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HEXAMINE COMBUSTION SYNTHESIS OF LANTHANUM NICKELATE

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ABSTRACT

This work presents the synthesis of $LaNiO_3$perovskite by simple combustion synthesis using hexamine as the fuel. The samples were characterized by X-ray Diffraction (XRD) and FT-IR. Inorder to identify the thermal decomposition and dissociation reactions, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed. The elemental analysis of the powder was assessed using Energy Dispersive X-ray analysis (EDS) technique. The morphological features of the powders were examined by Scanning Electron Microscopy (FESEM).

KEYWORDS: Combustion synthesis, Perovskite, X-ray Diffraction, Hexamine

INTRODUCTION

Perovskite type oxides are considered as promising materials because of their special chemical and physical properties than other oxide materials. These oxides have a general formula ABO_3 and contain both rare earth elements and 3-d transition metals in the +3 oxidation state where Ais the larger cation (M.A.Pena et al., 2001; I.V.Krylova 2002; P.Laccorre et al., 1991) and B is the smaller cation.Lanthanum Nickelate ($LaNiO_3$) exhibits very interesting properties and is used as cathodes, gas sensors , catalysts etc ...(P.Laccorre et al., 1991;M.S.Chenet al., 1996; R.N.Singh 1997; K.Barnard et al., 1990)

Conventionally, this compound is prepared by solid state reaction where the metal oxides are used as precursors and are ground to very fine mixture and subsequently sintered at very high temperature for longer duration to obtain a pure phase of lanthanum nickelate(S.K.Tuwarum et al., 1998; A.K.Norman et al., 1999). The final product in solid state processing results in larger particle sizes with inhomogenity. Inorder to reduce the reaction temperature and duration of sintering, many wet chemical methods have been tried such as co-precipitation method(G.HelenAnnal Therese et. al., 2005), sol-gel method (Tomas Grygar 1999) , molten salt synthesis (S.IgnatiusArockiam et. al., 2012) and combustion process (Yanping Wang et al., 2006). The objective of our investigation is to prepare nano-crystalline lanthanum nickelate powders by hexamine combustion process. Hexamine also called as hexa methylene tetramine, a heterocyclic organic compound widely used in organic synthesisis used as fuel. The combustion reaction can be represented as

$$(CH_2)N_4 + 10O_2 \longrightarrow 4CO + 2CO_2 + NO_2 + 6H_2O$$

Hexamine was used as a fuel for the preparation of lithium manganite ($LiMn_2O_4$) (A. Subramani et al. 2007), nano lithium nickelate particles (M. Kayavizhi et al., 2010), alumina nanofibres(Jiangqiang Wang et al., 2007), dispersed bimetallic carbides and nitrides(S. Chouziera et al., 2006) and borides(K, Amalajothi et al., 2008). To the best of our knowledge no one has made attempt to prepare pure crystalline lanthanum nickelate compound by combustion technique using hexamine as a fuel. Considering the importance of this material in advanced technological applications, we prepared

lanthanum nickelate compound using the above method.

EXPERIMENTAL

Nano powders of lanthanum nickelate were prepared by a wet chemistry route using nitrates of lanthanum and nickel.Hexamine was used as a fuel and a gelating agent. Initially aliquot amounts of analytical grade lanthanum nitrate ($LaNiO_3$) and nickel nitrate ($Ni(NO_3)_2.6H_2O$) were thoroughly mixed with hexamine. Then the mixture was dissolved in deionised water to obtain a precursor solution. The mixture solution was concentrated in a quartz crucible until the evaporation of free water and it ignites at high temperature. During ignition, a flame with copious gases was evolved from the reaction zone. Lanthanum Nickelate product was calcined at 800℃ for five hours using an electrical resistance furnace. After the completion of calcination, the samples were characterized by X-Ray diffraction (XRD) using Cu-Kαsource (Philips 8030 X-ray diffractor) FT-IR measurements were performed with a Perkin Elmer UK paragon-500 Spectroscope in the mid Infra-red region (4500-400 cm^{-1}). For each sample preparation approximately 2 mg of sample was dispersed in 300 mg of KBr powder and pressed into a pellet and used for the analysis. The elemental analysis of the powders using Energy Dispersive X-ray analysis (EDAX) techniques. This analytical tool was as attachment to the SEM (Scannning Electron Microscope) unit. The surface morphology was analysed by using a Scanning Electron Microscopy (JEOL-JSH-3.5(cf-Japan)). Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) of the assynthesized powders were carried out using a STA 1500 pl thermal sciences, version V4.30 analyser.

RESULTS AND DISCUSSIONS

TGA/DTA

The thermal behavior of the as-synthesized lanthanum nickelate compound was studied using thermogravimetry and differential thermal analysis. The TGA and DTA curves are shown in figure 1. The curve exhibit discrete regions of weight loss in the final product lanthanum nickelate compound from the amorphous powder. There is a gradual decrease in weight loss noticed between room temperature to 192.09 ˚C. Beyond this temperature, there is an enormous amount of loss in weight that has been observed upto 292.66 ˚C. The major weight loss in this region is attributed to the loss of water and dissociation of chemical compounds like oxides of nitrogen and carbon di oxide from the precursor and the fuel hexamine. Beyond this temperature, the loss in weight is found to be meagre indicating the transformation of amorphous powder into crystalline lanthanum nickelate compound. The DTA curve reflects the same information where an endothermic peak appeared at 257.30 ˚C indicates the chemical dissociation of inbound water molecules. An exothermic peak appeared at 261.38 ˚C specifically attributed to the decomposition reaction of hexamine and other nitrogen containing intermediates at that stage of the product formation process. The gradual decrease in DTA curve upto 800 ˚C exhibits the transformation into the final product crystalline lanthanum nickelate.

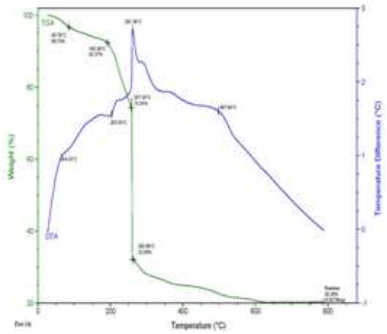

Figure 1: TGA/DTA Curves of lanio

X-Ray Diffraction (XRD)

The XRD patterns of synthesized nano powders of lanthanum nickelate exhibit sharp crystalline peak after calcinations at 800℃. It is shown in figure2. The as synthesized powders have shown sharp crystalline peak which reveals the completion of combustionreaction on the synthesis process. The analysis of this XRD data ascertains that the sample is single phased presenting orthorhombicperovskite crystal structure (A Jones et al., 2008; M. E. I. Baydi et al., 1995). The average crystalline size of the powders has been determined from the XRD pattern according to the Debye Scherrerequation(P.Ciambelli et al., 2001) and the lattice distortion calculated by the equation(Xiangting Dong et al., 1996)

$$2\omega^2\cos^2\theta = 4/\prod^2(\lambda/D)^2+32\varepsilon^2\sin^2\theta$$

Where θ – Diffraction angle, λ -X-ray wavelength equal to 0.154 nm, D-average crystal size calculated by scherrer equation, 2ω –Full Width at Half Maximum (FWHM in radian)

The variation of crystallinity of the synthesized lanthanum nickelate compound by the calcinations at different temperatures has been evaluated. It is noticed that the crystal size grows with the increase in calcination temperature. It is mainly because of the grain growth which occurs during the thermal treatment process. It has been represented in the form of graph by a straight line of lnDVs 1/T.

According to the Scott equation given below under the condition of homogenous growth of nano crystals (Huaming Yang et al., 2004) which approximately describes the growth rate of nanocrystals

$$D = C \exp (E/RT)$$

Where D is the crystal size, C is the constant, E is the activation energy for crystal growth, R is the ideal as constant and T is the absolute temperature.

There exists a linear relationship between lnD and 1/T. Accordingly E value could be derived from the slope of the straight line (E=41.9Kcal/mol). We can see that the growth of the $LaNiO_3$ nanocrystalheavily depend on the calcinations temperature.

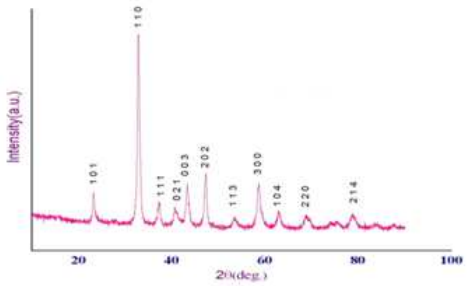

Figure 2: XRD Pattern of as Synthesized $LaNiO_3$ Compound

FT-IR Spectroscopy

The FT-IR spectrum is shown in figure 3. In this spectrum we could see 3 prominent bands and few weak bands at different wavelength region. From the FTIR spectrum, it has been observed that the strong frequency bands appeared at 1000-1550 cm^{-1} is responsible for the formation of lanthanum nickelate crystals. The bands appeared at 2374.50 cm^{-1} are responsible for La-O bands and a strong band at 2925.29 cm^{-1} are responsible for Ni-O bands. The other strong bands above 3000cm^{-1} represents the presence of inbound water molecules (Lacramioara Claudia Chioaru et al., 2008).

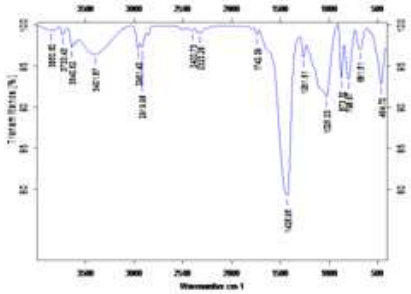

Figure 3: FT-IR Spectra of as-Synthesized $LaNiO_3$ Compound

Scanning Electron Microscopy

Scanning Electron micrographs of the synthesized lanthanum nickelate powders is shown in figure 4. It exhibits very fine agglomerated crystals with irregular morphology.

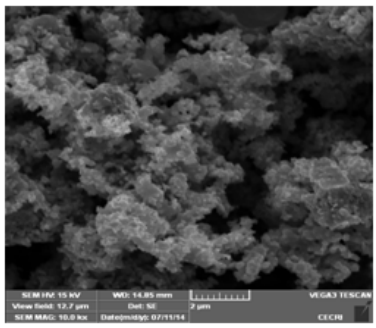

Figure 4: SEM Micrograph of as-Synthesized $LaNiO_3$ Compound

EDX Spectroscopy

Figure 5.shows the EDX spectrum of the as synthesized lanthanum nickelate compound.The spectrum shows the appropriate concentration of lanthanum, nickel and oxygen in the product. The spectrum affirms that the obtained product is pure without other impurity elements.

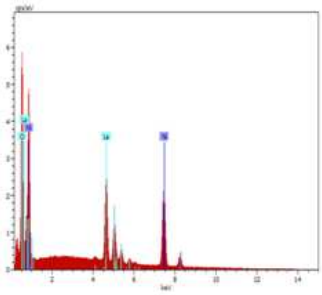

Figure 5: Energy Dispersive X-Ray Spectrum of $LaNiO_3$ Compound

CONCLUSIONS

$LaNiO_3$compound was successfully prepared by a comprehensive solution combustion synthesis technique. The TGA-DTA study discloses that the compound is formed at around 600 °C and the formation involves several exothermic reactions. XRD patterns and SEM micrographs divulge the formation of desired orthorhombic phase with the grain size in the range of nanometers. The EDS spectrum declares that the obtained product does not contain any impurities. The FTIR spectrum shows the characteristic vibration modes of $LaNiO_3$.

REFERENCES

1. M.A.Pena andJ.L.G.Fierro, *chem.rev.* **101,** 1981 (2001).
2. I.V.Krylova,*Russ .chem.bell.Int.Ef.*,**51**, 46 (2002).
3. P.Laccorre, J.B.Torrance, J.pannmetier, A.I.Nazzel, P.W.Wang and T.C.Huang ,*j.solid state chem.*, **91** 225 (1991).
4. M.S.Chen ,T.B.Wu and J.M.Wu, *Appl.Phys.Letts.*,**1430** (1996).
5. R.N.Singh.*Int.J.Hydrogen Eng.***22**, 557(1997).
6. K.Barnard, T.Fogger, R.D.turney and J.Williams ,*j.catal.*, **125,**265 (1990).
7. S.K.Tuwarum ,J.K.Koenig , G.Poiloerat , P.Chartier andR.N.Singh , *J.Appl.Electrochem*., **28,** 114 (1998).
8. A.K.NormanandM.A.Morris ,*J.Mater.process.technol.*,**92,**91 (1999).
9. G.HelenAnnalTherese ,M.Dinamani andP.VishnuKemath ,*J.Appl. Electrochem*.,**35**, 459 (2005).
10. Tomas Grygar ,*J. Solid State. Electrochem*.,3, 412 (1999).
11. S.IgnatiusArockiam, L.JohnBerchmans, S.Angappan,A.Visuvasamand V. Mani, *Materials science forum.*,**699**, 67 (2012).

12. Yanping Wang, JunwuZhu ,Xufie Yang , Lude Lu and Xin Wang. *Material research bulletin.*,**41,** 1565 (2006).
13. Subramani.A, Angayarkanni .N and Vasudevan.T ,mater. *Chem. Phys*., **102**,19 (2007).
14. M.kayavizhi and L.JohnBerchmans ,*e.journal of Chemistry*.,**7(S1)**,S137 (2010).
15. JiangqiangWang ,Youzhen Wang , MinghuaWiao , Songhai Xie and Kangnian Fan , *Lett*., **61**,5074 (2007).
16. S. Chouziera , P. Afanasiev ,M. Vrinata, T. Cserio and M. Roy-Auberger, *J solid State Chem*.,**179**,3314 (2006).
17. K. Amalajyothi and L. JohnBerchmans , *Int J Self-Propagating high Temperature synthesis.*,**74**, 218 (2008).
18. A jones andH.S.Islam, *J.Phys. Chem.C.*,**112,**4455 (2008).
19. M. E. I. Baydi, S. K. Tiwari, R. N. Singh, J. L. Rebspringer , P. Chartier, J. F. Koenig and G. Poillerat, *J. Solid State Chem*., **116**, 157-169 (1995).
20. P.Ciambelli , S. Cimino, S. De Rossi, M, L. Lisi, G.Minelli, I, P. Porta and G.Rosso, *Appl. Catal.B: Environ*., **29**, 239 (2001)
21. Xiangting Dong, Guangyan Hong and Decai Yu, *J. Inorg. Mater.*, **11,** 542 (1996).
22. Huaming Yang, XianghaoZhang ,WeiginAo , GuanghouQiu, *Mater. Res. Bull.*, **39,** 833 (2004).
23. Lacramioara Claudia Chioaru, IoanaJitaru and Mariana Bicher, *U.P.B. Sci. Bull., Series B.*, **70,** 1 (2008).