

Preparation and characterisation of β'' -Al₂O₃

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Abstract. Beta alumina solid electrolyte is a potential candidate in the fabrication of Na-S batteries. In the present study, it has been prepared in the form of discs by uniaxially as well as isostatically pressing and sintering in the temperature range 1585–1630°C, the highest sintered density of 3.25 g/cm³ has been achieved in the samples isostatically pressed and sintered at 1630°C. X-ray analysis of the samples shows formation of β'' -phase. Microstructure of the sintered samples reveals some darker regions which are attributed to low soda content. Resistivity at 300°C measured by the two-probe method at a frequency of 1 MHz on samples having vacuum-deposited silver electrodes is 15 ohm-cm, which is slightly higher than the value of 5–13 ohm-cm reported in literature using molten sodium electrodes. The activation energy of conductivity is 0.24 eV which is comparable to the literature value of 0.24–0.35 eV.

Keywords. Conducting ceramic; ionic conductor; sodium beta alumina; solid electrolyte.

1. Introduction

Beta-alumina ceramics have potential application in a variety of devices such as (a) electrolyte in the Na-S battery (Kummer and Weber 1968) for automotive propulsion or electric utility load levelling (b) thermoelectric devices (Weber 1974) and electrochemical devices for measuring sodium and oxygen activities. Amongst these, the sodium sulphur battery system based on beta alumina is the most advanced one.

The general formula for beta alumina is Na₂O · x-Al₂O₃, where x varies from 5–11. Two structural forms of beta type alumina exist (Kummer 1972). At x = 11 the composition yields β -alumina which starts converting in β'' -alumina as the sodium content increases and at x = 5, the β -phase is completely converted into the β'' -phase. β'' -alumina has higher ionic conductivity than β -alumina but is unstable at a temperature greater than 1500°C. As the sintering temperature of β'' -alumina is > 1500°C, some stabilizing agent like lithium oxide or magnesium oxide or both are added (Gordon *et al* 1977).

Lithium-stabilised β'' -alumina was synthesised from reactive α -alumina which was prepared at NPL, India (Das *et al* 1982). To compare the results, reactive α -alumina of M/s Reynolds, USA was also used to synthesise β'' -alumina.

2. Experimental procedure

β'' -Al₂O₃ was synthesised using two varieties of reactive α -Al₂O₃ (NPL, India; M/s Reynolds USA (which has particle size $\leq 0.7 \mu\text{m}$ and purity > 99.6 %)). The other two raw materials, sodium carbonate and lithium carbonate were of AR grade. The material was processed by using zeta process (Youngblood *et al* 1977) in which sodium-alumina

composition and a lithium alumina composition known as zeta alumina were processed and calcined separately and the two were then mixed in proper proportions to yield the desired composition.

The composition chosen for this experiment was 84.09% Al_2O_3 , 13.54% Na_2O and 2.37% Li_2O all taken in mole percent. $\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ prepared for making the above composition were separately calcined at 1340°C for 2 hr and the compositions dry-ball milled to a particle size of $< 1 \mu\text{m}$. The powder was then mixed with polyvinyl butyral and benzene, which acts as a binder for about 2 hr and the slurry dried in air. The material was granulated using a nylon sieve and pressed uniaxially and isostatically into discs (15 mm dia and 2.5 mm thickness). A flow chart of the zeta process is shown in figure 1. To study the effect of particle size on the density, the

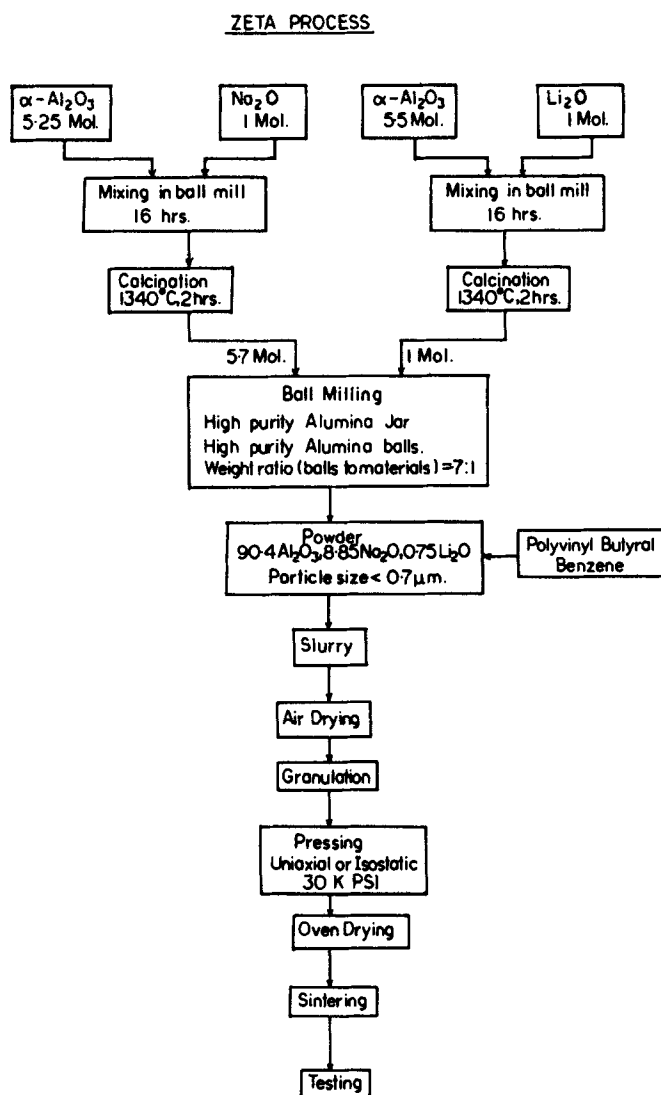


Figure 1. Flow chart of zeta process for the synthesis of $\beta''\text{-Al}_2\text{O}_3$.

Table 1. Particle size analysis of powders A–E.

Particle size (μm)	Materials (comm %)				
	A	B	C	D	E
+1.8	0.4	0.2	0.1	0	0
+1.15	4.2	3.4	2.3	1.2	1.2
+0.8	14.0	12.1	10.7	9.5	9.2
+0.65	26.3	22.6	21.3	19.9	20.2
+0.57	38.2	33.2	32.5	31.1	31.3
+0.5	49.2	43.2	43.0	42.3	42.3
+0.46	59.0	52.3	52.6	51.3	51.5
+0.43	67.5	60.5	61.0	59.3	59.5
+0.36	86.3	83.2	83.8	77.8	77.4
+0.33	94.0	90.3	89.9	85.6	86.4
+0.30	98.4	95.5	95.9	92.4	92.9
+0.28	100.0	98.8	99.2	97.6	97.5
+0.26	100.0	100.0	100.0	100.0	100.0
Mean Particle size	0.56	0.54	0.52	0.5	0.5

material was ground for various durations of time to yield different particle size distributions. Five such powders (table 1) having different particle size distribution were processed by pressing uniaxially and isostatically at different pressures. The pressed tablets were dried overnight in an oven (160°C) and then covered with coarse beta alumina powder and sintered in super kanthal furnace at a temperature ranging from 1585 – 1630°C for various time intervals (2–32 min). The temperature schedule of the sintering is shown in figure 2. The material was annealed at 1480°C for 4 hr for complete conversion into the β'' -phase. An almost similar two-step sintering schedule was adopted by Kvachkov *et al* (1981, 1982).

Rectangular samples ($33 \times 32.7 \times 2.7$ mm) for x-ray analysis were prepared by uniaxially pressing and sintering at a temperature ranging from 1585 – 1630°C . Tables 2a and 2b give the x-ray analysis and it is evident that mostly the β'' -phase is present (Ray and Subbarao 1975; ASTM 1967). The density of the sintered discs was measured by Archimedes principle by immersion in xylene.

For microstructural evaluation the discs were broken into small pieces and the broken faces examined under a scanning electron microscope (JEOL JSM-35 CF). Energy dispersive spectroscopy (EDS) mode was employed for the elemental analysis of aluminium and sodium.

The electrical resistivity was measured by employing evaporated silver full face electrodes and by using Siemen's Bridge at 1 MHz to avoid interface polarisation (Yao and Kummer 1967) in a temperature range of 20 – 300°C .

3. Results and discussions

3.1 Effect of compacting pressure on green density

Figure 3 depicts the effect of uniaxial as well as isostatic pressure on the green density of the materials (Kalsi *et al* 1983). The green density increases with pressure. The highest

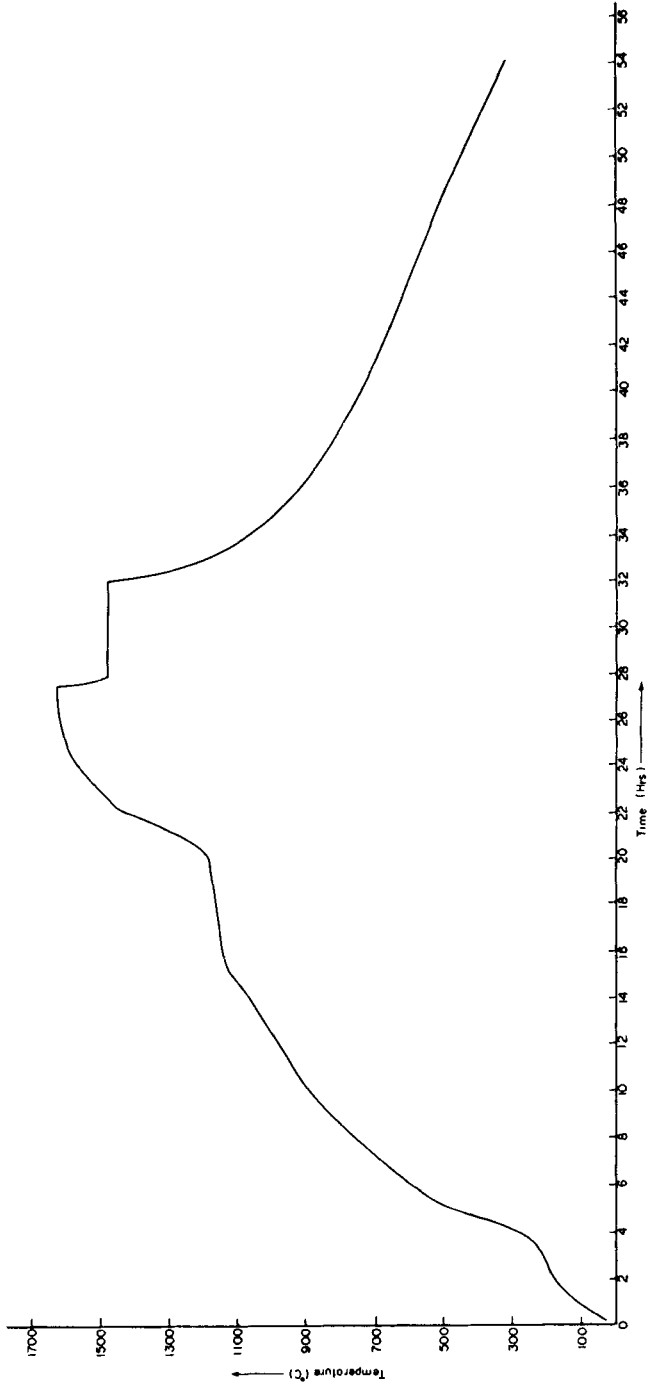


Figure 2. Temperature profile of sintering cycle.

Table 2(a). X-ray diffraction data for β'' -Al₂O₃ prepared from powder D.

dA°	I/I ₁	hkl
11-632	100	003
5-644	47	006
4-495	5	100
4-086	3	001
2-818	12	110
2-683	24	114
2-515	16	116
2-429	9	0014
		200
2-380	3	204
		118
2-254	13	110
2-132	9	1014
		207
2-040	9	209
1-973	5	2010
1-943	7	1016
1-596	6	2014
1-559	6	306
1-406	17	220

Table 2(b). X-ray diffraction data for β'' Al₂O₃ prepared from powder E.

dA°	I/I ₁	hkl
11-632	100	003
5-717	56	006
4-484	7	100
4-086	6	001
2-818	16	110
2-691	28	114
2-600	5	101
		0013
2-515	22	116
2-417	12	0014
		200
2-383	3	203
2-254	18	110
2-139	12	1014
		207
2-045	16	200
1-973	5	2010
1-943	8	1016
1-596	8	2010
1-559	8	306
1-486	4	309
1-404	25	220

green density of 2.27 g/cm³ was obtained in powder A (table 1) at a uniaxial compacting pressure of 3600 kg/cm² whereas at an isostatic pressure of 2600 kg/cm² a highest green density of 2.3 g/cm³ was obtained for the same powder.

The variation of green density with particle size presented in figure 3 shows that the density decreases with particle size.

3.2 Effect of compacting pressure on the sintered density

Variation of the sintered density with uniaxial and isostatic pressure is shown in figure 4. The highest sintered density of 3.22 g/cm³ was obtained for powder D (table 1) compacted at uniaxial pressure of 1800 kg/cm² and sintered at 1630°C, whereas for the isostatically pressed samples sintered at 1630°C, the sintered density is independent of the isostatic pressure in the range of 700–2600 kg/cm². The highest sintered density of 3.25 g/cm³ for powder D was obtained.

The variation of sintered density with particle size is also shown in figure 4 and it is clear that as the particle size decreases the sintered density increases.

3.3 Shrinkage studies

The shrinkage was measured as a function of uniaxial compacting pressure for all the five powders by sintering at 1630°C. The results are shown in figure 5. Shrinkage is higher at lower pressures with no significant change beyond 3000 kg/cm². Powder D exhibits the highest shrinkage followed by powder E (table 1).

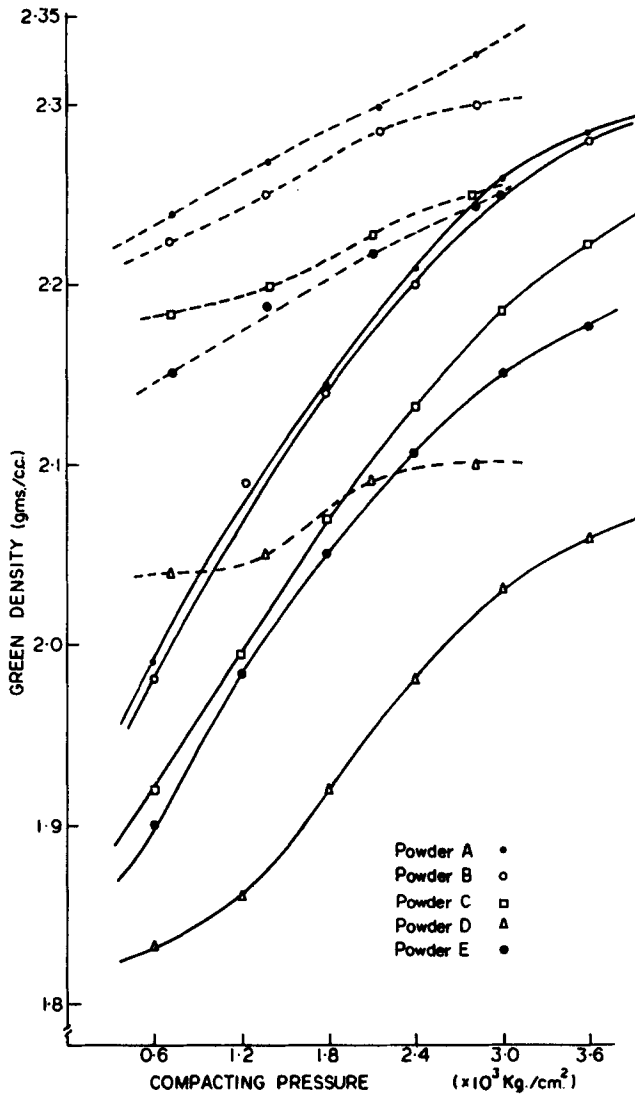


Figure 3. Effect of uniaxial (—) and isostatic (----) compacting pressures on the green density of specimens of different particle sizes.

3.4 Effect of sintering temperature on the sintered density

Figure 6 shows the variation of sintered density with sintering temperature for powders D and E. Initially the density increases rapidly with temperature up to 1615°C beyond which it begins to saturate.

3.5 Microstructural evaluation

Microstructure of the β'' -Al₂O₃ samples prepared from powders D and E and sintered at 1630°C is shown in figures 7a and 7b respectively. The microstructure consists of grains that are elongated but irregular. The overall structure is quite uniform across the

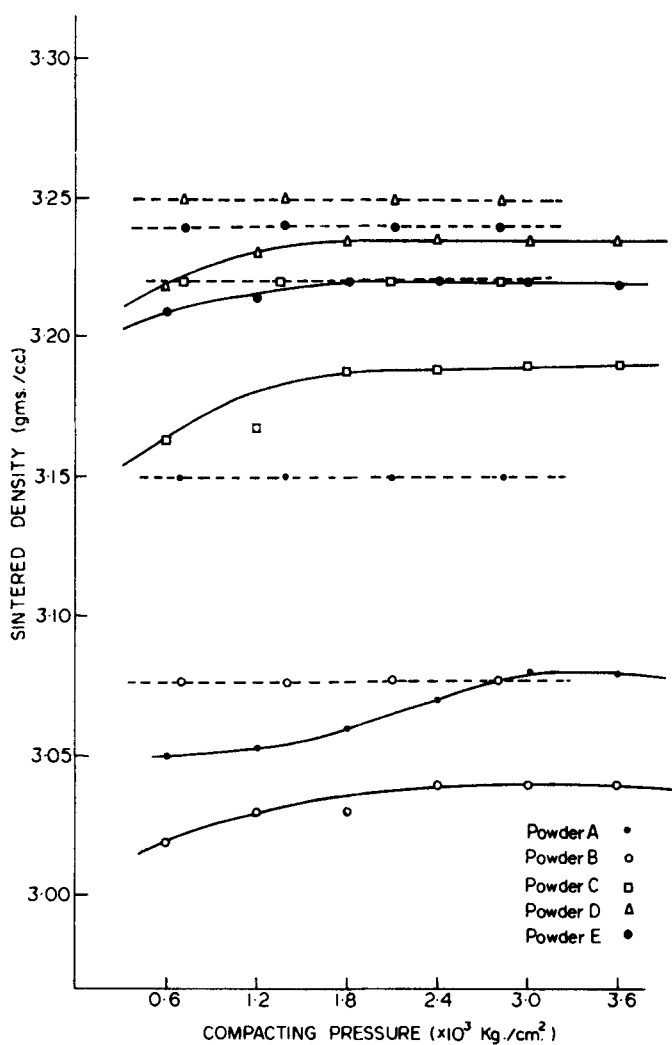


Figure 4. Variation of sintered density as a function of uniaxial (—) and isostatic (---) compacting pressures for all the five powders having different particle sizes and sintered at 1630°C for 20 min.

ceramic and the grains are randomly oriented. Grains as large as 10 μm could be seen. Similar microstructure has also been observed by Wynn and Miles (1971).

A common feature of the microstructure is the presence of a dark phase spread over the microstructure. Closer examination (EDS) for elemental analysis showed that these regions were soda-deficient portions and therefore the likelihood of some beta-phase cannot be ruled out. Recently it has been reported (Hodge 1983) that the relative amount of β and β'' phase is a function of cooling rate and the amount of β'' -phase increases with decreasing cooling rate. Further work is required to confirm and eliminate this secondary soda deficient phase from $\beta''\text{-Al}_2\text{O}_3$.

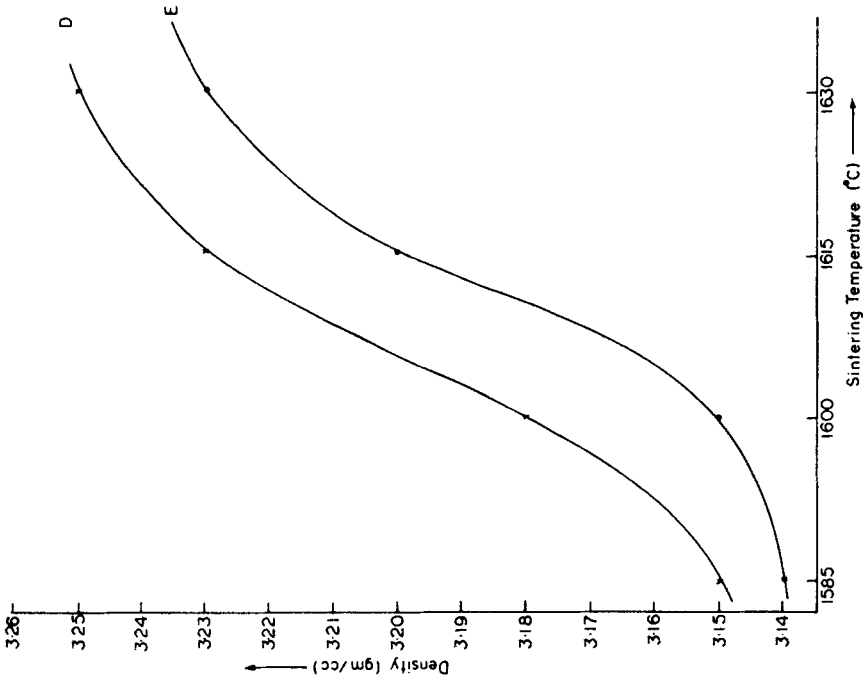


Figure 6. Variation of sintered density of powders D and E as a function of sintering temperature.

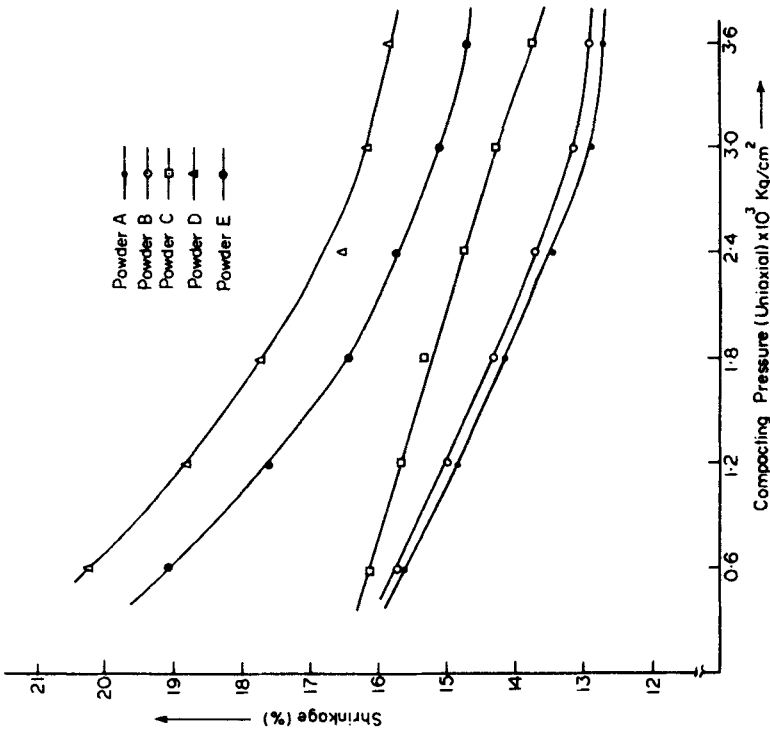


Figure 5. Variation of shrinkage with uniaxial compacting pressure for samples of different initial particle sizes and sintered at 1630°C for 20 min.



Figure 7. Microstructure of β - Al_2O_3 prepared from a. powder D and b. the powder E and sintered at 1630°C for 20 min.

4. Conductivity measurements

Ionic conductivity of beta alumina type superionic conducting material has been studied by several investigators (Wynn and Miles 1971; Demontt and Hancock 1971; Kummer 1972; Whittingham and Huggins 1971). Such measurements need either reversible electrodes *i.e.* molten sodium (Demontt and Hancock 1971) or $\text{NaNO}_2/\text{NaNO}_3$ (Sudworth *et al* 1973) eutectic mixture, in which case conductivity is independent of the frequency. For measurements made using platinum or silver blocking electrodes the conductivity becomes frequency dependent below 1 MHz. At 1 MHz and above it is independent of the frequency. In this study the measurements were made at 1 MHz using evaporated silver blocking electrodes; and resistivity of the order of 15 ohm-cm at 300°C was obtained.

The activation energy of conductivity was 0.24 eV which is close to the value reported (Kalsi *et al* 1983) for Li_2O doped compositions of $\beta''\text{-Al}_2\text{O}_3$. It may be pointed out here that this is slightly higher (Kalsi *et al* 1983) than those for the corresponding MgO-doped compositions. This difference could be due to the difference in structure or atomic jump mechanism which controls the ionic conductivity.

5. Conclusion

In $\beta''\text{-Al}_2\text{O}_3$ samples isostatically pressed and sintered at 1630°C a density of 3.25 g/cm³ has been obtained. A maximum shrinkage of 20% was observed in samples uniaxially pressed at 600 kg/cm² and sintered at 1630°C. X-ray analysis reveals the formation of β'' -phase. The microstructure reveals randomly oriented elongated crystals of $\beta''\text{-Al}_2\text{O}_3$ having some darker portions; which are regions of low soda content. The resistivity of the order of 15 ohm-cm at 300°C has been obtained. An activation energy of 0.24 eV was obtained which is close to the value reported in literature.

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