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Electrical properties of sodium beta-alumina ceramics synthesized by citrate sol-gel route using glycerine

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Abstract

Sodium beta-alumina is an efficient ion conducting solid electrolyte due to fast ionic conductivity arising from its favourable crystal structure. Other main requirements of a material to serve as solid electrolyte are fine grain structure, minimum porosity and good electrical properties at the operating temperature, which is usually about 300 °C. Mg-doped sodium beta-alumina powder was synthesized using citrate sol-gel route (wherein glycerine was used as a fuel) and calcined at different temperatures (950–1100 °C). The synthesized powders have β''-alumina as a dominant phase and particle size in range 75–95 nm. The obtained powders were compacted by uniaxial pressing at 100 MPa and sintered at 1500 °C for 3–10 h. Maximal density of the sintered samples was 92% TD and the primary phase was β''-alumina. The highest conductivity of 0.38 S/cm was measured at 300 °C and the lowest activation energy for conduction of 0.20 eV was obtained.

I. Introduction

Electrical energy storage (EES) devices are used for storing excessive amount of energy and releasing it when needed. These devices are essential for storing energy from unconventional energy sources, such as solar and wind energy, which are by their nature variable and uncontrolled. Na/S batteries using sodium beta-alumina as solid electrolyte are such devices capable of reversibly storing and releasing electrical energy without involving "Carnot" cycles [1]. Hence, in recent years, solid compounds exhibiting fast ionic conduction have attracted considerable attention both because of their application as solid electrolytes in batteries, fuel cells and other devices, and also to obtain a fundamental understanding of the fast ionic conduction process [2]. Materials for battery electrolyte application require not only high ionic conductivity and negligible electronic conductivity, but also high mechanical strength, chemical stability with respect to the battery electrodes, and low cost.

Sodium beta-alumina (SBA) ceramics constitute a family of oxides which exhibit a fast-ionic conductivity. This property makes SBA as one of the best solid electrolytes known today and suitable for use in sodium-sulphur (Na/S) batteries. The high-energy Na/S battery system has been under active investigation in many countries [3]. Derivatives known as beta-alumina are generally found in materials of the type β'-Al_2O_3 with the empirical formula of $Na_2O \cdot 11 Al_2O_3$, and β''-Al_2O_3 identified in the form $Na_2O \cdot 5.33Al_2O_3$ [2,3]. β''-alumina (beta prime-prime alumina) is an isomorphic form of aluminium oxide (Al_2O_3), a hard polycrystalline ceramic, which, when prepared as an electrolyte, is complexed with a mobile ion, such as Na^+, K^+, Li^+, Ag^+, Sr^{2+} or Ba^{2+} depending on application. Beta-alumina is a good conductor of its mobile ion, but poor electronic conductor. Thus, due to the unique structure and high ionic conductivity, β''-alumina has been used in Na/S battery [1,4]. Charge transport is determined by the structure of Na^+-beta-alumina in which two-dimensional conduction planes partially occupied by Na+ ions are separated by crystalline Al_2O_3 spinel blocks [5]. Activation energy values for ion transport in the conduction plane are low, between 0.12 and 0.27 eV, because of the correlated movement of interstitial Na^+ pairs, instead of a standard vacancy mechanism [2,5].

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The Na/S battery consists of sulphur at the positive electrode, sodium at the negative electrode as the active materials and the beta-alumina of sodium ion conductive ceramic that separates both electrodes [6]. The Na/S battery offers higher performance parameters than other secondary cells [7]. The β''-phase exhibits a higher conductivity and can be stabilized by adding large amounts of Na_2O to Al_2O_3 and further by doping with suitable oxides such as MgO and Li_2O. Conductivity can be optimized by doping, but also with the way of the sodium beta-alumina fabrication [8]. Conductivity of solid electrolyte (beta-alumina) depends on the concentration of mobile ion. Charge balance in undoped beta-alumina has been attributed to Al^{3+} vacancies and O^{2-} interstitials in the conduction plane. Lithium is one important element which has been shown by NMR line narrowing studies to reside in both conduction plane and spinel block [9]. The batteries viz. the used materials therein are still facing challenges of improvement to enhance performance of the batteries and lowering their cost for broad market penetration [1].

Processing of fine structured SBA ceramics has been focus of many investigations, as the nano-sized sodium beta-alumina has faster ionic conductivity than the micro-sized material [10]. Conventionally, SBA has been synthesized by solid-state reaction of α-alumina with Na_2CO_3 and small amounts of MgO or Li_2O as stabilizing agent. The main disadvantage of this process is formation of two-phase product consisting of β' and β''-alumina resulting from the reconstructive transformation of the hexagonal close packed stacking of oxygen ions of α-alumina to the cubic close packed stacking of oxygen ions in the spinel structure of the β''-alumina. Repetitive grinding, compaction and annealing are often necessary to obtain a single-phase material. Thus, the process is cost- as well as energy-intensive [7]. Some other processing routes, like alkoxide hydrolysis, sol-gel process, co-precipitation, solution combustion technique have also been reported in literature [8]. Even though the solution combustion synthesis method yields a single-phase material at much lower temperatures, still a higher temperature heat treatment is necessary for obtaining the required β''-structure [11]. Citrate sol-gel method has attracted interest lately as an alternative to conventional thermal processing route, because of its advantages such as excellent product homogeneity, better compositional control and lower processing temperature [8].

In the present work Mg-doped SBA was synthesized by citrate sol-gel route using glycerine as a reaction fuel, instead of ethylene glycol used in conventional processing route. Different processing parameters were used for preparation of dense Mg-SBA ceramics. DC conductivity values were experimentally measured and correlation between conductivity and the various processing parameters was investigated.

II. Experimental work

Mg-doped sodium beta-alumina (Mg-SBA) powder was prepared by citrate sol-gel method using AR grade aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9\,H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6\,H_2O$), sodium nitrate ($NaNO_3$), citric acid (CA) and glycerine. In the first step, stoichiometric amounts of $Al(NO_3)_3 \cdot 9\,H_2O$, $Mg(NO_3)_2 \cdot 6\,H_2O$ and $NaNO_3$ (with molar ratio of 10.33 : 0.67 : 1.67) were dissolved into distilled water. Then citric acid and glycerine were added into the prepared solution and three samples (S-112, S-113, S-114) with different molar ratio of citric acid, metallic ions and glycerine (1 : 1 : 2, 1 : 1 : 3 and 1 : 1 : 4, respectively) were obtained. The resulting solution was slowly evaporated in a water bath held at 80 °C with stirring until the formation of yellow or orange coloured transparent gels. The gels were in viscous form and formed by network of interlinked particles. Formation of orange coloured gel occurred after stirring solution for 3–3.5 h at 80 °C on magnetic stirrer. The gels were transferred into a pre-heated muffle oven at 400 °C, and powders with fine particles (having size of 75–95 nm determined by BET surface area analyser Smartsorb 92/93, Smart Instrument, Thane) were obtained. Subsequently, the formed fluffy powders were calcined at 950–1100 °C to remove unwanted volatile organic compounds. The change in powder colour from black to white suggested the complete removal of carbon.

Cold compaction method was used for preparation of sodium beta alumina ceramic pellets. Before compaction, the calcined powders were ground using agate mortar-pestle. The obtained Mg-SBA nanopowders, with small amount of binder (polyvinyl alcohol), were uniaxially pressed at 100 MPa to form pellets (13 mm diameter, 2 mm thickness). The samples were subsequently sintered up to 1500 °C for 3 and 10 hours in a sealed alumina crucible while keeping them embedded in SBA powder.

To identify the structure of the calcined powders and sintered pellets, X-ray diffraction was carried out using X-ray diffractometer with CuK_α source (Brucker AXS, D8 Advance X ray Diffractometer) in 2θ range of 10–80°. X-ray diffraction data were collected and analysed using JCPDS database. Field emission scanning electron microscopy (FE-SEM) (Bruker Detector, model Zesis Sigma) was carried out to study the morphology of ceramic samples. Electrical conductivity was obtained using impedance spectroscopy measurements at various temperatures. The measured AC conductivity values were plotted as a function of frequency at various temperatures and these were fit using Jonscher's power law to obtain DC conductivity at each temperature. However, here we will show only DC conductivity values obtained by this method for various samples.

III. Results and discussion

3.1. Structural characterization

XRD patterns of the Mg-SBA ceramics prepared from different powders (the samples S-114 calcined at 1000 °C and S-113 calcined at 1050 °C) and sintered at 1500 °C for 3 h are presented in Fig. 1. The XRD pattern reveals the presence of β'' as the primary phase and β' as the secondary phase in both samples. The co-existence of both β' and β'' phases was confirmed by X'pert High score plus analysis as a mixture of rhombohedral Na-β''-Al$_2$O$_3$ phase (JCPDS file no. 00-035-0438) and Na-β'-Al$_2$O$_3$ phase (JCPDS file no 00-032-1033). The XRD results also showed that a higher concentration of glycerine is useful for getting more crystalline β'' phase, as the samples S-113 has smaller and less sharp peaks of β''-alumina in spite of higher calcination temperature (1050 °C).

XRD patterns of another three Mg-SBA ceramic samples prepared from different powders (the samples S-112, S-113 and S-114, calcined at 1100 °C) and sintered at 1500 °C for 3 h are shown in Fig. 2. The coexistence of both β' and β'' was once again confirmed and higher intensity of peaks for the sample S-114 as compared to other two samples was observed.

All above XRD results (Figs. 1 and 2) reveal that the portion of β'' phase increases with increase in both calcination temperature and glycerine content. Similar co-existence of phases has been already reported and studied theoretically in terms of the β'/β'' equilibrium by Nafe *et al.* [11]. In another study, it was established that the β'/β'' equilibrium was sensitive to phase composition and sintering temperature [12].

Figure 3 shows density variation of the Mg-SBA ceramics sintered at 1500 °C for 3 and 10 hours. It can be seen that with the increase of sintering time relative density of ceramic pellets increases. Moreover, the increase of glycerine content in the precursor solution resulted in increase in relative density too. This can be attributed to the increase in β'' phase content which consequently, decreased mismatch in the sintering characteristics of β' and β'' phase. However, sintering at 1500 °C for 10 hours resulted in small decrease in relative density of some samples (prepared with higher glycerine content) which can be attributed probable to volatilization for this particular composition due to longer sintering time. However, further investigation is needed to understand the observed reduction in density for this particular composition.

Figures 4a and 4b show SEM micrographs of the Mg-SBA ceramics obtained from the S-113 powders calcined at two different temperatures (1050 and 1100 °C) and sintered at 1500 °C for 3 h. The change of grain shape from elongated to more equiaxed, a small increase in grain size and reduction in porosity (improved densification) can be recognised. An identical trend was also noted for the samples prepared from the S-114 powders (Figs. 4c and 4d). However, more uniform equiaxed grains with less porosity are observed in the case of the S-114 samples, which demonstrated the highest density of 92.5% TD.
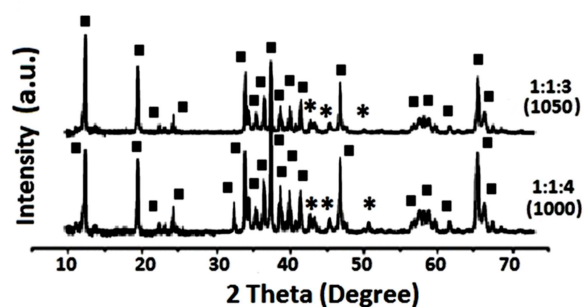

Figure 1. XRD patterns of Mg-SBA ceramics prepared from different powders (S-113 calcined at 1050 °C, S-114 calcined at 1000 °C) and sintered at 1500 °C for 3 h [■ = β''-alumina, * = β'-alumina]
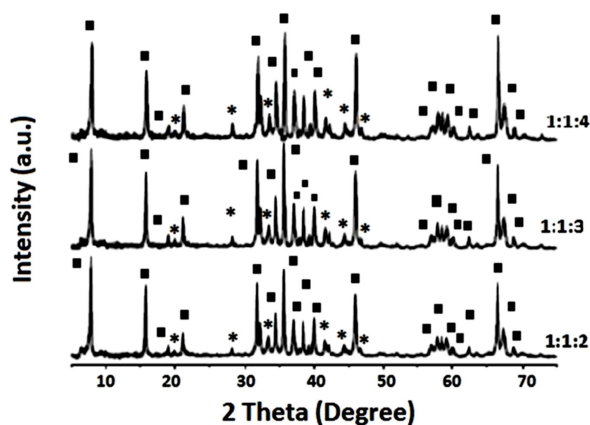

Figure 2. XRD patterns of Mg-SBA ceramics prepared from different powders (S-112, S-113, S-114 calcined at 1100 °C) and sintered at 1500 °C for 3 h [■ = β''-alumina, * = β'-alumina]
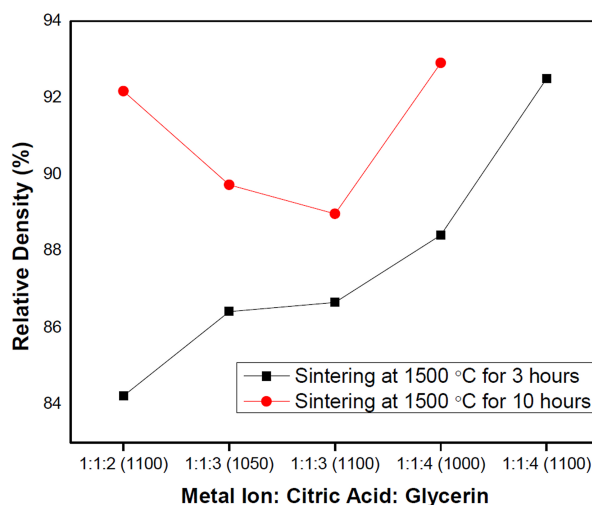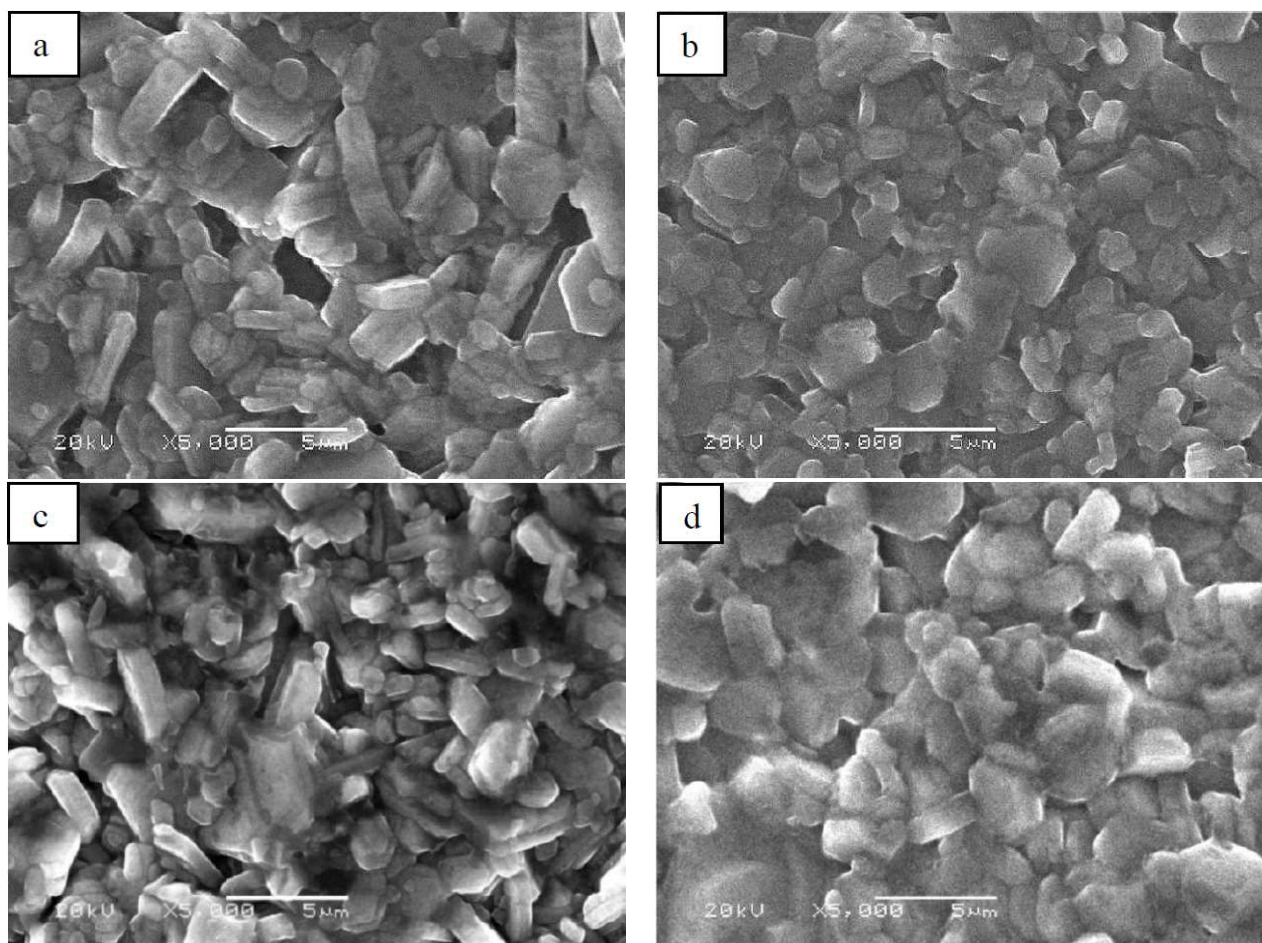

Figure 3. Relative density of Mg-SBA ceramics prepared from different powders and sintered at 1500 °C (numbers in parentheses indicate calcination temperature)

Figure 4. SEM micrographs of Mg-SBA ceramics prepared by sintering at 1500 °C for 3 h of different powders: a) S-113 calcined at 1050 °C, b) S-113 calcined at 1100 °C, c) S-114 calcined at 1000 °C and d) S-114 calcined at 1100 °C

3.2. Conductivity

DC conductivity of the Mg-SBA ceramics sintered at 1500 °C for 3 and 10 hours are presented in Figs. 5a and 5b, respectively. For practical application, DC conductivity of SBA electrolytes at 300 °C is very important because of its stable electrochemical behaviour in a cell. Thus, it can be seen that DC conductivity measured at 300 °C for the ceramics sintered at 1500 °C for 10 h is about 10% higher than for those sintered at 1500 °C for 3 h, which can be attributed to improved densification of these ceramics with longer sintering time. Moreover, difference in the relative density of ceramics arising from different glycerine content in precursor solution and calcination temperature does not have significant effect on the DC conductivity of these ceramics at 300 °C, which can be ascribed to sufficient mobility of sodium ions.

The temperature dependence of DC conductivity for all samples was analysed with Arrhenius' equation:

$$\sigma = \frac{\sigma_0}{T} \exp \frac{-E_a}{k_B \cdot T} \qquad (1)$$

where σ is conductivity, T is temperature, E_a is activation energy and k_B is Boltzmann constant. Activation energy for the conduction was computed from the slope of $\ln(\sigma T)$ vs. $1000/T$ lines, as shown in Fig. 6. The activation energy for the Mg-SBA ceramics lies between 0.20–0.23 eV, which is also in compliance with the values reported in the literature [1–3]. The lowest activation energy was calculated for the Mg-SBA ceramics prepared from the S-114 powders calcined at 1100 °C and sintering at 1500 °C for 10 h, which can be attributed to the presence of higher portion of β'' phase and higher density.

The obtained conductivity values of the Mg-SBA ceramics are in good agreement with those cited in literature, and even higher than the published results [14–17]. Thus, the electrical conductivity at 300 °C reported by Avinash *et al.* [18] is about 0.065 S/cm which is almost one order of magnitude lower than the values reported in this work. However, Avinash *et al.* [18] had an aim of fabricating tubes of β-Al$_2$O$_3$ and thus, various additives had to be used which affected electrical conductivity in their case. Similarly, Barrison *et al.* [19] have reported electrical conductivity of about 0.14 S/cm at 300 °C in their work, which is lower than the conductivity reported here. Reason for the lower conductivity in their case can be the formation of secondary phases like MgAl$_2$O$_4$ which could have brought down electrical conductivity. Similarly, conductivity reported by Srisurat *et al.* [20] is much lower, i.e. of the order
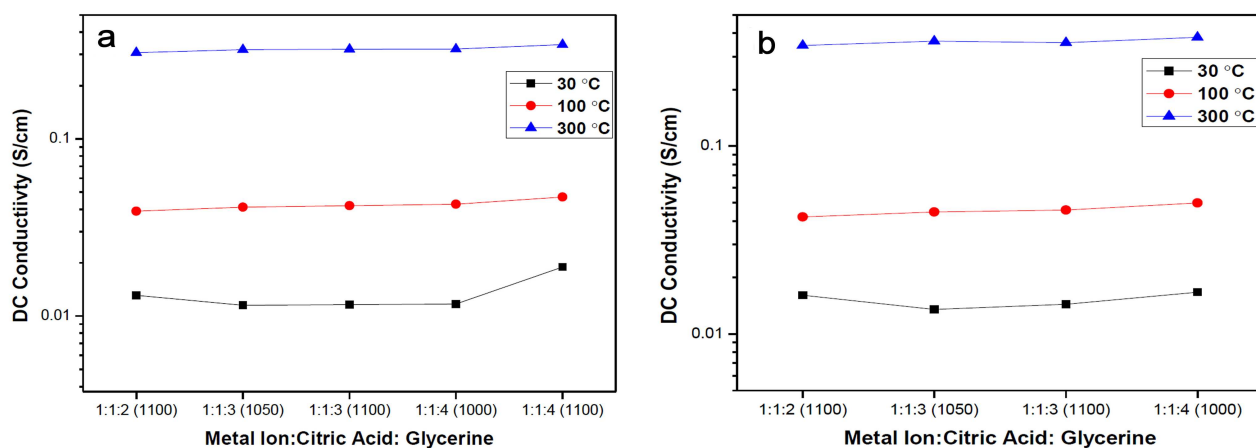
Figure 5. DC conductivity at various temperatures of Mg-SBA ceramics prepared from different powders and sintered at 1500 °C for: a) 3 h and b) 10 h (numbers in parentheses indicate calcination temperature)
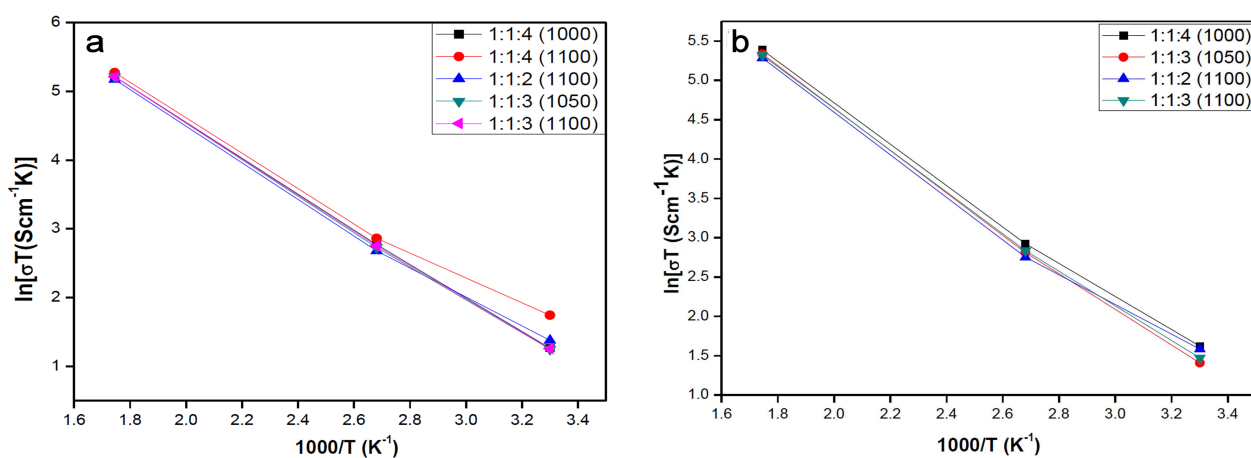

Figure 6. Arrhenius plots for Mg-SBA ceramics prepared from different powders and sintered at 1500 °C for different time: a) 3 h and b) 10 h (numbers in parentheses indicate calcination temperature)

of 10^{-6} S/cm which could be the yield of liquid phase sintering which might have caused grain boundary segregation and impediment to ionic motion. In short, the electrical conductivity obtained in our work is at par with most of the classic works reported in the literature where β'' is the primary phase after solid state sintering.

IV. Conclusions

Mg-doped sodium beta-alumina (Mg-SBA) nanopowders were synthesized using the citrate sol-gel process. Low cost glycerine was used instead of ethylene glycol as solvent. To the best of our knowledge this has been done for the first time. Utilisation of glycerine during synthesis of Mg-SBA resulted in getting particle size <100 nm which was considerably less as compared to initially used ethylene glycol which resulted in a particle size of >200 nm as measured by BET surface area analysis. The sintered density was found to increase with increase in the calcination and sintering temperature and also the sintering time. The maximum DC conductivity obtained using glycerine as solvent is 0.38 S/cm measured at 300 °C and minimum activation energy for conduction is 0.20 eV.

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