Synthesis, Structural And Electrical Studies Of Ba-Doped Al$_2$O$_3$ Prepared By Solution Combustion Synthesis.

[1]Belekar R. M., [1] Sawadh P. S. , [2]Mahadule R. K.

Abstract-Nano-crystalline Barium doped β-alumina as Ba$_x$Al$_{2-x}$O$_{3-\delta}$ (where x= 0.01,0.02,0.03) was successfully prepared via solution combustion synthesis using urea as a fuel and aluminium nitrate as precursor. These samples were characterized by powder XRD, SEM and TEM analysis. The electrical conductivity was measured using two probe dc technique within a temperature range 500^{0}C to 1100^{0}C. The 'Ba' is located in the glassy matrix which surrounds the crystalline phases. There it acts as a blocking ion and suppresses the easy mobility of alkali ions which are present as impurities. XRD analysis revealed spinel like structure of Ba-alumina. The insulating property of the material was found to be increasing with the concentration of 'Ba'. The activation energy calculated from Arrhenius plot of conductivity was around 0.89 eV.

Keywords: β-alumina, conductivity, blocking ion, activation energy, XRD, TEM, SEM.

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1. INTRODUCTION

Aluminous ceramic materials are widely used as structural and functional materials due to their chemical and physical properties like chemical inertness, high hardness and high electrical resistivity [1]. The scientific and technical interest in the properties exhibited by beta alumina has grown over the past few decades. These interests range from fields as diverse as batteries [2] to the chemi-luminescense [3] exhibited by some doped beta aluminas. The use of beta alumina as sensors has also been widely investigated [4]. While interest in the laboratory has centered around the ion exchange, conductivity [5-8] and structural properties [9-11] of these materials.

In the Na beta alumina structure, the unit cell is composed of two spinel blocks of O^{2-} and Al^{3+} ions, separated by a mirror plane. The Na$^+$ ions can easily move

in two dimensions along the layer between the spinel blocks. In the case of beta- alumina, the structure is the result of stacking of three spinel blocks and is usually stabilized by adding MgO or Li$_2$O. Some of the ion exchanged beta aluminas are unstable at high temperatures, for example Li beta alumina will decompose at approximately 1273K, and cannot be produced by direct synthesis. The ion-exchanged Ca beta alumina has also been seen to be more stable but in the closely related magnetoplumbite phase. It is however possible to produce a number of beta aluminas by solid state sintering [12].

Baβ-Al2O3 has been produced by both solid state [13, 14] and ion exchange [15] routes. The material has been shown to have a beta alumina type structure, with two types of structures being determined, phase 1 and phase 2 [14]. These two structures have been shown to have the nominal stoichiometry of BaAl$_{14}$O$_{22}$ and BaAl$_9$O$_{15}$, having been produced by the floating zone method [14]. While the composition of BaAl$_{12}$O$_{19}$ is also shown to have a beta alumina structure. The addition of BaCO3 to high surface area gamma alumina has been shown to produce a material that retains a high surface area at high temperatures [16, 17]. This technique has been used in the production of thermally stable catalyst supports [18].

Among the available chemical processes, self sustaining solution combustion synthesis is convenient in process, simple in experimental device and time saving. Solution combustion synthesis process involves an aqueous mixture containing suitable metal salts which are the precursors of the final desired oxide and a proper sacrificial organic fuel which acts as reagent reducer. Generally, hydrate nitrates are preferred to other salts because of their good solubility in water which allows them to obtain a highly homogeneous solution. Urea is the most convenient fuel that can be used in the combustion processes [19] because of its relatively low price, availability, commercially grade and safety.

2. EXPERIMENTAL

Self-propagating high temperature combustion synthesis is a novel technique that has been used successfully for the preparation of ceramic and phosphor materials. The main advantage of this method, compared to the solid state sintering method, is that the experiment is completed within 10 min. The basic principle of the method is the decomposition of an oxidizer, e.g., a metal nitrate, in the presence of a fuel. The fuel gets ignited by the oxidizer to yield oxide materials derived from the metal salts. The fuel used in the present study was urea which acts both as fuel and carbon source.

The stoichometric amount of Aluminum nitrate, barium nitrate and urea were dissolved in 25 ml of water contained in a beaker and placed on a hot plate for 15 minutes, as the solution dehydrates to form a disposition like a gel. Then the beaker was placed in a preheated muffle furnace at 400°C. The solution boils, ignites with a flame and the entire reaction was completed within 5 minutes. The powder was highly amorphous, a portion of the sample was calcinated at 800° C

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- [1]Raju Belekar, Reseach Scholar and Asst. Professor at Bapurao Deshmukh College of Engg., Wardha, Maharshtra, India, E-mail:rajubelekar@gmail.com

and the XRD pattern of this powder confirms the formation of   Ba-Al_2O_3.

3. RESULTS AND DISCUSSION
3.1 X-ray diffraction study:

The peaks shows corresponding peaks of both α-Al2O3 and Ba β-Al2O3. The peaks become less sharp as value of 'x' increases. The crystallinity of both Ba-Al2O3 and α-Al2O3 phases decreases as evident by typical peaks of Ba-Al2O3 at d-values of 4.48, 2.79, 2.69, 2.51 A° and typical peaks of α-Al2O3 at 3.47, 2.55, 2.13 A° . In many earlier studies on preparation of barium aluminates formation of various alumina phases such as θ-Al2O3, δ-Al2O3 and γ-Al2O3 have been reported at 1200–1400⁰C [20, 21] while in this study only α-Al2O3 phase is formed. It is quite interesting to note that with increase in values of 'x' from x= 0.01 to x= 0.03 the intensity of the peak decreases. As observed at 1200⁰C, the mean crystalline diameter for mono-aluminate increases and those of α-Al2O3 decrease with the increase of Ba/Al ratio.
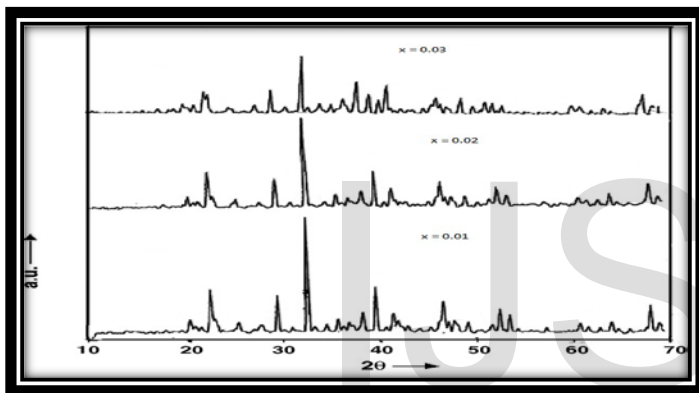

Figure 1 XRD Pattern of $Ba_xAl_{2-x}O_3$

The crystal structure of Ba-β-Al2O3 is very similar to that of Na-β-Al2O3 [22, 23] , Four layers of close-packed oxygen atoms with aluminium in the tetrahedral and octahedral interstices form spinel-like structural blocks. These blocks are separated by mirror planes in which the Ba is located. The spinel-blocks are held together by bridging-oxygen atoms which are also situated in the mirror plane. The crystal structure of Ba-β-Al2O3 belongs to the space group P63/mmc.

3.2 SEM/ TEM Analysis:

After the calcination step at 800°C ceramics produced from powder shows a homogenous microstructure. The matrix consists of Al2O3 with a grain size of about 50 –150 nm (fig. 3). The barium is uniformly distributed in this porous matrix. The Al2O3 grains are connected via sintering necks. After 1 h at 800°C the ceramic consists of a still very porous Al2O3 matrix, which does not show any signs of grain growth or further densification. Embedded in this matrix are BaAl2O4 grains which also do not show any grain growth.
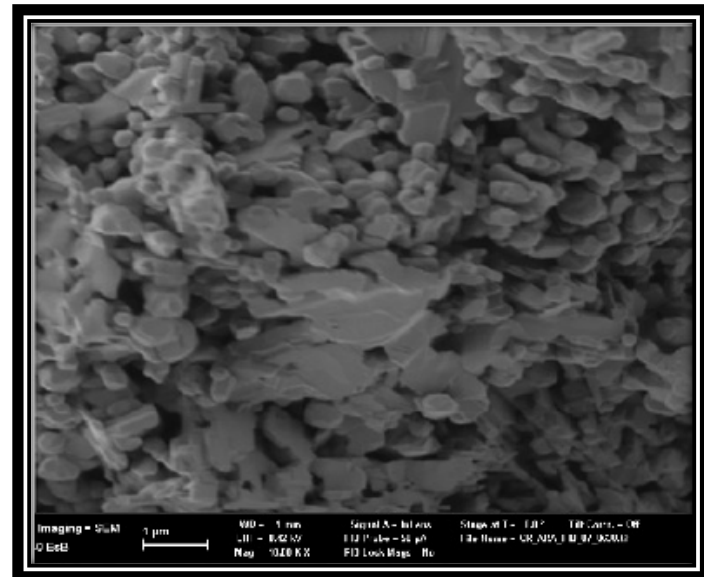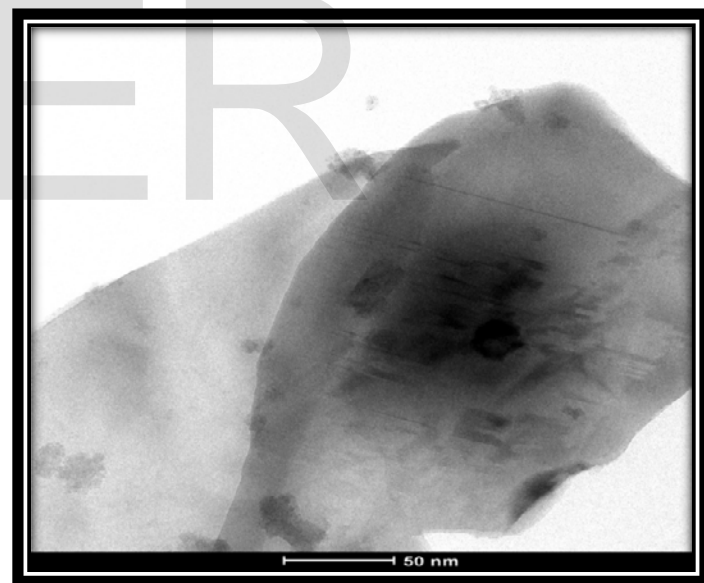

Figure 2 SEM micrograph of Ba-Al_2O_3

Figure 3 TEM image of Ba Al_2O_3

The sample calcinated for 3 hours at 800°C exhibits the first Ba-β-Al2O3 crystals. They are homogenously distributed within the matrix of Al2O3 and BaAl2O4 grains which both still do not show any grain growth. The homogenously distributed and randomly oriented Ba-β-Al2O3 crystals are characterized by a columnar to plate-like morphology and internal porosity. Prolonged sintering times lead to the formation of more Ba-β-Al2O3. The

crystals show a remarkable grain growth. After 30 h of sintering time crystals have grown to about 20 µm whereas the Al2O3 matrix does not show any coarsening or further

3.3 Electrical measurement of Ba doped alumina:
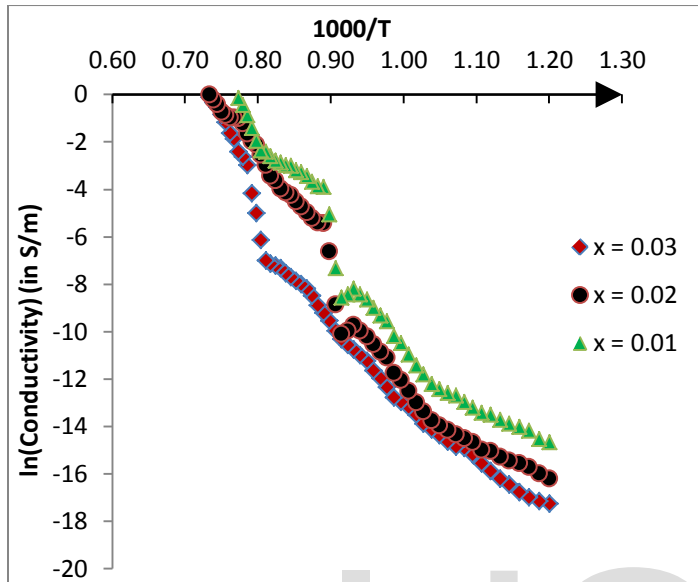

Figure 4. Arrhenius plot for conductivity.

The addition of Ba to electrical aluminous porcelain leads to improved electrical resistivity. The Ba is located in the glassy matrix which surrounds the crystalline phases. There it acts as a blocking ion and suppresses the easy mobility of alkali ions which are present as impurities.

As shown in fig. 4, during heating, the conductivity is nearly the same at all supplied rates up to a temperature of 670 °C. Above 670°C the conductivity attributed to a heating rate of 0.167 K/min increases. Above 800°C the conductivity increases strongly. At temperatures above 1050°C the conductivities during heating and cooling are the same for different rates. At temperatures below 1050 °C, the conductivities measured during cooling are notably larger than during heating in the entire temperature range studied. Below the temperature of 830^{0}C, the slope of the plot decreases notably and ln[conductivity] (-7.4 to -5.3) is larger than supplying larger rates (<-8.5). The Arrhenius plot of the bulk conductivity of a Ba-Al2O3 sintered pellet is shown in Fig. 4. In the 500–900^0 C range an activation energy of 0.89 eV is determined, in agreement with previous results for Li–β-alumina (0.86 eV) and for Mg-β-alumina (0.9 eV) [24]. Another feature of the Arrhenius plot shown in Fig. 4 is a deviation of the straight line for temperatures higher than 900^0 C. High-temperature in situ X-ray diffraction in that range did not show any evidence of structural phase transition.

4. CONCLUSION

densification. Longer sintering times also lead to reduced internal porosity within the Ba containing crystals.

Barium doped Al2O3 was successfully prepared by self sustaining solution combustion synthesis. The formation of Ba β- alumina phase was conformed from X-ray diffraction study. The crystal structure of Ba-β-Al2O3 belongs to the space group P63/mmc. It is seen that prolonged sintering of the samples leads to the formation of more Ba-β-Al2O3, further it also leads to the increase in average grain size. The addition of Ba improves the insulating behavior of alumina. The conductivity of the material was found to be increases on sintering. This increase in conductivity has been explained on the basis of formation of smaller grains and more grain boundaries that lead to the increase in concentration of defects. And also formation of space charge region between ionic solid and dispersed insulating particle could be the reason for the enhancement. The observed lesser activation energy in dispersed system indicates that the probability of formation of vacancies is more rather than that of interstitials in the extrinsic motion region.

5.   REFERENCES:

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