

## **Effect of fuel to oxidizer ratio on synthesis of Alumina powder using Solution Combustion Technique-Aluminium Nitrate & Glycine combination**

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### **ABSTRACT**

*The combustion synthesis is a technique using glycine as fuel and Aluminium Nitrate as an oxidizer is able to produce alumina powders in Nano scale. Thermodynamic modelling of the combustion reaction shows variation in amount of gases produced and in flame temperature (combustion temperature) with variation in fuel to oxidizer ratio. Amorphous structure and Nano scale particles size found after XRD and SEM analysis.*

**Keywords:** Solution Combustion, Metal oxide, Combustion synthesis, Self propagating high temperature synthesis, Nano-ceramics.

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### **INTRODUCTION**

#### **Solution Combustion**

The solution combustion (SC) method of preparing oxide materials is a fairly recent development compared to SSC or SHS techniques. Today, SC is being used all over the world to prepare oxide materials for a variety of applications. During the short span (15 years) of SC synthesis history, hundreds of papers on SC of oxides have been published, many from the author's laboratory. There are many oxide materials prepared by rapidly heating aqueous solutions containing stoichiometric amounts of respective metal nitrate (oxidiser) and fuels like urea / hydrazides (carbo hydrazide (CH), oxalyl dihydrazide (ODH), malonic acid dihydrazide (MDH), tetra formal tris azine (TFTA)[2].

A wide range of technologically useful oxides (alumina to zirconia) were prepared with interesting magnetic, dielectric, electrical, mechanical, catalytic, luminescent and optical properties. It was possible to prepare oxide materials with desired composition, structure (spinel, perovskite, garnets, etc.) by SC[24,25]. Interestingly, some of the fuels used were found to be specific for a particular class of oxides e.g. glycine & urea—for alumina and related oxides; CH—for zirconia and related oxides; ODH—for Fe<sub>2</sub>O<sub>3</sub> and ferrites, TFTA—for TiO<sub>2</sub> and related oxides; glycine—for chromium and related oxides, etc.

All these fuels serve two purposes:

- (a) They are the source of C and H, which on combustion form CO<sub>2</sub> and H<sub>2</sub>O and liberate heat.
- (b) They form complexes with the metal ions facilitating homogeneous mixing of the cations in solution.

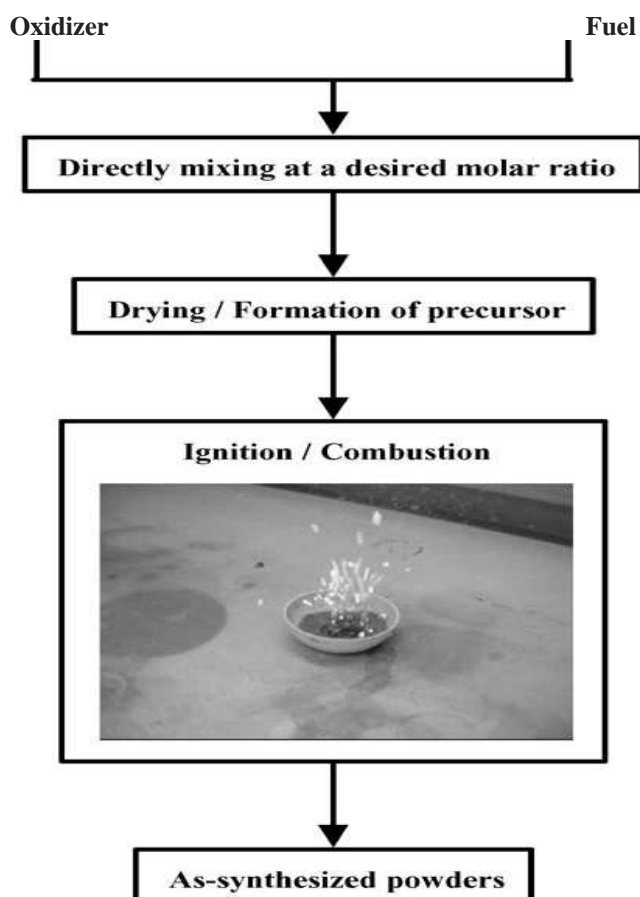
The exothermicity ( $T_{ad}$ ) of the redox reaction varies from 1000 to 1800 K. Depending upon the fuel used, the nature of combustion differs from flaming to non-flaming (smouldering). Among the fuels used and their applications. Not surprisingly, urea occupies the centre stage, probably due to its ready availability and high exothermicity [21-22]. Most of the oxides prepared by the urea method are alumina-based e.g.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> products. Another development in

alumina synthesis by the urea process is the preparation of nanosize  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by microwave initiated SC. The process yields nanosize alumina, since combustion is accompanied by controlled release of gases and dissipation of heat. The ease of doping metal ion in oxides by SC has not only yielded ZTA, but has also resulted in the facile synthesis of metal and alloy doped alumina, aluminates, pigments and phosphors. Combustion of aluminium nitrate-urea in the presence of halide salts of Pt, Pd, Ag and Au yielded uniformly dispersed M/Al<sub>2</sub>O<sub>3</sub> composites. These exhibit better catalytic properties towards oxidation of CO and hydrocarbon and reduction of NO<sub>x</sub> compared to the conventionally prepared ones[22,23]. Further, it is possible to selectively reduce M<sup>n+</sup>/Al<sub>2</sub>O<sub>3</sub> composites by hydrogen to obtain M or alloy dispersed alumina[11]. Similarly, a variety of ceria and ceria-based oxide materials have been prepared by the SC method using ODH fuel. Some important oxides prepared are: CeO<sub>2</sub>-ZrO<sub>2</sub> (oxygen storage capacitor), M<sup>n+</sup>/CeO<sub>2</sub>; M= Pt, Pd, Ag, and Au and Ce<sub>1-x</sub>Pt<sub>x</sub>O<sub>2</sub>. Ceria is a well-known catalyst support and Pt/CeO<sub>2</sub> is used in catalytic converters (three-way catalyst TWC) in controlling pollution from car exhausts[13][14].

The solution-combustion is a two-step process

- (i) formation of a precursor and
- (ii) auto-ignition.

The formation of the precursor (viscous liquid or gel), is a primary condition for an intimate blending of the starting constituents and preventing the random redox reaction between a fuel and an oxidizer. The very high exothermicity generated during combustion manifests in the form of either a flame or a fire and hence, the process is termed as auto-ignition process. The nature of the fuel and its amount, are some of the important process parameters, for getting the transparent viscous gel without any phase separation or precipitation [4]. Thus, the basic characteristics of the fuel are that it should be able to maintain the compositional homogeneity among the constituents and also undergo combustion with an oxidizer at a low ignition temperature. The commonly used fuels are: Glycine, Citric acid, Urea, Ascorbic acid etc [15-20].



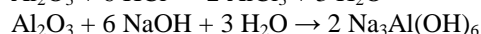
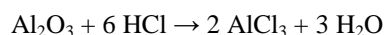
Figure[1] :-COMBUSTION PROCESS FLOW CHART [5].

### Alumina

Aluminium oxide is an amphoteric oxide with the chemical formula Al<sub>2</sub>O<sub>3</sub>. It is commonly referred to as alumina ( $\alpha$ -alumina), or corundum in its crystalline form, as well as many other names, reflecting its widespread occurrence in nature and industry. Its most significant use is in the production of aluminium metal, although it is also used as

and abrasive owing to its hardness and as a refractory material owing to its high melting point. Aluminium oxide is an electrical insulator but has a relatively high thermal conductivity ( $30 \text{ Wm}^{-1}\text{K}^{-1}$ ) for a ceramic material. In its most commonly occurring crystalline form, called corundum or  $\alpha$ -aluminium oxide, its hardness makes it suitable for use as an abrasive and as a component in cutting tools [5]. Aluminium oxide is responsible for the resistance of metallic aluminium to weathering. Metallic aluminium is very reactive with atmospheric oxygen, and a thin passivation layer of alumina (4 nm thickness) forms in about 100 picoseconds on any exposed aluminium surface.<sup>[6]</sup> This layer protects the metal from further oxidation. The thickness and properties of this oxide layer can be enhanced using a process called anodising. A number of alloys, such as aluminium bronzes, exploit this property by including a proportion of aluminium in the alloy to enhance corrosion resistance[12]. The alumina generated by anodising is typically amorphous, but discharge assisted oxidation processes such as plasma electrolytic oxidation result in a significant proportion of crystalline alumina in the coating, enhancing its hardness.

Aluminium oxide is completely insoluble in water. However it is an amphoteric substance, meaning it can react with both acids and bases, such as hydrochloric acid and sodium hydroxide.



Aluminium oxide was taken off the United States Environmental Protection Agency's chemicals lists in 1988.

Aluminium oxide is on EPA's Toxics Release Inventory list if it is a fibrous form.[7]

## MATERIALS AND METHODS

### Chemical Composition and Parameters:-

#### [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 $25^\circ \text{C}$
Oxidising-reducing valency-	-15

#### [b] Glycine-

Symbol-	$\text{C}_2\text{H}_5\text{NO}_2$
Molecular Weight-	75 g/mole
Solubility in distilled water-	250g/litre at $25^\circ \text{C}$
Oxidising-reducing valency-	+9

### Stoichiometric oxidizer to fuel molar ratio:

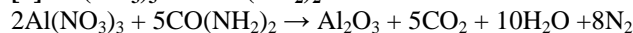
#### $\text{Al}(\text{NO}_3)_3$ (oxidizer) & $\text{C}_2\text{H}_5\text{NO}_2$ (fuel) :

$$\text{Oxidizer/fuel ratio} = \frac{\sum \text{all oxidizing \& reducing elements in oxidizer}}{\sum \text{oxidizing \& reducing elements in fuel}} = \frac{15}{9} = 1.66$$

Hence, the stoichiometric aluminium nitrate: glycine molar ratio is 1:1.66, required for the complete solution combustion.

### Chemical equations:

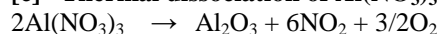
#### [a] $\text{Al}(\text{NO}_3)_3$ & $\text{CO}(\text{NH}_2)_2$ :



#### [b] $\text{Al}(\text{NO}_3)_3$ & $\text{C}_2\text{H}_5\text{NO}_2$ :



#### [c] 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)- 22.5g, Glycine –6g

22.5g of  $\text{Al}(\text{NO}_3)_3$  is mixed with 36ml of distilled water, dissolve to prepare homogeneous solution using magnetic stirrer. Similarly 6 g of glycine in 30ml of distilled water.

Volume of  $\text{Al}(\text{NO}_3)_3$  solution = 48ml

Volume of glycine = 36ml

$\text{Al}(\text{NO}_3)_3$  divided as 16ml + 16ml + 16ml in three equal proportions.

**In Stoichiometry ratio 7.5g of  $\text{Al}(\text{NO}_3)_3$  requires 2.5g of GLYCINE for complete combustion.** Three different samples with different oxidizer / fuel ratio were levelled as:

1C-----Fuel lean

2C----- Fuel lean

3C-----Fuel rich

Beaker lable	$\text{Al}(\text{NO}_3)_3$ solution (ml)	Glycine solution(ml)	$\text{Al}(\text{NO}_3)_3$ in grams	glycine in grams	Stoichiometric Fuel %
1C	16	6	7.5	1	40
2C	16	12	7.5	2	80
3C	16	18	7.5	3	120

#### Mixing & Furnace Heating:

All the precursor samples 1C, 2C, 3C 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<sup>0</sup>c -450<sup>0</sup>c, until solution become free from water to form final product (foam).

#### 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
1C	No flame, small amount of sparking, light black product formed
2C	Little flame, blackish product formed
3C	Little flame, dark black product formed

From flame observation during combustion reaction inside the furnace, it is clear that there is variation in amount of flame, with variation in oxidizer to fuel ratio.

From this flame observation it is clear that, no any one of samples (fuel lean to fuel rich) produces sufficient flame as was expected in combustion process.

Black product indicates the in-complete combustion probably due to characteristics of fuel employed.

The color of the powder as-synthesized was also found to change with the fuel-to-oxidant ratio. This is attributed to the carbonaceous residue which remains from glycine due to insufficient oxidizer specimen quantity.

This incomplete combustion of the reactant can be thought of due to the temperature dissociation of nitrate, not only due to- the main fuel reaction. This lack of exothermicity in case of glycine can be thought of due to large carbon content in glycine process.

#### XRD analysis:

XRD patterns of the combustion product were recorded using a Siemens D500 with  $\text{Cu}_{\text{K}\alpha}$  radiations.(See figure 2,3,4)

The XRD of the as-synthesized powder indicates the amorphous structure, which denotes the absence of crystalline phase from precursor solution for all fuel to oxidizer ratios. The formation of crystalline alumina in-situ did not occur for any one of fuel/oxidizer combination because the temperature generated was not enough to promote some crystallization as expected.

Fig-2:- XRD of powder sample 1C.

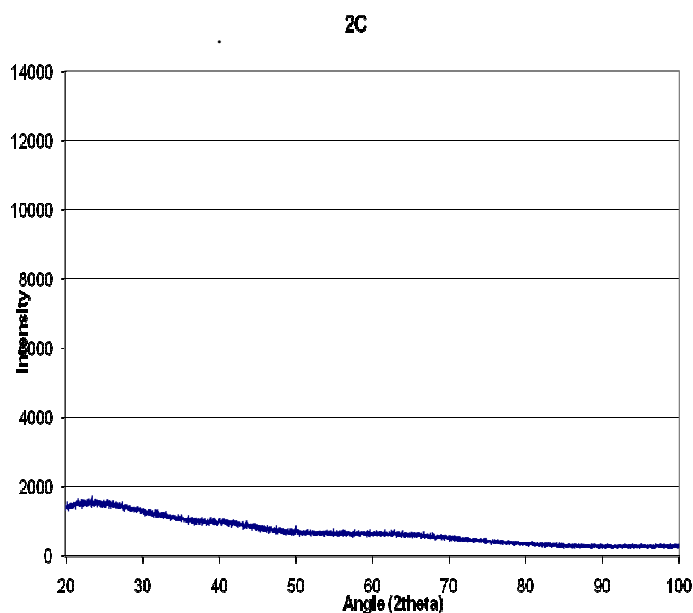


Fig-3:- XRD of powder sample 2C

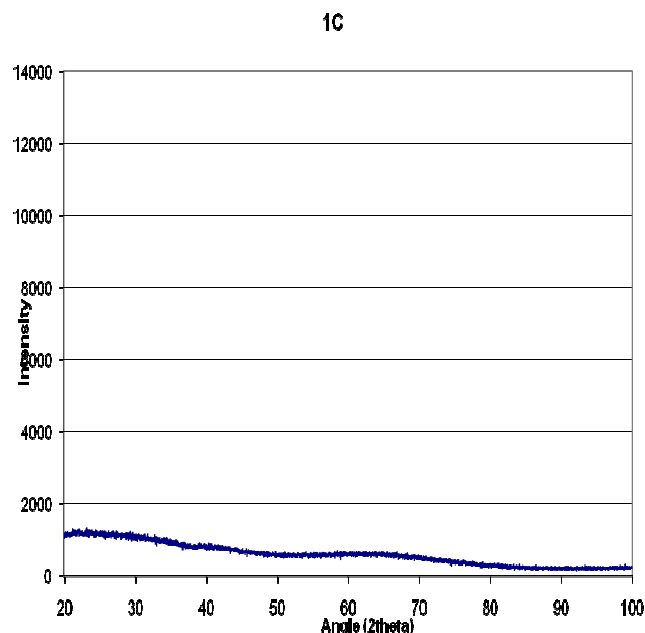
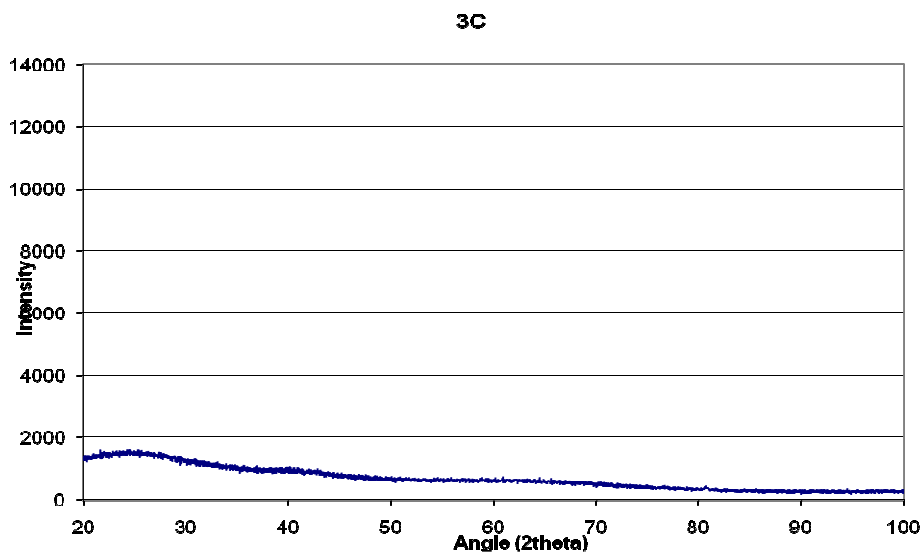


Fig-4:- XRD of powder sample 3C.

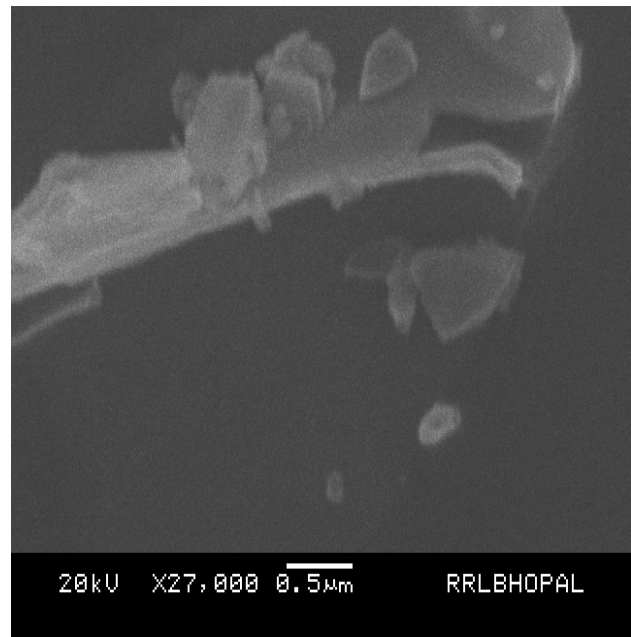
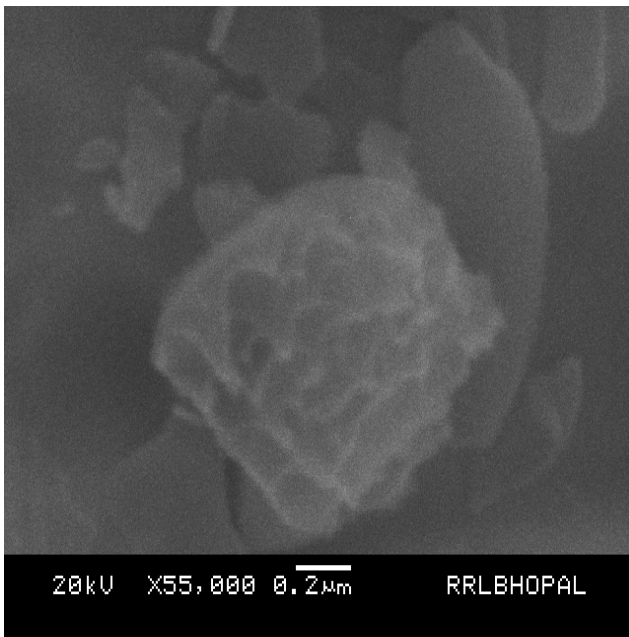


#### SEM analysis:

SEM analysis shows formation of foamy agglomerate particles (low magnification) and presence of larger voids in their structure (high magnification). Formation of these features is attributed to the evolution of a larger amount of gas during combustion. In case of glycine all experiments, results in negligible flame and black product, thus there is lack of sufficient temperature required for the formation of large agglomerates and thus results in amorphous product. All the experiments with glycine give rise to small range of distribution of particles size, with few agglomerates. SEM for these samples is shown in figure 5,6,7. Range of particles size is from 50nm-150nm in fuel lean samples, it is from 50nm-250nm in case of fuel rich due to combustion of reactant by temperature dissociation of nitrate. Hence amorphous structured nano-phase metal-oxide confirmed.

**High Magnification**

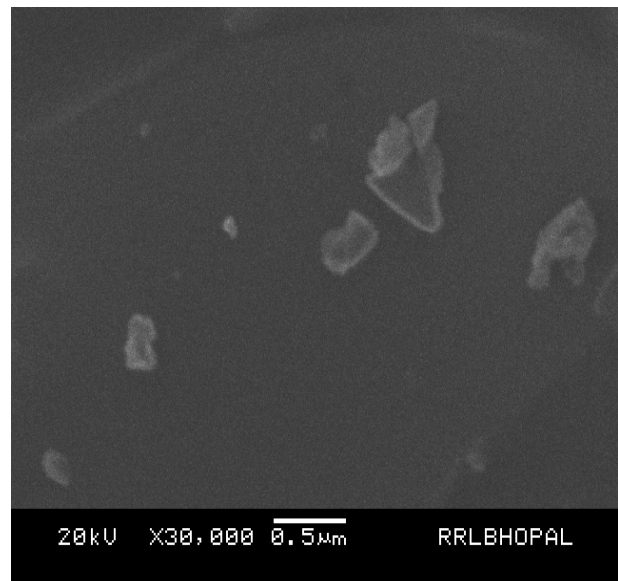
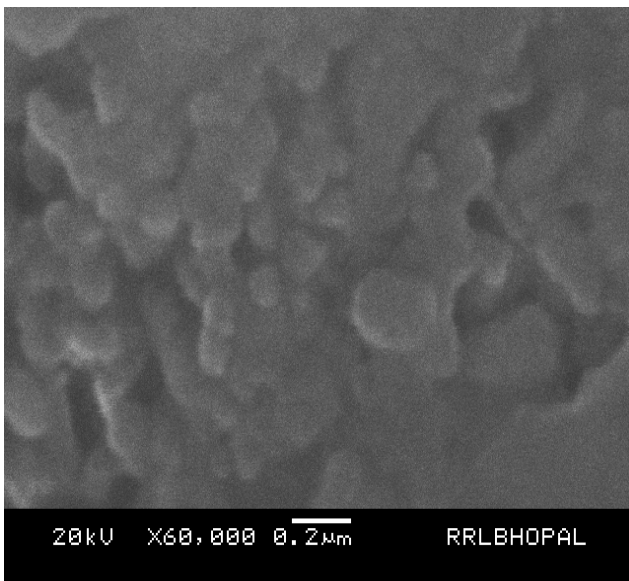
**Low Magnification**



**Figure-5:-SEM of powder sample 1C.**

**High Magnification**

**Low Magnification**



**Figure-6:-SEM of powder sample 2C.**

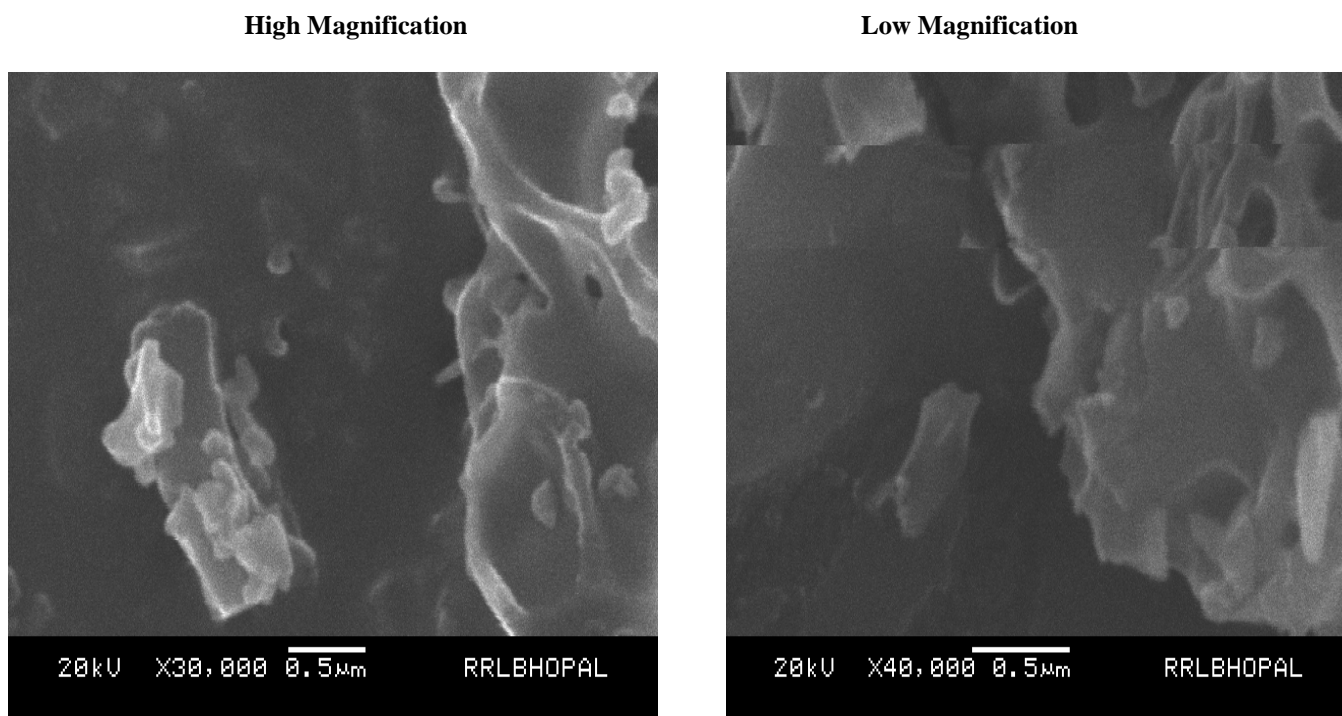


Figure.-7:-SEM of powder sample 3C.

### CONCLUSION

XRD analysis shows that Glycine has an outstanding potential for synthesis of Alumina powder with amorphous structure. SEM analysis confirmed the formation of Alumina with particles size in range of Nano scale. Also the observations during solution combustion process shows that there is increase in amount of gasses produced and also in flame temperature with increase in fuel/oxidizer ratio.

Crystallinity can be obtained by further calcination at desired temperature. Glycine as a fuel lacks only towards complete combustion as desired in solution combustion process. This leads to lack of crystallinity in product phase and lower flame temperature during combustion process.

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