

## **Combustion Synthesis of Nanocrystalline Al<sub>2</sub>O<sub>3</sub> Powder using Aluminium Nitrate and Urea as reactants—influence of reactant composition**

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### **ABSTRACT**

*Combustion synthesis technique for synthesis of Aluminium oxide using urea as fuel and Aluminium Nitrate as an oxidizer is found to be easy & economical route & is able to produce Nano phase alumina powder. In present experiment urea is found to have outstanding potential towards solution combustion. Exothermicity is excellent and exothermic flame temperature increase with increase in oxidizer/ fuel ratio. A well defined crystalline structure and Nano scale particles size found after XRD and SEM analysis. Overall Urea-Nitrate combustion synthesis has an outstanding potential for producing pure Alumina powder. Crystallinity is excellent in case of urea, which leads to use in applications require high strength crystalline material.*

**Keywords:** Metal oxide, ceramic oxides, Combustion synthesis, SHS (Self propagating high temperature synthesis), Solution Combustion, Nano-ceramics.

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### **INTRODUCTION**

As is known, most of the conventional ceramics productions follow the classical processes of powder metallurgy - the sintering process for inert powders at high temperatures giving consolidated materials. For this to achieve, the other processes involving various pre treatment are being used in industry – plasmochemical synthesis and sputtering, hot uniaxial pressing, hot isostatic pressing in gasostats (HIP), gas-phase deposition (PVD and CVD), etc [1]. A common feature observed in all these processes is the strong external heating to accelerate processing. Because of this heating mechanism, the ceramic technologies are regarded as energy intensive ones. In recent years, a new approach based on the utilization of highly calorific charges and setting-up an auto wave mode by a local initiation became popular. As a result, inorganic materials (including ceramics) can be synthesized due to the layer-by-layer self-heating to high temperatures by utilising internal energy. The auto wave propagation mode is confirmed by heat transfer from hot to cold combustion material (reactants). The process is characterized by a distinctly defined combustion front progressing through a charge and thus converting it to final products (i.e. - chemical compounds, materials). These processes are commonly known as Self Propagating High Temperature Synthesis (SHS).

The solution combustion (SC) route to preparing metal oxide is a fairly recent development compared to SSC or SHS techniques. Now a day, Solution Combustion is being used all over the world to prepare oxide materials for a variety of applications. During last 10-15 years of SC (solution combustion) synthesis history, so many papers on SC of oxides have been published. There are many oxide materials prepared by rapidly heating aqueous solutions containing stoichiometric amounts of respective metal nitrate (oxidiser) and fuels like urea, hydrazides (carbohydrazide (CH), oxalyl dihydrazide (ODH), malonic acid dihydrazide (MDH), tetra formal tris azine (TFTA)[2]. Solution Combustion involves two steps:

- (i) Generation of heat of combustion, and
- (ii) Gas evolution.

Flame temperature helps in crystallization and formation of the desired final phase. However, a very high flame temperature can adversely affect the internal characteristics of powder like increase in the crystallite size, formation of hard agglomerates and thereby reduction in the surface area and sinterability [3]. The exothermicity ( $T_{ad}$ ) of the redox reaction varies from 1000 to 1800 K. Depending upon the fuel and also on nature of combustion differs from flaming to non-flaming. Among the fuels used and their applications. Not surprisingly, urea occupies the centre stage, probably due to its high exothermicity during solution combustion process [21-22]. Most of the oxides prepared by the urea method are alumina-based e.g.  $\alpha$ - $\text{Al}_2\text{O}_3$  products. Another development in alumina synthesis by the urea process is the preparation of Nano size  $\alpha$ - $\text{Al}_2\text{O}_3$  by microwave initiated SC. In short, recent investigations on SC have led to the preparation of Nano phase materials [15-20]:

- (a) With precursors like metal acetates and UREA/Glycine, one can control combustion and prepare nano phase oxides.
- (b) Combustion can be started by microwave, which yields uniform, narrow size distribution products.
- (c) Carcinogenic hydrazine-based hydrazide fuels can be avoided.

### Alumina

Alumina is the widely used metal oxide ceramic. It has wide range of applications including spark plugs, abrasion resistant tiles, tap washers, seals, electronic substrates, grinders, cutting tools, bio-ceramics, (hip-joints), body armour, laboratory ware and wear parts for the textile and paper industries. Very large tonnages are also used in the manufacture of monolithic and refractories. It is also used mixed with other materials such as flake graphite where even more severe applications are envisaged, such as pouring spouts and sliding gate valves.[25-26]

### Experimental:

#### MATERIALS AND METHODS

##### [a] Aluminium Nitrate non-hydrate (GR)

Symbol-	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Molecular Weight-	375 g/mole
Solubility in distilled water-	637g/litre at 25 <sup>0</sup> C
Oxidising-reducing valency-	-15

##### [b] Urea-

Symbol-	$\text{CO}(\text{NH}_2)_2$
Molecular Weight-	60 g/mole
Solubility in distilled water-	1080g/litre at 25 <sup>0</sup> C
Oxidising-reducing valency-	+6

##### Stoichiometric oxidizer to fuel molar ratio:

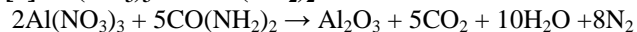
$$\text{Oxidizer/fuel ratio} = \frac{\sum \text{all oxidizing \& reducing elements in oxidizer}}{\sum \text{oxidizing \& reducing elements in fuel}} = \frac{15}{6}$$

$$= 2.5$$

Hence, the stoichiometric Aluminium nitrate/ Urea molar ratio is 1:2.5, required for the complete combustion of precursor.

##### Chemical equations:

##### [a] $\text{Al}(\text{NO}_3)_3$ & $\text{CO}(\text{NH}_2)_2$ :



##### [b] Thermal dissociation of $\text{Al}(\text{NO}_3)_3$ :



##### Precursor Preparation :

In present work variation from stoichiometric ratio i.e. fuel lean & fuel rich is used to study the effect of oxidizer / fuel ratio on combustion synthesis of Nano phase alumina powder. To prepare precursor, we have,

$\text{Al}(\text{NO}_3)_3$  (non-hydrate GR)- 15g,

Urea -5.5 g

15g of  $\text{Al}(\text{NO}_3)_3$  is mixed with 24ml of distilled water, dissolve to prepare homogeneous solution using magnetic stirrer. Similarly 5.5 g of Urea in 5.5ml of distilled water.

Volume of  $\text{Al}(\text{NO}_3)_3$  solution = 33ml      Volume of urea solution = 9 ml       $\text{Al}(\text{NO}_3)_3$  solution is divided as 11ml + 11ml + 11ml in three beakers

**In Stoichiometry 7.5g of  $\text{Al}(\text{NO}_3)_3$  requires 3g of Urea for complete combustion**

1A----- Fuel lean  
2A----- Fuel lean  
3A----- Fuel rich

Beaker lable	$\text{Al}(\text{NO}_3)_3$ solution (ml)	Urea solution(ml)	$\text{Al}(\text{NO}_3)_3$ in grams	Urea in grams	Stoichiometric Fuel %
1A	11	1.5	5	0.80	40
2A	11	3	5	1.60	80
3A	11	4.5	5	2.40	120

#### Mixing & Furnace Heating:

All the precursor samples 1A, 2A, 3A are mixed for 2-3 minutes, using magnetic stirrer, one by one. The each sample is subjected to furnace heating in the temperature range from  $350^\circ\text{C}$  -  $450^\circ\text{C}$ , until solution become free from water to form final product (foam).



Fig-1:- Solution combustion process inside digitally controlled furnace

#### Sample Preparation:

All the three foamy products formed after solution Combustion process are grounded thoroughly to form a homogeneous powder, without agglomerated particles. Powder is used for XRD & SEM characterisation.

## RESULTS AND DISCUSSION

### Flame observation

Sample	OBSERVATIONS
1A	Very small flame , white product
2A	Flame for 3-4 seconds, white foamy product
3A	High flame for 7-8 seconds, white foamy product

From flame observation during combustion reaction inside the furnace, it is clear that there is large amount of variation in exothermic flame temperature, with variation in oxidizer to fuel ratio. Sample 1A (**Fuel lean**), gives very small flame, which indicates that there is small extent of exothermic reaction takes place during combustion. This combustion can be thought of partially due to temperature dissociation of nitrate. In case of sample 2A contains large ratio of fuel than 1A, gives flame for 3-4 seconds and white product. High flame indicates that combustion takes place with high exothermicity and results in complete combustion of the reactant material.

In the similar way, sample 3A (**fuel rich**), gives very high flame for 7-8 seconds, and results in white product. White product again indicates complete combustion. Higher flame reveals the fact that increasing the percentage of fuel in precursor, increases the exothermicity of reaction. This increase in exothermicity and flame, promotes crystallinity, which is indicated by XRD analysis of the samples.

#### XRD Analysis:

The XRD of the as-synthesized powder shows that, in case of experiment 1A containing 40% of stoichiometric value of fuel, amorphous product is formed. Formation of amorphous phase is due to lack of sufficient temperature (**Low flame-1A**) required to promote alumina crystallization. Crystalline phase forms when the sufficient amount of temperature required to promote crystallization, reaches during combustion reaction (**High flame as in 2A, 3A**). Fig.2 shows amorphous character of the product phase, whereas there is large extent of crystallinity in case of 2A, 3A (fig.3, fig.4). All these observations reveal the fact that increasing the percentage of fuel (Urea) in precursor increases the exothermic flame temperature and hence crystallinity in the product phase.

**SEM analysis:** The SEM analysis of powder samples (1A, 2A, 3A) is shown in figures (5, 6, 7) below. Overall analysis shows foamy agglomerated particles with a wide distribution of particle size (low magnification) and presence of larger particle size in their structure (high magnification). Formation of these features is attributed to the amount of flame temperature during combustion process. In case of fuel leans **sample 1A**, there is formation of small particles in the range of 50nm to 200nm. The formation of very small particles can be related to small burning during combustion reaction, which leads to amorphous structure (fig.5). In case of experiment **2A**, there is wide distribution of particles ranging from 50nm to 300nm. Formation of large particles indicates high combustion flame and thus crystallinity (fig.6). Similar distribution of particles found in **3A**, with increasing crystallinity and particles size (fig.7). Formation of large particles is due to fact that small particles agglomerated at high temperature.

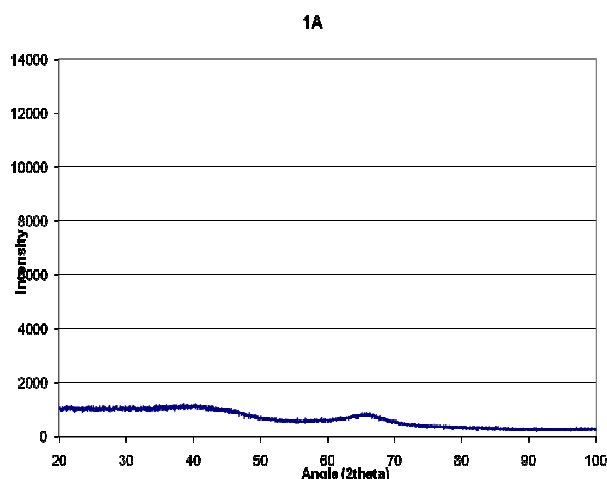


Fig-2: XRD of powder sample 1A.

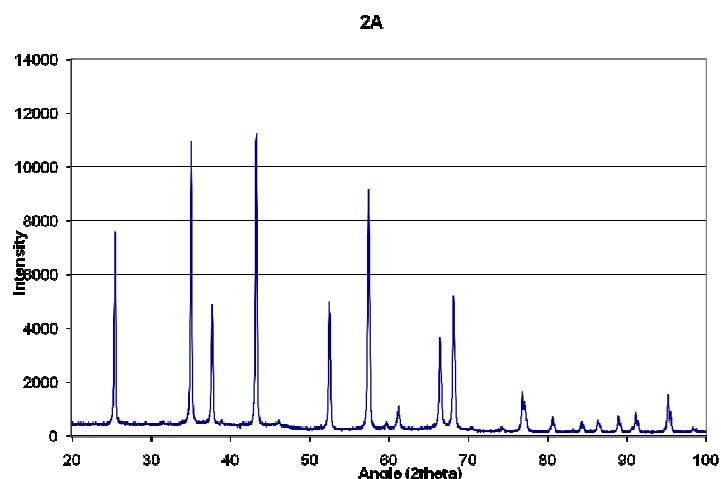


Fig-3: XRD of powder sample 2A.

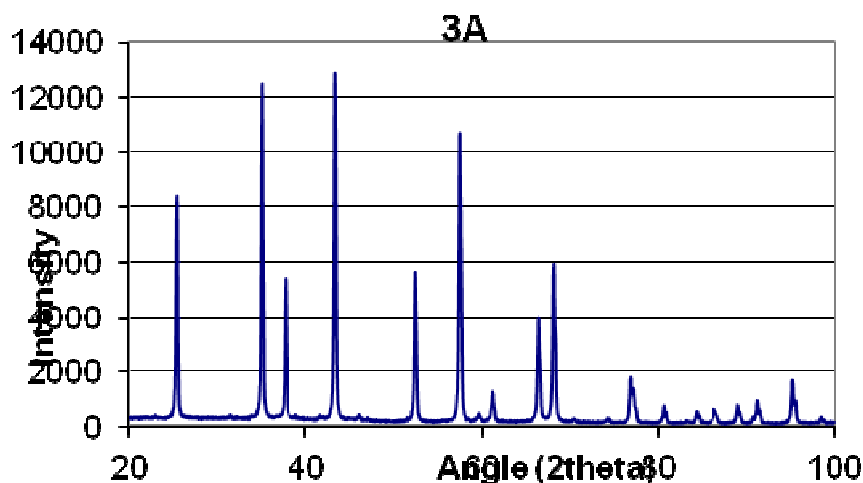
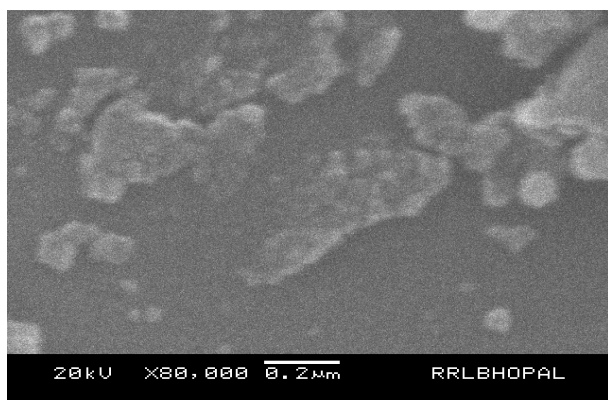


Fig-4: XRD of powder sample 3A.

High Magnification



Low Magnification

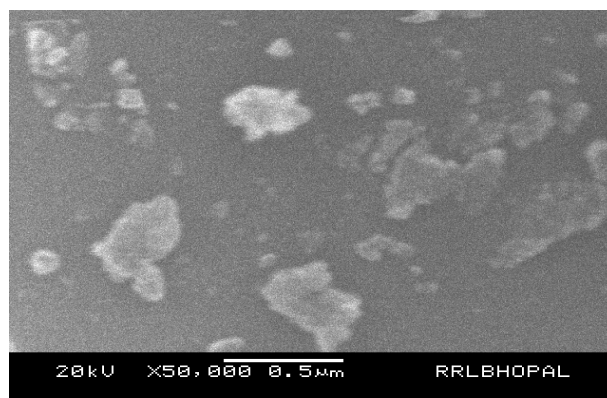
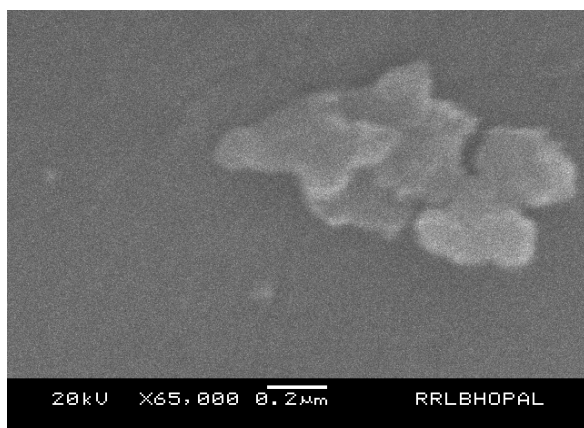


Figure-5:-SEM of powder sample 1A.

High Magnification



Low Magnification

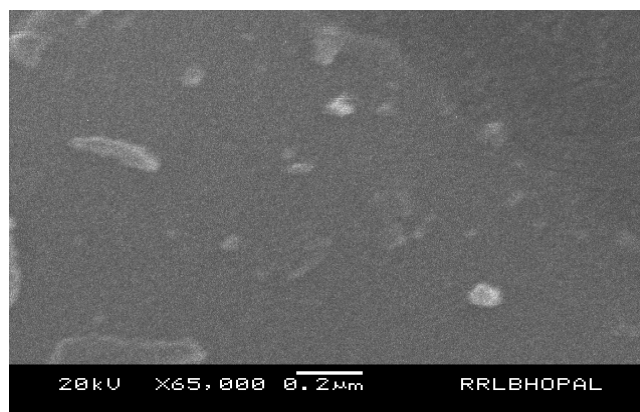
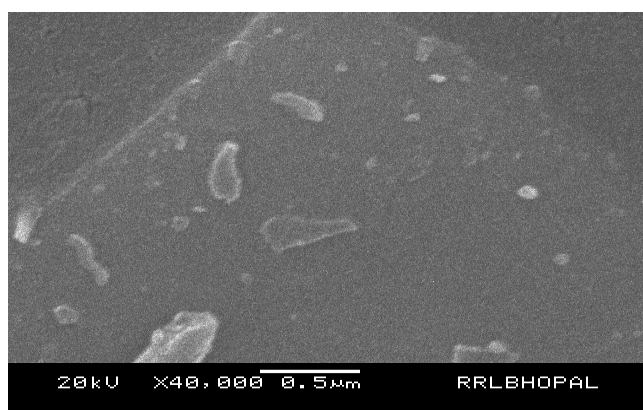


Figure-6:-SEM of powder sample 2A

High Magnification



Low Magnification

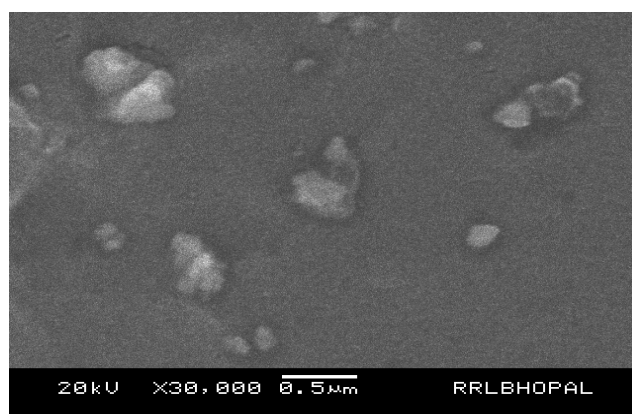


Figure-7:-SEM of powder sample 3A.

## CONCLUSION

Urea-Nitrate combustion synthesis has an outstanding potential for producing crystalline alumina powder. Crystallinity is excellent which leads to use in applications require well crystalline high strength material. Wide distribution of particle size in Nano-scale obtained. XRD and SEM analysis of samples with different oxidizer/fuel ratio shows increase in exothermic flame temperature and hence in crystallinity with increase in percentage of fuel in precursor. Overall study shows that urea is an excellent fuel for synthesis of crystalline alumina powder through

combustion route. Product formed have wide range of applications in areas requires crystalline high strength Nano-phase material.

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### REFERENCES

- [1] K. C. Patel, S.T. Aruna, T.Mimani, *Current opinion in solid state and material science* **2002**, 6, 507-512.
- [2] A. E. Sytschev, A. G. Merzhanov. *International Journal of Self-Propagating High-Temperature Synthesis*, (2009), 18:3, 200-206, Online publication date: 1-Sep-2009.
- [3] A.G. Merzhanov, *Journal of materials processing technology*, (1996),(56) 222-241.
- [4] K C Patil, *Bull. Mater. Sci.*, **1993**, Vol. 16, NO. 6, pp. 533-54.
- [5] C.C. Hwang, T.Y. Wu, *Journal of material science*, **2004**, 39, 6111-6115.
- [6] Kashinath C Patil, T Aruna Singanahally and Ekambaram Sambandan, *Current Opinion in Solid State & Materials Science*, **1997**,2:156-165
- [7] Mauro Epifani, Melissano Enrico, Pace Giovanni, *Journal of the European Ceramic Society*, (2007), (27), 115-123.
- [8] "Alumina: The Different Types of Commercially Available Grades", Azom.com Retrieved on **2011-01-29**.
- [9] S. Cava, S.M. Tebcherani, I.A. Souza, *Materials Chemistry and Physics*, (2007), 103, 394-399.
- [10] J.C. Toniolo, M.D. Lima, *Materials Research Bulletin*, (2005), 40, 561-571.
- [11] M.D. Lima, R. Bonadimann, *Journal of the European Ceramic Society*, (2006), 26, 1213-1220
- [12] He J., Schoenung J.M., *Mater. Sci. Eng.*, **A 2002**, 336, 274-319.
- [13] A. Sharma, O. P. Modi and G K Gupta, *Advances in Applied Science Research*, **2012**, 3 (4):2151-2158
- [14] A. S. Mukasyan, S. T. Aruna, *Current Opinion in Solid State and Materials Science* **2008**, 12, 44-50.
- [15] A.S. Mukasyan, A.S. Rogachev, *Prog Energ Comb Sci*, **2008**, 34, 377-416.
- [16] K.C. Patil, S.T. Aruna, S. Ekambaram, *Curr. Opin. Solid State Mater Sci.*, **1997**, 2, 158-165.
- [17] A.G. Merzhanov: SHS research and development handbook. Chernogolovka, Russia: Russian Academy of sciences, **1999**.
- [18] K.C. Patil, M. Muthuraman, S.T. Aruna, *Mater Res Bull*, **2000**, 35, 289-96.
- [19] Bahadur, S. Rajkumar and A. Kumar, *J. Chem. Sci.*, **2006**, Vol. 118, No. 1, pp. 15-21.
- [20] K.C. Patil, S. Ranganathan, T.V. Anuradha, T. Mimani, *Scripta Mater*, **2001**, 44, 2237-2241.
- [21] A.A. Borisov, A.G. Merzhanov, De Luca L.T., Redox methods in SHS practice in self-propagating high temperature synthesis of materials. New York: Taylor & Francis; **2002**.
- [22] J. McKittrick, L.E. Sheab, C.F. Bacalski, *Displays*, (1999), 19, 169-172.
- [23] Kishori Deshpande, Alexander Mukasyan and Arvind Varma, *Chem. Mater.*, **2004**, 16, 4896-4904
- [24] J. Bai, F. Meng, C. Wei, *Ceramics – Silikáty*, (2011), 55 (1) 20-25.
- [25] A. S. Lanje, S. J. Sharma, R. B. Pode, R. S. Ningthoujam, *Pelagia Research Library, Der Chemica Sinica*, **2011**, 2(5), 22-29.
- [26] S.V. Bangale, S.M, S.R. Bamane, *Der Chemica Sinica*, **2011**, 2 (4), 303-311.