

A New Method of Identification of Chelation in CGYO a Precursor for Dense Membranes using Fourier Transform Infrared Spectroscopy

Savinder. Preet Kaur

^{RT#}Department of Science Mata Sahib Kaur Khalsa College,
Talwandi Bhai, India

Abstract:- Glycine nitrate combustion method was used to synthesize $Ce_{0.8}Gd_{0.1}Y_{0.1}O_{1.9}$ powders using Glycine as fuel and nitrates as oxidizers. Soluble metal- glycine complexes result due to chelation examined by vibrational changes detected by infrared spectroscopy.

Keywords:- CGYO, GNP I.R

I. INTRODUCTION

The glycine nitrate method[1,2] is based on the exothermicity of the redox reaction between the fuel – Glycine [3] and oxidizer-nitrate. This paper reports the study of $Ce_{0.8}Gd_{0.1}Y_{0.1}O_{1.9}$ (CGYO) a potential electrolyte of solid oxide fuel cell with the aim to understand the details of the combustion synthesis pathways with emphasis of study of vibrational changes occurred during chelation.

II. EXPERIMENTAL

Stoichiometric solutions of cerium nitrate, yttrium nitrate and gadolinium nitrate corresponding to composition $Ce_{0.8}Gd_{0.1}Y_{0.1}O_{1.9}$ were dissolved in distilled water in a glass beaker according to the previously calculated composition of the final powder. Different amounts of glycine were added to the nitrate solution such that the ratio of glycine to nitrate per mole become 0.5, 0.7, 0.8, 0.9, 1.0, 1.2 and 1.4 mole g/n. Details of the synthetic procedure of GNP process are described elsewhere.

The resulting powder was calcined at 700°C for 2 hrs in order to remove carbonaceous residues. The powders obtained range $2\theta = 20- 80^\circ$ using Nickel filter. The morphology of powders was studied by Scanning Electron Microscopy (JEOL, Model: JSM 6100 and LEO 435 VP, UK). The infrared spectra in the range of 4000–400 cm^{-1} were recorded on an (PERKIN ELMER MODEL: Spectrum RX11 FT-IR, USA) FTIR spectrometer. The residual C content of all calcined powders were studied by the Elemental Analyzer (Perkin Elmer, 2400).

III. RESULTS

A. FT-IR Analysis

The Glycine exists as a neutral molecule in the gas phase while, it exists as a Zwitterion in solution and in the solid state[4]. It has ionized carboxyl group (COO-) and an amine salt (NH⁺). Further, glycine exhibits

polymorphism. It exist in three forms; stable α -, β - and the unstable γ -form[5]. Figure 1(a) shows FTIR of pure glycine. α and γ – glycine is identified by its broad peaks at 892.1 cm^{-1} however the extra peak at 910 cm^{-1} is characteristic peak of α - form. The spectrum of glycine show the presence of peaks in the NH⁺ stretching mode was found with broadband with after combustion were Phase purity and crystal structure of the obtained materials were determined by XRD. The patterns were recorded with standard (PHILIPS, Model: PW1710, Cu anode, 35 KV, 20mA) diffractometer using Cu-K α radiation with scanning multiple peaks between 3100-2600 cm^{-1}

IV. DISCUSSION

The C-H region of 910 cm^{-1} this suggests that Glycine (Fig.1) used is existing in α - form. The stretching vibrations were observed at 2917.5 cm^{-1} . A signal of 1651.9 cm^{-1} corresponds to NH⁺ deformation and 1520 cm^{-1} corresponds to symmetric deformation. Two signals at 1615 cm^{-1} and 1411.1 cm^{-1} were attributed to asymmetric and symmetric stretch modes of the COO- group. Other signal of deformation of the COO- mode was at 500.5 cm^{-1} .

This confirms that glycine exist in the zwitterion form in the crystals. Carboxylic acid does not coordinate when it is in its neutral state - COOH. The amino nitrogen coordinates only when it has a lone pair of electron, as it does in the -NH₂ state. It cannot coordinate when the amino group of the amino acid is in its protonated state, NH⁺.

Amino acid chelates are produced by reaction between α - amino acid and metal ions to form a ring structure. During chelation, the shape of amino acid ligand changes into a ring structure with the loss of hydrogen atom from the amine moiety.

The only way to prove that chelation has occurred is to identify the bonds between the metal and ligands i.e. to prove that the amino and carboxyl bonds are both present in the molecule. There is change in the amino moiety of the zwitterion amino acid when it changes from NH⁺ to NH₂ configuration, which is essential for chelation to occur. It results in a broad peak shift in the I.R spectra [6] where two bonding energies are important one that of carbon and other nitrogen.

When these two atoms participate in chelation, their energies changes due to their restricted movements. One

change which is observed in the spectrum, is the broadening of the peak at 3000 cm^{-1} . Figure 1 shows FTIR pattern of α -glycine, Figure 2 shows the molecular structure of chelate complex and Figure 3 shows the changes in FTIR spectra of powder obtained after the decomposition of nitrates from the $\text{C}_{0.8}\text{G}_{0.1}\text{Y}_{0.1}\text{O}_{1.9}$ solution having 0.5; 0.7; 0.8; 0.9; 1.0; bound to the metal. Chelation can be identified by examining the vibrational changes, which help to identify the bonds. Peak at 500.5 in glycine also diminishes as the carboxyl moiety participates in the chelate bond. As the amount of glycine increases, it is expected that glycine may form complex with Cerium.

In nanosized powders, the surface species absorption can compete with the absorption of bulk species. Therefore, the characterization of these powders cannot be complete without the identification of the surface chemical species. FTIR can be utilized to analyze the surface contamination. Typically, there will be contamination from CO_2 , water and hydrocarbons. Especially oxide surfaces that are always more or less hydrolyzed can easily absorb water molecules and CO_2 to form carbonate species. As synthesized particles of CGYO contain residual carbon content and when these powders were calcined at 700°C all powders were free from organics as evident from FTIR in Figure 3.

The mean crystallite size ranges from 7 to 21 nm showing that the method is effective for synthesis of nanosized powders. So the present study demonstrates the potentiality of GNP method to synthesize nanosized CGYO with emphasis mainly on to prove chelation and comparing samples for the organic content.

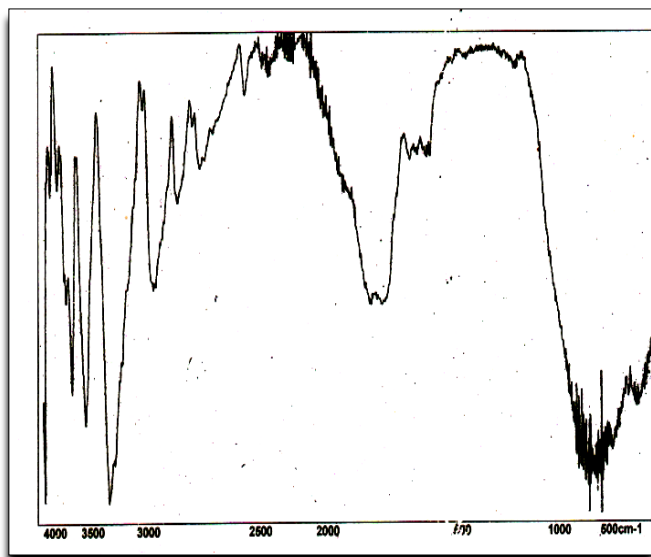


Fig. 1: FTIR pattern of α - Glycine

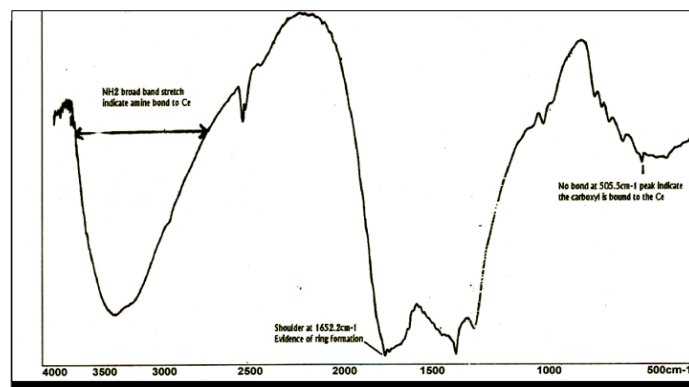


Fig. 2 : FTIR pattern of complex

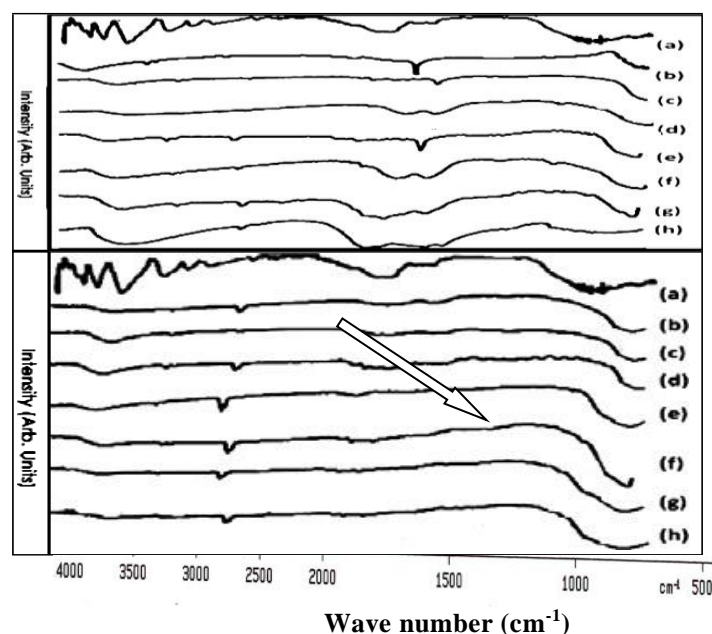


Fig. 3: FT-IR of complex of cerium with glycine, 0.5,0.7, 0.8, 0.9, 1.0, 1.2 and 1.4 mol uncalcined and calcined $\text{C}_{0.8}\text{G}_{0.1}\text{Y}_{0.1}\text{O}_{1.9}$

V. CONCLUSION

It is concluded that through bond analysis, (Ce)Metal-(Glycine)Amino acid chelation can be confirmed and chelation characteristics can be identified through FT-IR Spectroscopy. So in the course of the observation of bonds, in the complex, chelation can be identified and quantified.

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