Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 21, Sayı 3, 816-819, 2017

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 21, Issue 3, 816-819, 2017

DOI: 10.19113/sdufbed.31721

Investigation of the Production of Beta-Al_2O_3 Solid Electrolyte from Seydişehir α-Al_2O_3

Selin ENGÜRLÜ[1], Zeynep TAŞLIÇUKUR ÖZTÜRK*[2], Nilgün KUŞKONMAZ[1]

[1] Yildiz Technical University, Faculty of Chemical and Metallurgical Engineering, Metallurgical and Materials Engineering Department,34210, Istanbul
[2]Gedik University, Faculty of Engineering, Metallurgical and Materials Engineering Department, 34876, Istanbul

(Alınış / Received: 24.01.2017, Kabul / Accepted: 09.09.2017, Online Yayınlanma / Published Online: 24.10.2017)

Keywords
α-Al_2O_3,
Calcination,
Sintering,
β-Al_2O_3,
Dielectric properties

Abstract: In this study, we report the production of β˝-Al_2O_3 solid electrolyte by using Seydişehir α-Al_2O_3. Alumina has to be low grain-sized to ensure α-β phase transformation. Therefore, grain refining process was applied to high grain sized Seydişehir alumina by jetmill grinding. Seydişehir alumina was calcined at 1200 ^{0}C for 2 hours. After calcination, calcined Al_2O_3 and Na_2CO_3 were mixed during 2 hours in the mill. The samples were pressed and sintered to obtain β˝-Al_2O_3. β˝-Al_2O_3 was obtained after sintering at 1550°C for 1 hour. Due to the formation of β˝-Al_2O_3, it is observed that dielectric properties increased.

Seydişehir α-Al_2O_3'dan Beta-Al_2O_3 Katı Elektrolit Üretiminin Araştırılması

Anahtar Kelimeler
α-Al_2O_3,
Kalsinasyon,
Sinterleme,
β-Al_2O_3,
Dielektriksel özellikler

Özet: Bu çalışmada, Seydişehir α-Al_2O_3 kullanılarak β˝-Al_2O_3 üretimi yapılmıştır. α-β faz dönüşümünü sağlamak için alüminanın düşük tane boyutuna sahip olması gerekmektedir. Bu nedenle, iri taneli Seydişehir alüminaya jet mil öğütme yöntemi ile tane küçültme işlemi uygulanmıştır. Seydişehir alüminası 1200 ^{0}C'de 2 saat kalsine edilmiştir. Kalsinasyon işleminden sonra, kalsine Al_2O_3 ve Na_2CO_3 bilyalı değirmende 2 saat boyunca karıştırılmıştır. 1550°C'de 1 saat sinterlemeden sonra β˝-Al_2O_3 elde edilmiştir. β˝-Al_2O_3'nın oluşmasıyla birlikte dielektriksel özelliklerin arttığı gözlenmiştir.

1. Introduction

Alumina is a ceramic material that has high melting temperature, strength and hardness. In recent years, Seydişehir alumina has been attracting considerable amount of attention about construction of technical ceramic materials. The alumina which is produced by Seydişehir Aluminium factory is not eligible to produce technical ceramic material because of large particle size distribution, high impurity content, intermediate alumina phases contain a high proportion. For these reasons, studies focus on improving the quality of Seydişehir alumina powder and developing the sintering properties for the utilization of Seydişehir alumina in technical fields. [1,2].

Two different phases, the β and β˝, have been determined in the pseudo-binary Na_2O-Al_2O_3 system. They are used as the solid electrolyte membrane in Na-S batteries, electric vehicles, chemical sensors. β-Al_2O_3 is a layered crystal structure, $Na_2O.x\ Al_2O_3$ ($5 \leq x \leq 11$), and it is a nonstoichiometric compound. The β and β″-phases have closed packed structures with 2 and 3 spinel blocks respectively, separated by the conduction planes, which contain sodium and oxygen. Above 1550°C, the β˝ phase decomposes onto β and the decomposition is not reversible [3-6]. Sodium beta-alumina ceramics are the best solid electrolytes known today because of its fast-ionic conductivity. [6-9].

The conventional method for production of Na-β-aluminas, compound involves a high-temperature reaction of α-alumina with Na_2CO_3 in presence of small quantities of Li_2O, Na_2O or MgO as the stabiliser. Significant soda loss occurs as the reaction is carried out at high temperatures, which results in reduced conductivity of the products. Na_2O is added as a stabilizer. The mixture is calcined and sintered to obtain a beta-alumina solid electrolyte with uniform quality and high strength. [9-14].

The purpose of this study was to prepare beta alumina solid electrolytes in the Na_2O–Al_2O_3 system by using Seydişehir alumina and investigate the effect

*Corresponding author: ztasli@gmail.com

of the Na_2O content on the forming of beta alumina and the ionic conductivity of the solid electrolyte Na-beta-Al_2O_3. Therefore, Seydişehir alumina can be used as a technical ceramic.

2. Material and Method

The raw material, α-Al_2O_3 powder(Seydişehir Alumina), was jet milled for 30 min. The flow chart of the experimental procedure is given Figure 1. The particle size of the powder before and after jet milling was measured by Malvern Mastersizer 2000S. The resulting mixture was calcined at 1200°C for 2 h in Linn High Therm furnace. Sodium carbonate was added to α-Al_2O_3 powder. Mixing ratio was 9:1. So, 10 grams of Na_2CO_3 were added to 90 grams of Al_2O_3. The powder was ball milled with zirconia balls for 2 hours. 3 gr powder was weighed and prepressed in a 2 cm diameter mould under 50 MPa. In Figure 2(a), the mould and the pressed sample Figure2(b) could be seen.

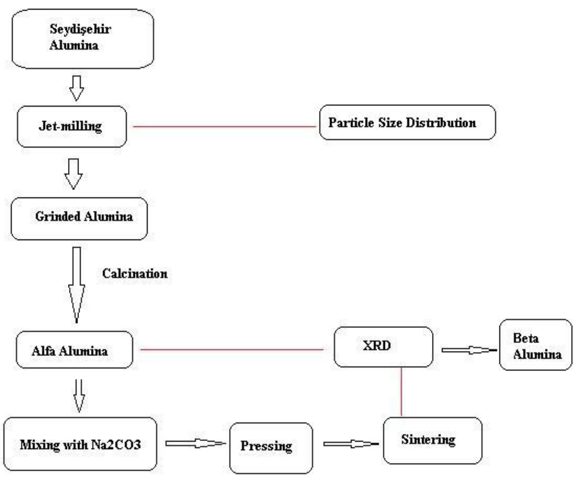

Figure 1. Flow chart of experimantal procedure

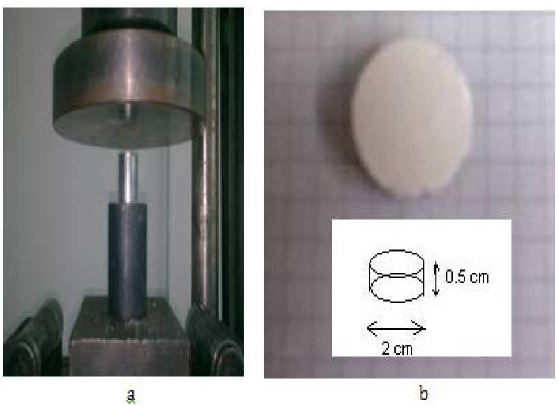

Figure 2. a) 2 cm diameter mould b) Pressed sample

After pressing, the specimens were sintered at 1550°C for 1 h. X'Pert PRO MRD Panalytical diffractometer with Cu-Kα X-ray radiation was used to investigate the crystal phases of the samples. Computer controlled Hewlett-Packard 4194A impedance/gain-phase analyzer was used in dielectric measurements which are performed at room temperature.

3. Results

The chemical analysis of Seydişehir alumina is given in Table 1. Bulk density and absolute density of Seydişehir alumina are 1.00-1.10 gr/cm^3 and 3.30-3.60 gr/cm^3, respectively.

Table 1. Chemical analysis of Seydişehir alumina powder

Chemical analysis	LOI (1100^{0}C)	Al_2O_3	SiO_2	Fe_2O_3	Na_2O
(%) max	1	98.5	0.030	0.035	0.50

Alumina has to be low grain-sized to ensure α-β phase transformation. Therefore, grain refining process was applied to high grain sized alumina by jetmill grinding. The avarage grain size of the powder was 82.088 μm before jet-milling. After 30 min jet-milling, average grain size of the powder was 4.618 μm as shown in Figure 3.

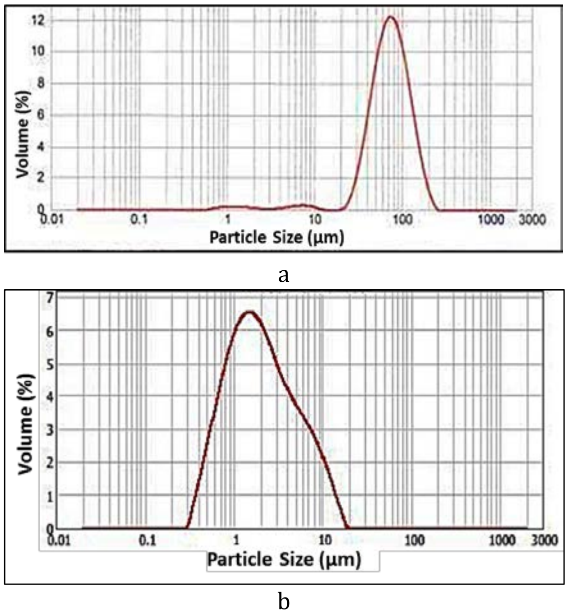

Figure 3. Particle size distribution of Seydişehir alumina a) before jet milling b) after jet milling

According to XRD analysis in Figure 4, it was seen that Seydişehir alumina did not consist of completely α-Al_2O_3 before calcination. After calcination at 1200 ^{0}C for 2 h, the transition phases transformed to α-Al_2O_3. Technical alumina ceramics could reach to the desired quality by calcination and grinding under controlled conditions.

XRD analysis presented in Figure 5 showed that β″-Al_2O_3 was formed, and Na_2O and $Na_2MgAl_{10}O_{17}$ phases were also detected. It was indicated that the Na_2O content had an intensive effect on the β″-phase content at high temperature. The higher Na_2O content led to the more β″-phase transformation[15].

The ionic conductivity of the solid electrolyte Na-beta-Al_2O_3 has been studied since a long time[16]. Figure 6 shows the relationship between the paralel impedance of samples (α-Al_2O_3 and β″-Al_2O_3) and the frequency. Depending on parallel measurements of frequency, frequency is defined as the critical point, the critical frequency of these two materials, the transaction process moves from the low frequency region to high-frequency region due to increasing of beta alumina. Critical frequency value of alpha alumina is approximately 19,810 khz and critical frequency value of beta alumina is 171,911 khz.

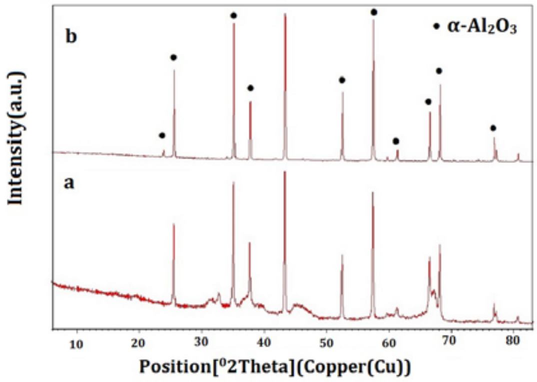

Figure 4. XRD patterns of the specimen a) before calcination b) after calcination at 1200°C for 2 h.

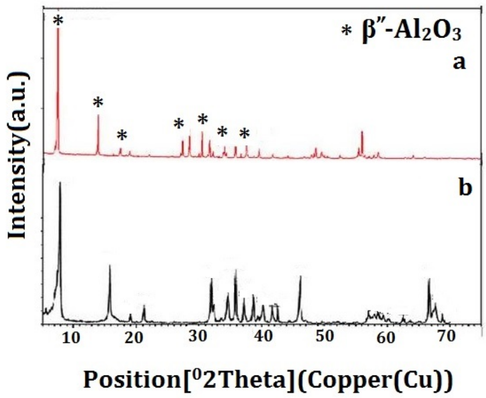

Figure 5. XRD patterns of the specimen sintered at a)1550°C for 1 h b) reference specimen

4. Discussion and Conclusion

Seydişehir alumina was used as raw material to produce beta-Al_2O_3. Jet milling method was applied for obtaining fine powder. The powder was calcined at 1200 ^{0}C for 2 h to form α-Al_2O_3. α-Al_2O_3 was ball milled with Na_2CO_3 to form β″-Al_2O_3. Pressed specimens were sintered at 1550 ^{0}C for 1 h. According to XRD analysis, β″-Al_2O_3 was formed. Dielectric properties were also measured as a function of frequency. The transaction process moves from the low frequency region to high-frequency region due to increasing of beta alumina. For better results, sintering temperature and time could be increased or hot pressing technique could be used.

Acknowledgment

This research was supported by Scientific Research Foundation of Yildiz Technical University with the Project no 2011-07-02 YULAP06.

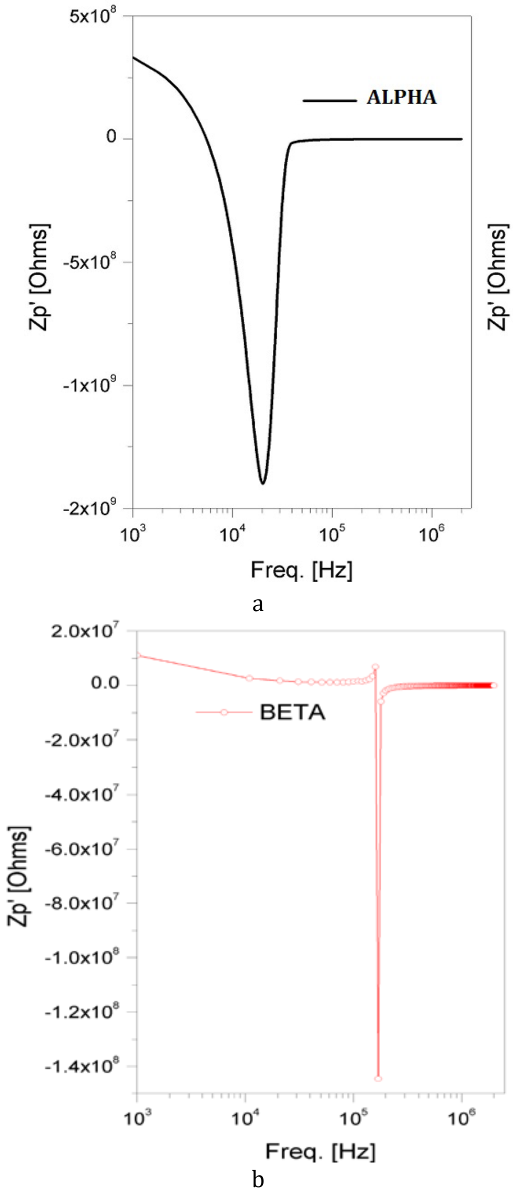

Figure 6. Parallel impedance of the specimen change depending on frequency a) α-Al_2O_3 calcined at 1200 ^{0}C for 2 hours b) Beta-Al_2O_3 sintered at 1550 ^{0}C for 1 hour.

References

[1] Erten, R., Emrullahoğlu, C.B., Yazıcı, Z.O., Emrullahoğlu, Ö.F.2004. An investigation on injection molding of Seydişehir alumina. Key Engineering Materials, 264-268(2004), 2523-2526.

[2] Tambaş, T., Özgen, S. Seydişehir alüminasının slip döküm parametrelerinin belirlenmesi.2007. İTÜ Dergisi/Mühendislik, 6(2007), 83-94.

[3] Subasri, R., Nafe, H.2003. An alternative approach to characterize the equilibrium in a biphasic α-Al_2O_3/Na-β-Alumina mixture as a function of sodium activity. Electrochimica Acta, 48(2003),3535-3540.

[4] Song, H.I., Kim, E.S., Yoon, K.H.1988. Phase transformation and characteristics of beta alumina. Physica B,150 (1988), 148-159.

[5] Roth, W.L., Devries, R.C. 1977. Comparison of the thermal stability of β and β˝-alumina high pressures. Journal of Solid State Chemistry, 20 (1977), 111-118.

[6] Chengfei, Z, Jinhua, X., Guanghui, J. 2015. Effect of Na_2O content on properties of beta alumina solid electrolytes. Materials Science in Semiconductor Processing, 31 (2015), 487- 492.

[7] Dunn, S., Kumar, R.V., Fray, D.J.2000. Thermodynamic studies of the ionic conductor Ba β - Al_2O_3. Solid State Ionics, 128(2000), 141-144.

[8] Sartori S, Martocci A, Muffato A, Guglielmi M.2004. Sol-Gel synthesis of Na Beta- Al_2O_3 powders. Journal of the European Ceramic Society, 24(2004), 911-914.

[9] May, G.J.1978. The development of Beta-alumina for use in electro-chemical cells: A Survey. Journal of Power Sources,3(1978), 1-22.

[10] Dae-Han, L, Sung-Tae, L., Jin-Sik, K., Sung-Ki, L.2017.Analysis of properties of partially stabilized zirconia-doped Na^+-beta-alumina prepared by calcining-cum-sintering process. Materials Research Bulletin, (2017)

[11] Jayaraman, V., Periaswami, G., Kutty, T.R.N. 2008. Gel- to- crysallite conversion technique for the syntheses of M-β/β˝-Alumina (M:Li,Na,K,Rb,Ca or Eu).Materials Research Bullettin, 43(2008), 2527-2537.

[12] Jones, I.W., Miles, L.J. Production of beta alumina ceramic. United States Patent 1975.

[13] Lu, X., Xia, G., Lemmon, J.P., Yang, Z.2010. Advanced materials for sodium-beta alumina batteries: Status, Challenges and Perspective. Journal of Power Sources, 195(2010), 2431-2442.

[14] Subasri, R., Mathews, T., Sreedharan, O.M., Raghunatan, V.S.2003. Microwave processing of sodium beta alumina. Solid State Ionics, 158 (2003), 199-204.

[15] Chengfei, Z., Jinhua, X., Guanghui, J. 2015. Effect of Na_2O content on properties of beta alumina solid electrolytes, Materials Science in Semiconductor Processing, 31 (2015), 487–492.

[16] Shqau, K. 2003. Characterization of the electronic conduction parameter of cation conducting solid electrolytes. Bericth Nr.141 Max-Planck-Institut für Metallforschung. Stuttgart University, Stuttgart, Germany, 2003.