materials which has a spinel structure AB_2O_4. This mixed metal oxide spinel has shown exceptional ability to serve as an oxygen evolution electrode and has been studied quite extensively by electrochemical methods for this purpose[13,14]. $NiCo_2O_4$ can be utilized as electrode material in sodium and sodium ion cells as well as electrocatalyst in advanced alkaline water electrolyzer due to its high electrical conductivity and desirable optical properties in the infrared regions[15]. However, there appear limited studies on $NiCo_2O_4$ for energy storage in supercapacitors. It is highlighted that incorporation of nickel into cobalt oxide would further enhance the electrical conductivity of the prepared samples[16,17].

The possibility of synthesis of $NiCo_2O_4$ as a high-dispersity material using the nickel cobalt phenylacetate hydrazinate as precursor is studied in the present paper.

Material and Methods

Preparation of nickel cobalt phenylacetate hydrazinate: Stoichiometric quantities (1:2 molar ratio) of metal nitrate hydrate $Ni(NO_3)_2.nH_2O$ and $Co(NO_3)_2.6H_2O$ were dissolved in 50 ml of water. The resultant solution was treated with 50 ml of aqueous solution containing the phenylacetic acid and hydrazine hydrate. The complex was precipitated after 20-30 minutes, filtered off, washed with distilled water, alcohol, ether and air dried.

Preparation of cobaltites: The cobaltite, $NiCo_2O_4$ has been obtained as residue by heating the precursor at 400˚C in a pre-heated silica crucible for about 15 minutes. While heating, the precursor should be added in small portions to the crucible in order to avoid explosions, since it decomposes violently.

Quantitative methods: The hydrazine content in the sample was determined by titration using KIO_3 as the titrant[20]. The percentage of nickel and cobalt in the precursor was estimated by the standard methods given in the Vogel's textbook[18].

Results and Discussion

Chemical formula determination of nickel cobalt phenylacetate hydrazinate: From the IR spectrum of the prepared complex, it is observed that the N-N stretching frequency is seen at 975 cm^{-1}, which unambiguously proves the bidentate bridging nature of the hydrazine ligand[19]. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1604 and 1404 cm $^{-1}$, respectively with the $_{\Delta}\upsilon$ $_{(\upsilon_{asymm-}\ \upsilon_{sym})}$ separation of 200 cm^{-1}, which indicate the monodentate linkage of both carboxylate groups in the dianion. The N-H stretching is observed at 3255 cm^{-1}. The IR data thus confirms the formation of nickel cobalt phenylacetate hydrazinate complex. The chemical formula, $NiCo_2$ $(PhAc)_2$ $(N_2H_4)_2$ has been assigned to the complex, nickel cobalt phenylacetate hydrazinate based on the observed percentage of hydrazine (15.62), nickel (4.90) and cobalt (9.90) which are found to match closely with the calculated values 16.21, 4.95 and 9.94 for hydrazine, nickel and cobalt respectively.

Thermal analysis: From the thermal decomposition data of the prepared complex, it is seen that the compound decomposes exothermically to yield the corresponding cobaltite, $NiCo_2O_4$ as the final product. The observed weight loss matches very well with the expected values. The major weight loss of 84.07% on the TG curve from 378 to 410°C is attributed to the decarboxylation of dehydrazinated phenylacetate precursor.

Cobaltites: The chemical analysis of the cobaltite prepared from the precursor shows that the nickel and cobalt in the residue are present in 1:2 ratio. Formation of cobaltite by the thermal decomposition of the mixed metal complex was confirmed by XRD patterns. The Infrared analysis of the residue shows two absorption bands in the region 660-665 and 555-562 cm^{-1} corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of cobaltites[12]. Further investigation has been carried out by obtaining X – ray powder diffraction pattern of the residue. The X-ray pattern of $NiCo_2O_4$ is shown in figure 1.

Conclusion

The synthesis of transition metal oxides via the metal–phenylacetate hydrazinate precursor is a convenient synthetic route to prepare nanosized mixed metal oxides. In this method hydrazine complex exhibits an autocatalytic behaviour after ignition in air. The precursor decomposes autocatalytically on ignition forming nanosized $NiCo_2O_4$.

The chemical analysis, total weight loss and infrared spectral analysis of the complex confirm the formation of the complex $NiCo_2(PhAc)_2(N_2H_4)_2$ .The TG-DTA analysis shows that the complexes have good thermal stability with initial decompose temperature at above 250°C.

The TG studies of the complex show the formation of single phase $NiCo_2O_4$ nanoparticles, which is also confirmed by XRD studies.

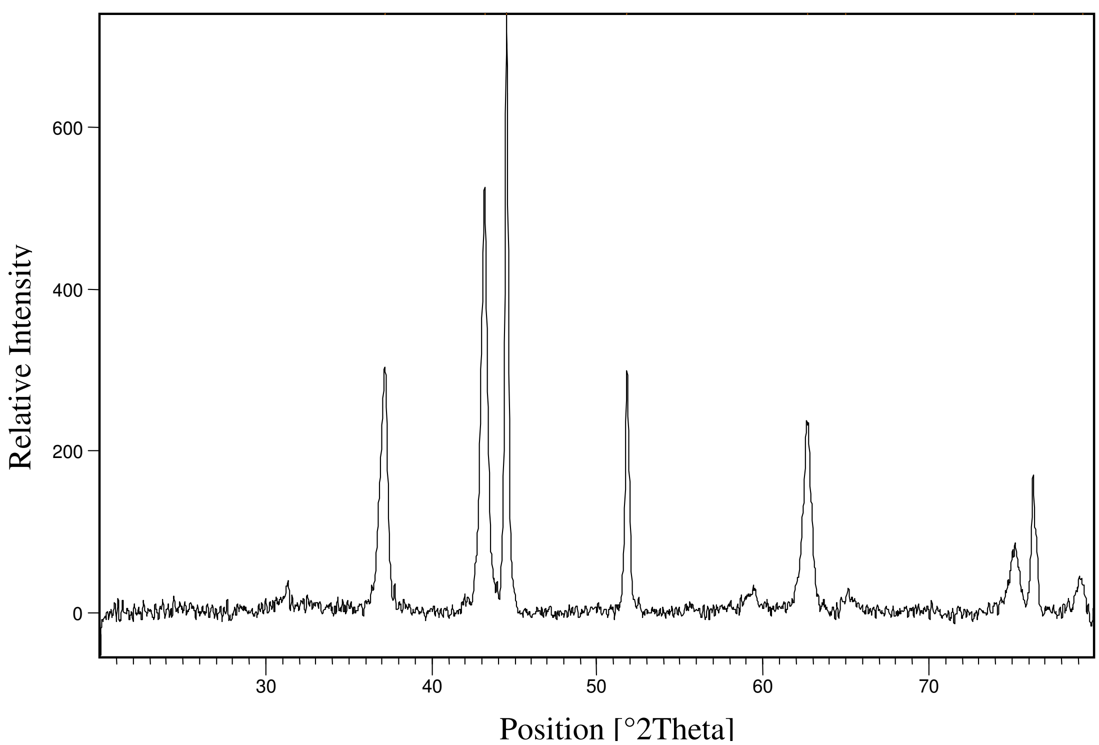

Figure-1
XRD pattern of $NiCo_2O_4$

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