

EFFECT OF FUELS ON THE COMBUSTION SYNTHESIS OF NiAl_2O_4 SPINEL PARTICLES

K. Christine Stella and A. Samson Nesaraj*

* drsamson@karunya.edu

Received: February 2010

Accepted: June 2010

Department of Chemistry, Karunya University (Karunya Institute of Technology & Sciences), Coimbatore 641 114, India.

Abstract: Spinel constitute an advanced group of materials with great technological appeal, being able to be applied as magnetic materials, semiconductors, pigments, catalysts, refractories and electronic ceramics. In this paper, we reported the preparation of NiAl_2O_4 spinels by low temperature combustion technique using glycine and urea as fuels. The resulting powder was characterized by XRD, particle size analysis and SEM. The XRD patterns show that the combustion technique was excellent to prepare single – phased cubic NiAl_2O_4 particles and the crystallite sizes were found to be around 14 nm. From the particle size analysis, it was found that the 50 % of the particles lie below 30 μm . The micrographs show the formation of fluffy agglomerates composed of fine particles.

Keywords: Nickel Aluminate Spinel, Combustion technique, Characterization

1. INTRODUCTION

Oxide spinels have been investigated in the solid state sciences of their usefulness as pigments, refractory, catalysts and electronic ceramics [1]. Interest in the synthesis of spinels like NiAl_2O_4 has increased due to its excellent strength and good wettability with metals at high temperature, besides the general merits spinel materials have. In particular, the nickel aluminate can be used as a good ceramic skeleton for infiltration of metals at high temperature [2]. Several preparation methods have been studied to obtain crystalline nickel aluminate spinels with small particle size, such as sol gel synthesis [3-4], sonochemical method [5], microwave heating [6], polymer solution route [2] and solid state reaction [7]. The sol – gel method provides powder with small particle size and high surface area, however, this method releases dangerous gases which require care during processing. The solid state reaction needs very high temperature for sintering and larger powder time consumption; also, the powder produced has low surface area which is undesirable, for instance, in catalyst materials. The advantage of the solution combustion technique is the quasi-atomic dispersion of the component cations in liquid precursors, which facilitates synthesis of the crystallized powder with low particle size and high purity at low temperatures.

In this study, nickel aluminate spinels were synthesized by the solution combustion technique using fuels urea and glycine, and the characteristics of the synthesized powders were examined and discussed.

2. EXPERIMENTAL PROCEDURE

In recent years, solution combustion technique has come up as a quick preparation method to produce homogeneous, very fine crystalline ceramic powders, without the intermediate decomposition steps. NiAl_2O_4 spinel particles have been prepared by solution combustion technique using glycine and urea as fuels. Based on the theory proposed by Jain et.al, the stoichiometric compositions of the redox mixtures for the combustion were calculated using the total oxidizing (O) and reducing (F) valencies of the components which serve as the numerical coefficients for the stoichiometric balance, so that the equivalence ratio, Φ_c (i.e., $\text{O:F} = 1$) is unit and the energy released by the combustion is maximum [8]. Based on the propellant chemistry, the species Ni^{2+} , Al^{3+} , C and H are considered to be reducing species with corresponding valencies +2, +3, +4 and +1. Elemental oxygen is considered to be an oxidizing species with valency -2. The valency of nitrogen is considered to be zero [9]. Based on these considerations, nickel nitrate and

aluminium nitrate will have the oxidizing valencies of – 10 and – 15 respectively. The fuels such as, urea and glycine will have the reducing valencies of + 6 and + 9 respectively [10].

In a typical experiment, stoichiometric amounts of nickel nitrate and aluminium nitrate were dissolved in minimum quantity of distilled water along with appropriate quantity of urea / glycine (fuel and complexant). The complexation of metal ion by the metal molecule increases the solubility of metal ion in solution. A stoichiometric composition denotes a fuel (urea or glycine) to metal nitrate ratio at which the fuel can react completely with all of the metal nitrates in the mixture, in such a way that no residual fuel or nitrate remains in the product materials [11]. The mixed solution was heated in a mantle at around 80 – 90 °C and the volume was reduced to one half. Afterwards, the resulting solution was introduced into a muffle furnace maintained at 600 °C. Initially the solution foils boils and undergoes dehydration followed by decomposition with evolution of gases (N_2 and CO_2). Then, it burns to yield voluminous and foamy homogeneous residue [12]. During the burning reaction, the flame temperature is reported to be above 1000 °C [11]. The gases evolved not only yield fine particles of $NiAl_2O_4$ but also help to dissipate the heat which inhibits sintering of the product. Thus, combustion reaction was completed within a few minutes. The foam was then lightly ground in agate mortar with pestle to obtain fine particles. The flow chart for the preparation of $NiAl_2O_4$ is given in Figure 1. The stoichiometric proportion of precursor materials used for the synthesis of $NiAl_2O_4$ spinels is indicated in Table 1.

The stoichiometric redox reactions between metal nitrates and glycine or urea to product $NiAl_2O_4$ spinels can be represented by the

following theoretical equations.

To prepare $NiAl_2O_4$ as urea as fuel (No. 1) :



To prepare $NiAl_2O_4$ as glycine as fuel (No.2):

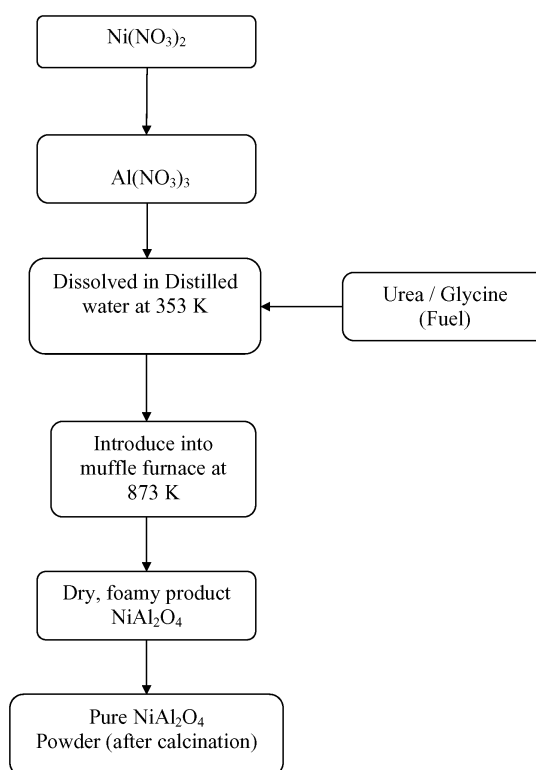
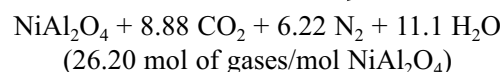
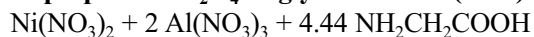


Fig. 1. Flow chart for the preparation of $NiAl_2O_4$ powder by combustion synthesis

Table 1. Stoichiometric proportion of the precursor materials used for the synthesis of $NiAl_2O_4$ powder

| Weight of $Al(NO_3)_3$ (g) | Weight of $Ni(NO_3)_2$ (g) | Weight of glycine (g) | Weight of urea (g) | Weight of as synthesized $NiAl_2O_4$ powder (g) | % weight loss at 800° C |
|----------------------------|----------------------------|-----------------------|--------------------|---|-------------------------|
| 8.52 | 3.66 | 4.16 | – | 1.9685 | 1.05 % |
| 8.52 | 3.66 | – | 5.0 | 2.0208 | 2.34 % |

The as-synthesized powder was carried out in clean alumina crucibles and calcined in air at 800°C for 4 hours to remove the deposited carbon and the unreacted organic residues and to get phase pure compound [13]. Calcination of the as-synthesized powder implies a very significant weight loss (1 - 2%). The calcination data is indicated Table 1. The powder XRD study was carried out using a Shimadzu XRD6000 X-ray diffractometer at a scan speed of 5 deg/min using $\text{CuK}\alpha$ radiation. The crystallite sizes of the ceramic powders were calculated by Scherrer's formula. The particle size of the powder was measured using a Horiba Laser Scattering Particle Size Analyzer (LA-910) using triple distilled water as medium. A Horiba LA-910 laser diffraction analyzer was used to measure the average particle size of the oxide materials. The morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Role of Fuels on the Mechanism of Product Formation

It is well recognized that the fuel is an important component for the preparation of oxides by combustion synthesis. Urea and glycine are the most popular and attractive fuels for producing highly uniform, complex oxide ceramic powders with precisely controlled stoichiometry. The mechanism of formation NiAl_2O_4 with fuels such as urea and glycine is indicated below.

Mechanism of product formation when urea as fuel:

When a mixture of nickel nitrate, aluminium nitrate and urea with required stoichiometry is heated rapidly at 600 °C, it undergoes melting and dehydration in the first 2 minutes. Later it decomposes with frothing as a result of the formation of $\text{Ni/Al(OH)(NO}_3)_2$ gel along with other products like urea nitrate, biuret, HNCO , and NH_3 . This mixture then foams due to the generation of gaseous decomposition products as intermediates, leading to enormous swelling. The gaseous decomposition products are a

mixture of nitrogen oxides, NH_3 , and HNCO . These gases are known to be hypergolic in contact with each other. The foam could be made up of polymers like cyanuric acid, polymeric nitrate, etc. which are combustible. In the third minute, the foams breaks out with a flame because of the accumulation of the hypergolic mixture of gases. With an insitu temperature build up of greater than 1000 °C the whole foam further swells and burns to incandescence. At such high insitu temperature the foam decomposes to yield NiAl_2O_4 (the high temperature form). This mechanism is proposed based on the reported literature for the preparation of α - Alumina particles [14].

Mechanism of product formation when glycine as a fuel:

The glycine fuel serves two purposes in the preparation of NiAl_2O_4 in the combustion process: first, it complexes the metal cations (Ni and Al), increasing their solubility and preventing selective precipitation as the water evaporates: and secondly, it serves as fuel for combustion, being oxidized by the nitrate anions and by oxygen from the air. The glycine molecule has a carboxylic acid group at one end and one amine group at the other end. Possibly the cations (Ni and Al) are largely complexed by the carboxylic acid end and by the amine group. Water molecules in the cation's coordination sphere are replaced by the amine-ends of the glycine molecules. The number of glycine molecules which join the transition metal's coordination sphere is dependent upon the ratio of glycine to cations in the solution. Complexation prevents the metal salts (nickel nitrate and aluminium nitrate) from precipitation at low water concentrations. When the solution is boiled down until its viscosity increases to a honey-like consistency, the concentrated solution has amorphous structure with the cations intimately mixed on a molecular scale. As the last water is evaporated, the solution begins to swell, forming a viscous foam. The foam ignites spontaneously to yield ash (fine) particles of NiAl_2O_4 . The above mechanism is proposed as per the reported literature for the preparation ceramic oxides by glycine nitrate combustion method[15].

4. XRD STUDIES OF NiAl_2O_4 POWDER

Figure 2 and 3 show the XRD patterns obtained for NiAl_2O_4 powder prepared by combustion synthesis using urea and glycine as fuels and calcined at 800 °C for 4 hours. All the peaks in the XRD pattern are very sharp showing the well crystalline behaviour of the heat treated powders. The XRD patterns of NiAl_2O_4 powder are compared with the reported data. The identified phases present in the patterns of NiAl_2O_4 are of cubic spinel-type (ICDD: 71-0963). Two impurity phases at $2\theta = 44.96$ and 62.98 (which are marked with asterisks) were observed in the NiAl_2O_4 powder prepared using urea as a fuel, however, no impurity phases were detected in the XRD pattern of NiAl_2O_4 powder prepared using glycine as a fuel. From the XRD data, it was found that full crystallization of NiAl_2O_4 could be achieved by combustion synthesis process using glycine as fuel. Jeevanandam et.al. prepared single phase NiAl_2O_4 spinel by sonochemical method at 950°C for 14 hours [5]. Also, it was reported that NiAl_2O_4 powder is prepared by a solid state reaction after prolonged heat treatments [16]. It was found that the 'd' values agreed well with the standard values [16]. The lattice parameters are calculated from 2θ peaks in the XRD pattern.

The unit cell volumes calculated for NiAl_2O_4 remained almost equal. The theoretical density has been calculated using the lattice parameters with formula [18].

$$D_{\text{th}} = z \frac{M}{N \times V}$$

where 'M' (in atomic-weight units) is the mass of one unit of the chemical formula, 'z' is the number of such chemical units in one unit cell of the crystal, 'N' is the Avagadro's number and V (in \AA^3) is the volume of the crystalline unit cell as determined by X-ray diffraction. These values were also agreed well with the reported data. The crystallite sizes of the NiAl_2O_4 powder have been calculated from the XRD peak intensity analysis using Scherrer formula [19].

$$D = z \frac{0.9 \lambda}{\beta \cos \theta}$$

where 'D' is crystallite size in nm, ' λ ' is the radiation wavelength (for $\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$), ' θ ' is the diffraction peak angle and ' β ' is the broadening of the line ("half width") measured at half its maximum intensity (in radians). The crystallite sizes calculated for NiAl_2O_4 are small ($\sim 14 \text{ nm}$). The crystallographic parameters obtained on NiAl_2O_4



Fig. 2. XRD pattern obtained for the NiAl_2O_4 powder prepared by combustion synthesis using urea as a fuel

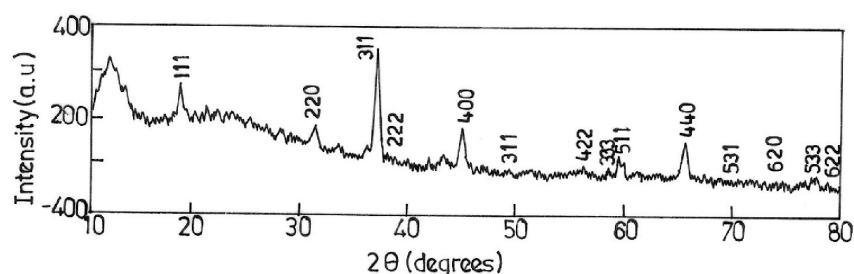


Fig. 3. XRD pattern obtained for the NiAl_2O_4 powder prepared by combustion synthesis using glycine as a fuel

Table 2. Crystallographic parameters obtained on NiAl_2O_4 powder

| S. No. | Properties | Standard XRD data for NiAl_2O_4 powder [15] | XRD data of NiAl_2O_4 powder prepared with urea as a fuel | XRD data of NiAl_2O_4 powder prepared with glycine as a fuel |
|--------|---|---|---|--|
| 1. | Crystal structure | Cubic | Cubic | Cubic |
| 2. | Unit cell parameter (\AA) | $a = 8.0462$ | $a = 8.0499$ | $a = 8.0367$ |
| 3. | Unit cell volume (\AA^3) | 520.922 | 521.641 | 519.079 |
| 4. | Theoretical density (g/cm^3) | 3.0249 | 3.0252 | 3.0107 |
| 5. | Crystallite size(nm) | - | 14.83 | 14.23 |

Table 3. Particulate properties obtained on NiAl_2O_4 powder

| Sl. No. | Sample | Bulk density (g/cc) | Tap density (g/cc) | Mean particle diameter (μm) | Median particle diameter (μm) |
|---------|--|---------------------|--------------------|--|--|
| 1. | NiAl_2O_4 powder prepared with urea as a fuel | 0.6315 | 0.8900 | 30.922 | 110.330 |
| 2. | NiAl_2O_4 powder prepared with glycine as a fuel | 0.1719 | 0.2772 | 24.419 | 107.840 |

powder are indicated in Table 2. It was found that the crystallographic properties obtained for the NiAl_2O_4 powder are in good agreement with the reported data [17].

5. PARTICULATE PROPERTIES

5. 1. Density Measurements

The bulk and tap density values of NiAl_2O_4 powder were measured as described in literature [20] and the data is presented in Table 3. From the density data, it is drawn that the NiAl_2O_4 powder is fluffy and fine [21].

5. 2. Particle Size Measurements

The particle size distribution curves of NiAl_2O_4

powder prepared with urea and glycine as fuels are indicated in Figures 4 and 5. The frequency percentage is on the left hand side of the plot indicated by the line. The % on the right hand side of the plot corresponds to the particle distribution (histogram) indicated by the bars. The particle characteristics of NiAl_2O_4 from particle size analysis is presented in Table 3. In which, median particle diameter represents the particle diameter equal to 50 % of the cumulative distribution and mean particle diameter represents the arithmetically averaged value of the frequency distribution. From the curve (Fig. 4), it was clear that the particles lie between $0.087 \mu\text{m}$ to $592.4 \mu\text{m}$. Also, it was found that 30 % of the particles are present below $19.264 \mu\text{m}$, 50 % of the particles are having the particle size less than $30.922 \mu\text{m}$ and 90% of the particles are having the particle size less than

**Fig. 4.** Particle size pattern obtained for the NiAl_2O_4 powder by combustion synthesis using urea as a fuel

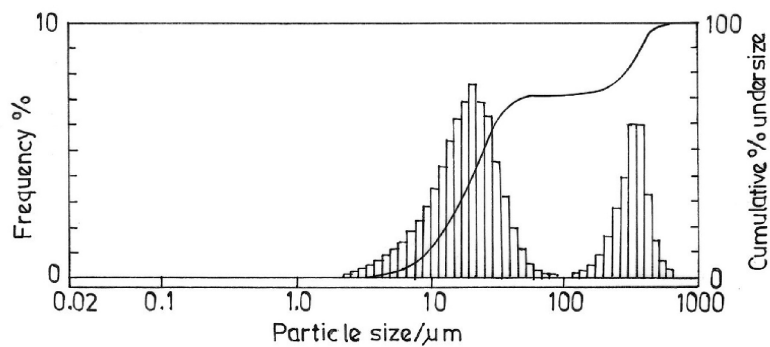


Fig. 5. Particle size pattern obtained for the NiAl_2O_4 powder by combustion synthesis using glycine as a fuel



Fig. 6 (a-h) SEM pictures obtained on NiAl_2O_4 powder synthesized by combustion synthesis using urea as a fuel

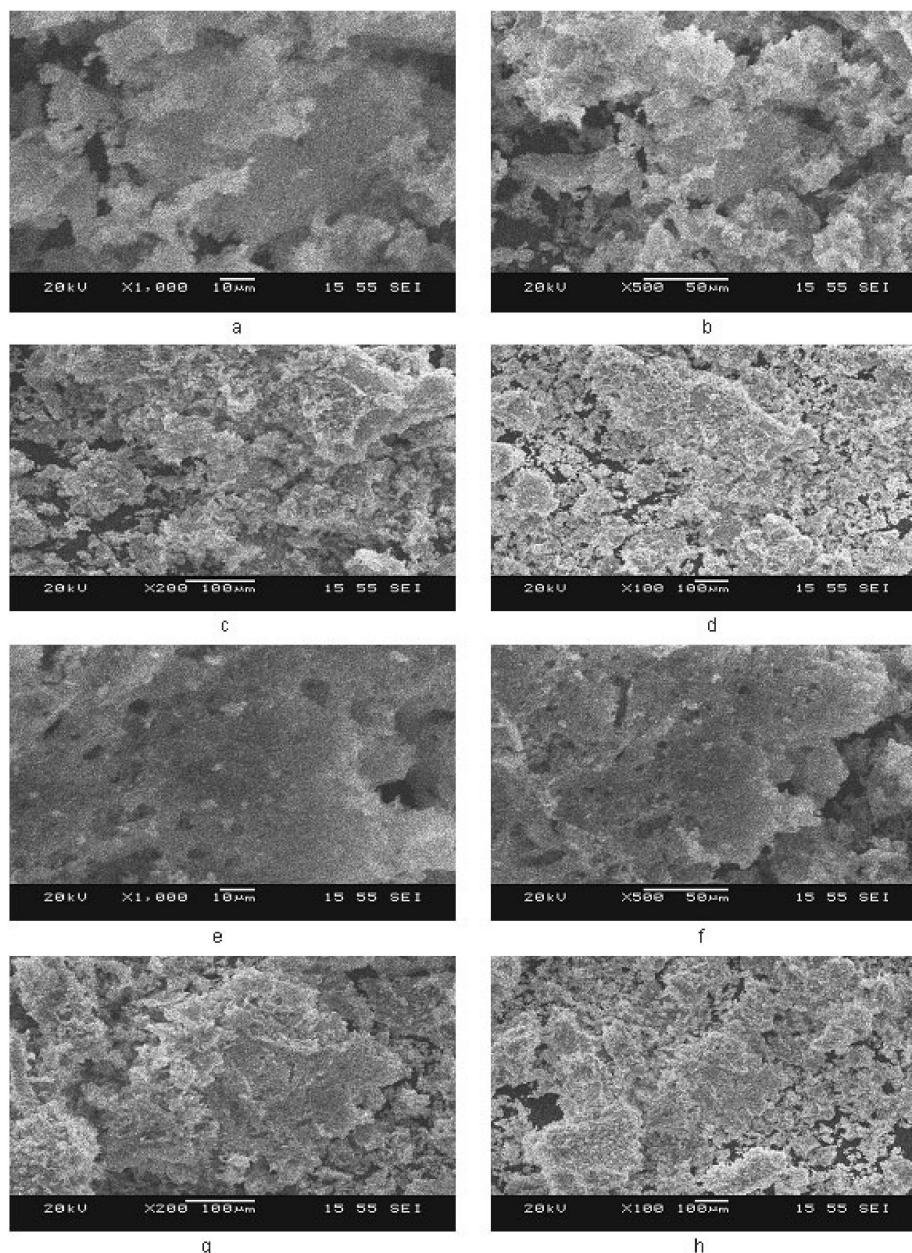


Fig. 7 (a-h) SEM pictures obtained on NiAl_2O_4 powder synthesized by combustion synthesis using glycine as a fuel

287.236 μm . From the curve (Fig. 5), it can be seen that the NiAl_2O_4 particles are found in the range between 0.058 to 678.5 μm . Also, it was found that 50 % of the particles are present below 24.419 μm . The larger particle size (> 300 μm) of NiAl_2O_4 powder was due to the agglomeration of particles at high temperatures treatment [22]. From the particle characteristics data, it was found that the NiAl_2O_4 powder prepared with glycine as fuel is found to be finer than the powder prepared with

urea as a fuel, the same phenomena was reported earlier in literature for the preparation of $\text{Li}_2\text{CoMn}_3\text{O}_8$ [23].

6. SCANNING ELECTRON MICROSCOPIC STUDIES

It was reported that combustion synthesis produces particles of a very uniform size [24]. The SEM pictures of the NiAl_2O_4 powder reveals agglomerated, porous and flaky morphologies of

particles [25]. It was reported that the flame temperature is responsible for agglomeration in ceramic oxides [26] and the evolution of large amount gaseous products during combustion produces highly porous voluminous powders [27]. Figures 6 and 7 show the microstructures of NiAl_2O_4 powder synthesized using urea and glycine as fuels. The SEM micrographs of NiAl_2O_4 powder exhibit flaky morphology as reported [28]. Fig. 6 reveals the presence of interconnecting grains in the NiAl_2O_4 powder. Larger particles were also seen in the powder prepared with urea as a fuel. Fig. 7 shows the fluffy and foamy like morphology found in the powder prepared with glycine with fuel. In the literature, the observed particle size differences / microstructure of oxides prepared by solution combustion technique using various fuels is usually explained based on the differences in the number of moles of gases liberated during the reaction. In our case, it is found that 30.64 and 26.20 moles of gases liberated when urea and glycine are used as fuels in the combustion process. The marked difference in particles size and dissimilar microstructure of NiAl_2O_4 prepared with two different fuels may be due to the evolution of gases during the combustion reaction and eventually which alters the properties of the combustion product. Also, it is clear that the nature and course of the decomposition products of the fuel and oxidiser appear to control the combustion behavior. In our case, the glycine process yields oxides with low particle size, because of the formation of stable product during combustion without much sintering as reported earlier [29].

6. CONCLUSION

Combustion synthesis of NiAl_2O_4 spinel particles using urea and glycine as fuels are dealt with. The powder XRD data obtained on NiAl_2O_4 powder are in good agreement with the standard reported data. However, the powder prepared with urea as fuel has few impurity peaks. The particulate properties obtained on NiAl_2O_4 powder suggest that the as-formed materials are porous. The SEM pictures show the presence of fluffy morphology found in the powder. Based on

the physical characterization of the powder, it is concluded that combustion synthesis with glycine as fuel can be used effectively to produce fine NiAl_2O_4 spinel particles.

ACKNOWLEDGEMENT

ASN thanks Karunya University for promoting this research activity.

REFERENCES

1. Gama, L., Ribeiro, M. A., Barros, B.S., Kiminami, R.H.A., Weber I.T. and Costa, A.C.F.M., *Synthesis and characterization of the NiAl_2O_4 , CoAl_2O_4 and ZnAl_2O_4 spinels by the polymeric precursors method. J. Alloys and Compds.*, 2009, 483, 453.
2. Kim, J.W., Shin, P.W., Lee, M.J. and Lee, S.J., *Effect of particle size on the strength of a porous nickel aluminate fabricated by a polymer solution route. J. Ceramic Processing and Research*, 2006, 7, 117.
3. Arean, C.O., Mentruit, M. P., Lopez, A.J., and Parra, J.B., *High surface area nickel aluminate spinels prepared by a sol-gel method. Colloids and Surfaces A: Physicochemical and Engg. Aspects*, 2001, 180, 253.
4. Meyer, F., Hempelmann, R., Mathur, S. and Veith, M., *Microemulsion mediated sol-gel synthesis of nano-scaled MAl_2O_4 ($\text{M}=\text{Co}, \text{Ni}, \text{Cu}$) spinels from single-source heterobimetallic alkoxide precursors. J. Mater. Chem.*, 1999, 9, 1755.
5. Jeevanandam, P., Kolytyn Yu and Gedaanken, A., *Preparation of nanosized nickel aluminate spinel by a sonochemical method. Materials Science and Engineering B*, 2002, 90, 125.
6. Mohammadpour Amini, M. and Torkian, L., *Preparation of nickel aluminate spinel by microwave heating. Materials Lett.*, 2002, 57, 639.
7. Yamakawa, A., Hashiba, M. and Nurishi, Y., *Growth of zinc aluminate on the surfaces normal to the various crystal axes of an alumina single crystal. J Mater. Sci.*, 1989, 24, 1491.
8. Jain, S. R., Adiga, K. C. and Pai Vernekar, V.R., *A new approach to thermochemical calculations of condensed fuel-oxidizer mixture. Combustion and Flame*, 1981, 40, 71.
9. Purohit, R. D., Sharma, B. P., Pillai, K. T. and

- Tyagi, A. K., *Ultrafine ceria powders via glycinenitrate combustion. Mater. Res. Bull.*, 2001, 36, 2711.
10. Tanu Mimani, Fire synthesis: Preparation of alumina products. *Resonance*, 2000, 5, 50.
11. Kingsley, J. J., Manickam, N. and Patil, K.C., *Combustion synthesis and properties of fine particle fluorescent aluminous oxides. Bull. Mater. Sci.*, 1990, 13, 179.
12. Samson Nesaraj, A., Arul Raj, I. and Pattabiraman, R., *Synthesis and characterization of LaCoO₃ based cathode and its chemical compatibility with CeO₂ based electrolytes for Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC). Ind. J. Chem. Tech.*, 2007, 14, 154.
13. Kumar, M., Arul Raj, I. and Pattabiraman, R., *Y₂Zr₂O₇ (YZ)-pyrochlore based oxide as an electrolyte material for intermediate temperature solid oxide fuel cells (ITSOFCs)—Influence of Mn addition on YZ. Mater. Chem. Phys.*, 2008, 108, 102.
14. Chemistry of nanocrystalline oxide materials: Combustion synthesis, properties and applications, ed. Patil, K.C., Hegde, M.S., Rattan, T., and Aruna, S.T. World scientific publishing co. private limited, Singapore, pp. 46 – 47
15. Samson Nesaraj, A., 'Studies on materials and components for the Intermediate Temperature Solid Oxide Fuel Cells (ITSOFC)' Ph.D. Thesis, Alagappa University, India, October 2002.
16. Kou, L. and Selman, J.R., *Electrical conductivity and chemical diffusivity of NiAl₂O₄ spinel under internal reforming fuel cell conditions. J. Applied Electrochem.*, 2000, 30, 1433.
17. Downs, R.T., Bartelmehs, K.L., Gibbs, G.V., and Boisen, M.B., Jr. *Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. American Mineralogist*, 1993, 78, 1104.
18. Christine Stella, K. and Samson Nesaraj, A., *Low Temperature soft chemical synthesis of bright blue CoAl₂O₄ spinel particles. J. Nep. Chem. Soc.*, 2010, 25, 62.
19. Shaji Kumar, M.D., Srinivasan, T.M., Ramasamy, P., and Subramanian, C., *Synthesis of lanthanum aluminate by a citrate-combustion route. Mat. Lett.*, 1994, 25, 171.
20. Munro, R. G., Malghan, S. G., Hsu, S. M., *Variances in the measurement of ceramic powder properties. J. Res. Natl. Inst. Stand. Technol.*, 1995, 100, 51.
21. Dhak, D. and Pramanik, P., *Particle size comparison of soft-chemically prepared transition metal (Co, Ni, Cu, Zn) aluminate spinels. J. Amer. Ceram. Soc.*, 2009, 89, 1014.
22. Chun-bo Liu, Lian-sheng Yu, Xian-liang Jiang, *Particle growth mechanism of nanocrystalline zirconia powder during high temperature heat treatment. Trans. Nonferrous Metals Soc. China*, 2007, 17, 1022.
23. Kalaiselvi, N., Ashok Kumar, M., Prasath, M. S., Renganathan, N.G., Raghavan, M. and Muniyandi, N., *Evaluation of fuels for the synthesis of Li₂CoMn₃O₈. Ionics*, 2002, 8, 447.
24. Hiroyuki Ishikawa, Kouya Oohira, Tatsuo Nakajima, Tomohiro Akiyama, *Combustion synthesis of SrTiO₃ using different raw materials. J. Alloys and Compds.*, 2008, 454, 384.
25. Auger, M.A., Savoini, B., Muñoz, A., Leguey, T., Monge, M.A., Pareja, R. and Victoria J., *Mechanical characteristics of porous hydroxyapatite/oxide composites produced by post-sintering hot isostatic pressing. Ceramics International*, 2009, 35, 2373.
26. Wey, C., Powell, E. A. and Jagoda, J. I., *The Effect of Temperature on the Sooting Behavior of Laminar Diffusion Flames, Combustion Science and Technology*, 1984, 41, 173.
27. Dinesha, M.L., Jayanna, H.S., Mohanty, S. and Ravi, S., *Structural, electrical and magnetic properties of Co and Fe co-doped ZnO nanoparticles prepared by solution combustion method. J. Alloys and Compds.*, 2010, 490, 618.
28. Aruna, S.T. and Rajam, K.S., *Mixture of fuels approach for the solution combustion synthesis of Al₂O₃-ZrO₂ nanocomposite. Mater. Res. Bull.*, 2004, 39, 157.
29. Lenka, R.K., Mahata, T., Sinha, P.K. and Tyagi, A.K., *Combustion synthesis of gadolinia-doped ceria using glycine and urea fuels. J. Alloys and Compds.*, 2008, 466, 326.