# Effect of Milling Time on Structural and Dielectric Properties of $Al_2O_3$

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## ABSTRACT

Aluminum oxide ($Al_2O_3$) is a ceramic material that is well known for its high temperature property, high level of hardness, as well as great stability against corrosion (Li et al. 2016, Amirsalari et al. 2015). The ball milling effects on the structural and dielectric properties of $Al_2O_3$ samples prepared by solid-state reaction are studied. The samples are prepared with different milling times from 0 to 12h. XRD results reveal that nano ball milling has remarkable effects on the crystal structure by changing its preferred orientation and crystallite size. The values of dielectric constant increase with increasing frequency due to space charge polarization. It is observed that milling time has significant impact on dielectric values. Variation in dielectric properties is attributed to change in grain boundary capacitance and grain size.

## 1. INTRODUCTION

Aluminium oxide ($Al_2O_3$) is a promising ceramic material because of its properties such as high temperature and hardness (Pantelis et al. 2000, Hartfield-Wunsch et al. 1994, Niemi et al. 1994). In addition, it has large stability against corrosion, low leakage current, high breakdown strength and a low dielectric loss which makes it a suitable material for fabrication of capacitors having high energy density. High energy density capacitors are necessary for fast progress in electronic equipment (Ding et al. 2003, Wu et al. 2008). With the fast progress in the surface modification and coating technology, compositions containing $Al_2O_3$ are outstanding protective coatings because of resistance against thermal, corrosion and mechanical wear by means of their excellent arrangement of high hardness, melting point, chemical and thermal stability, in addition to wear and corrosion resistance (Li et al. 2006). However, $Al_2O_3$ can be used in CMOS technologies which is important both for electronic and optics (Seredin et al. 2015). The electrical parameters of materials depend upon the physical properties of material. Physical properties of materials change significantly with chemical composition and microstructure, which can be carefully controlled during the growth. The powder characteristics such as chemical purity, morphology and particle size have remarkable effect on the physical properties of ceramic.

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Several researchers tried to develop low cost synthesis methods for making pure submicron powders with controlled size distribution. Among these methods, ball milling is a significant technique used to make sub–micrometer particles. During the milling process, the grinding specimen is accelerated to higher velocities that transfer a high kinetic energy from the balls to the sample; as a result of it fine powder is produced. Ball sizes, rotation speed, and milling time have great influence on the experimental results. This method has many benefits for example its simplicity, cost effective and can be used to any type of materials (Kong et al. 2000, German 1996). High-energy ball milling is most suitable technique to produce solid-state reactions as compared to the conventional procedures of powder preparation (Suryanarayana 2001). In the ball milling, milling time is an important factor. Powder characteristics such as morphology, structure, grain growth and physical properties are influenced by milling time. In the present work, influence of milling time on the structural and dielectric properties of aluminum oxide has been studied.

## 2. Experimental details

Samples of aluminium oxide ($Al_2O_3$) were prepared by the standard solid-state reaction method. Commercially available high-purity (99.99%) aluminium oxide ($Al_2O_3$) powder from Reacton (rare earth metals and compounds) was used. The powder was ball-milled [Fritsch, Germany] by using ten stainless steel balls at a frequency of 25Hz for 1 h. Then powder was pressed/pelletized by hydraulic press at pressure of $2.54\times10^6$ Pascals to prepare the pellet having area (0.54 $cm^2$). Further, the pellet was sintered at 1500 $^oC$ for 2 h in air. The samples prepared in this study are listed in Table 1. The microstructure of fabricated samples of aluminum oxide was analyzed by scanning electron microscopy (Hitachi S3400N). The Impedance analyzer (Wayne Kerr 6500 B) was employed to determine the frequency dependent dielectric parameters. Finally, in the same manner four different samples labeled as c, d, e & f were prepared by various milling times. The milling time, thickness and area of samples are summarized in Table I.

Table 1: Summary of the samples obtained in this study.

| Sample ID | Ball-milling time (h) | Thickness (cm) | Area ($cm^2$) |
|---|---|---|---|
| a | 0 | 0.066 | 0.526 |
| b | 1 | 0.186 | 0.538 |
| c | 3 | 0.076 | 0.559 |
| d | 6 | 0.114 | 0.545 |
| e | 9 | 0.136 | 0.551 |
| f | 12 | 0.104 | 0.555 |

## 3. Results and discussion

Figure 1 illustrates XRD patterns of the $Al_2O_3$ samples milled for different times. All XRD peaks identify rhombohedral structure of $Al_2O_3$ with the help of JCPDS card (pdf 10-0173). It is noted that there is change in number of diffraction peaks such as peaks diffracted at angle 2θ values 66.58° and 68.30° corresponding to (214) and (300) plane. However these are present only in samples a and b. As the milling time was increased from 1 hour, these two peaks were not observed. All the other diffraction peaks were observed in all samples with different intensities and with minor change in diffraction angles. The change in number of peaks and shift in diffraction angles is due to distortion of the lattice. It is a possibility that milling produces defects in crystalline solid, which consequently generate inhomogeneous strain (Vijatovic Petrovic et al. 2012, Thakur et al. 2007). This strain promotes the lattice deformation. The high intensity peak corresponding to (104) plane is consistent with literature (Parchovianskŷ et al. 2014). The crystallite size and dislocation density of high intensity peak is plotted as a function of milling time as shown in Fig. 2. The crystallite size increases with increasing milling time due to decrease in strain that reduces the dislocation density. Crystallite size attained maximum value at 3 hour milling and it became almost constant with further increase in milling time. The constant trend in crystallite size with increase in milling time proposes that the system entails a mechanism due to production of microstrain and specific energy of grain. These reveal plastic defects in the lattice.

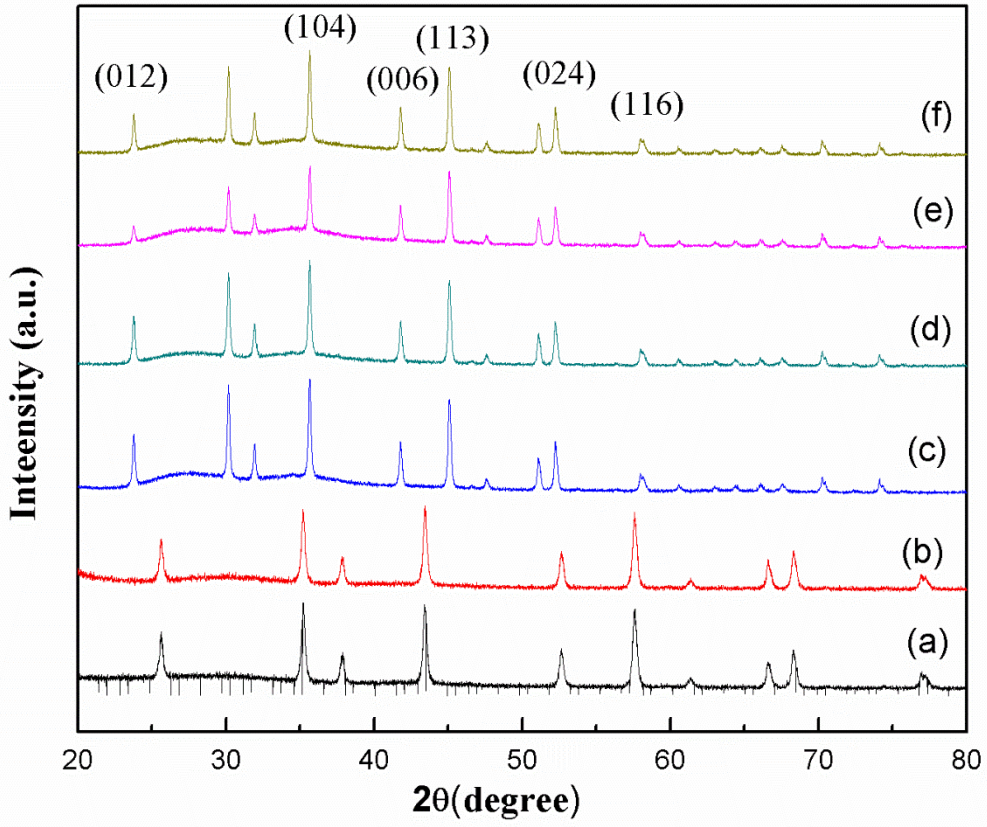


Fig. 1: X-ray diffraction pattern of samples a-f.

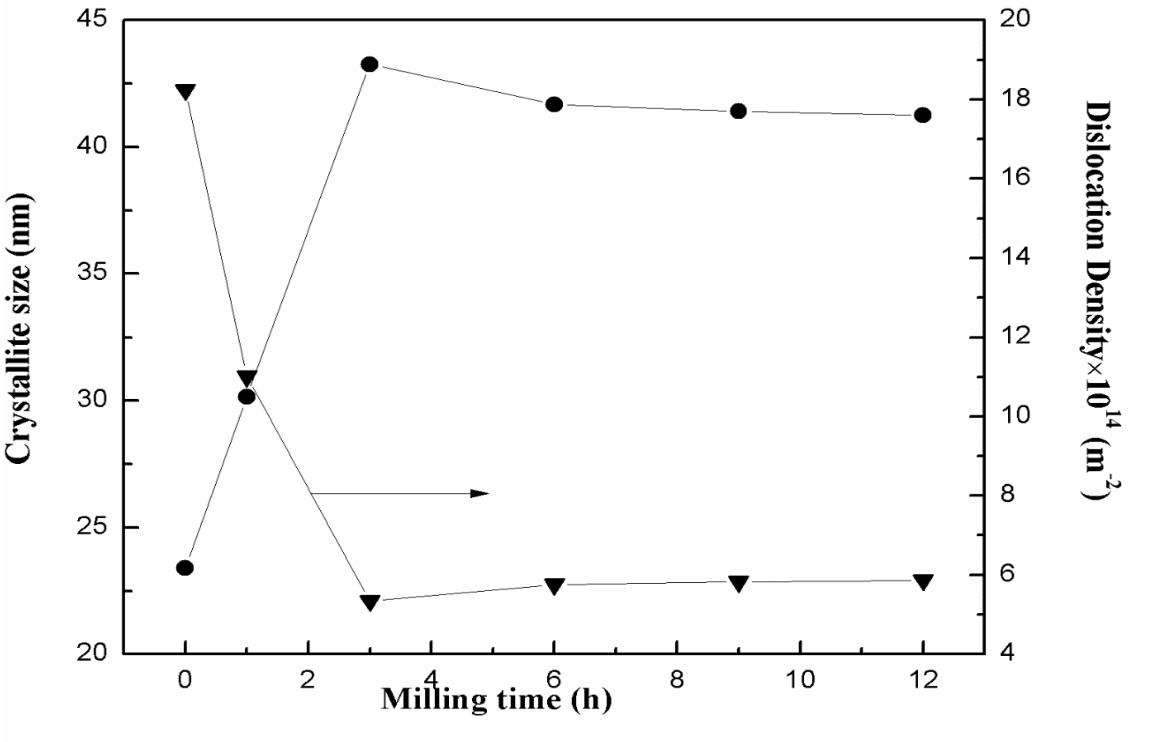


Fig. 2 Crystallite size and dislocation density of highest peak with increasing milling time.

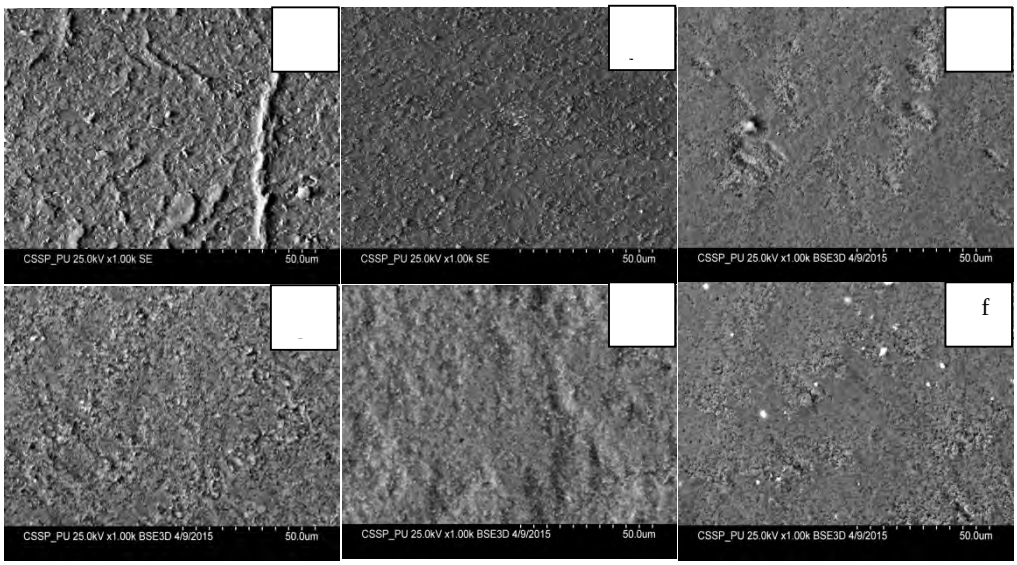


Fig. 3 SEM micrographs of samples a-f.

Figure 3 displays SEM images of samples a-f with different milling time. It is specifically observed that micro composites made by unmilled $Al_2O_3$ reveal rough surface with lots of cracks and pores. Surface roughness is reduced in case of micro composites made by milled $Al_2O_3$ samples. There is rise in number of grains with minor change in the grain size as a milling time increase. This observation supports the XRD results.

Frequency dependent dielectric measurements in the frequency range of 1 KHz to 10 MHz were taken at room temperature. The parallel capacitance values were obtained to calculate the dielectric constant ($\epsilon$) using the relation (Chelkowski 1980):

$$\epsilon = \frac{C \times d}{\epsilon_o \times A} \qquad (1)$$

where C, d, $\epsilon_o$ & A are the capacitance of the capacitor, thickness of the pellet, permittivity of free space and flat surface area of the pellet, respectively. The calculated values of dielectric constant as a function of frequency for all samples are plotted in Figure 4. The frequency dependence of dielectric constant shows a continuous increase with increase in frequency with pronounced dispersion at higher frequency. It is clear from Figure 4 that the variation of dielectric constant as a function of frequency is not consistent with literature (Mozalev et al. 2014, Huanga et al. 2011). Similar trends have been reported in different materials by several researchers (Qian et al. 2010, El Hiti 1999) suggesting a strong relationship between lattice distortion and dielectric behavior of materials.

The dielectric constant depends only on the capacitance because thickness and surface area are fixed. The change in dielectric constant is because of space charge polarization. The space charge polarization is due to the grains having high conductivity detached by grain boundaries; the grain boundaries have low conductivity. The role of grain dominates considerably at low frequency while grain boundaries are more effective as compared to the grains at high frequency. Consequently, dielectric constant increased with increase in frequency. At high frequency grain boundary defects and voids play active role. The lattice deformation leads to inconsistency of charges, which changes capacitance of the specimen. Defects are produced by lattice deformation because of different particle sizes through milling. Defects or traps have an ability to capture and emit electrons that change the charge density. It was found that dielectric constant value decreases with increase in milling time. Initially, particle sizes are increased with the increased with milling time and hence it is quite possible for these ions to polarize to the maximum extent causing an increase in the dielectric constant. Further increase in milling time reduces the dielectric constant thereby hindering the polarization. The overall low values of dielectric constant observed might be attributed to nanosized particles of the specimen that introduce more defects. This variation in dielectric constant of different samples is also consistent with XRD and SEM results.

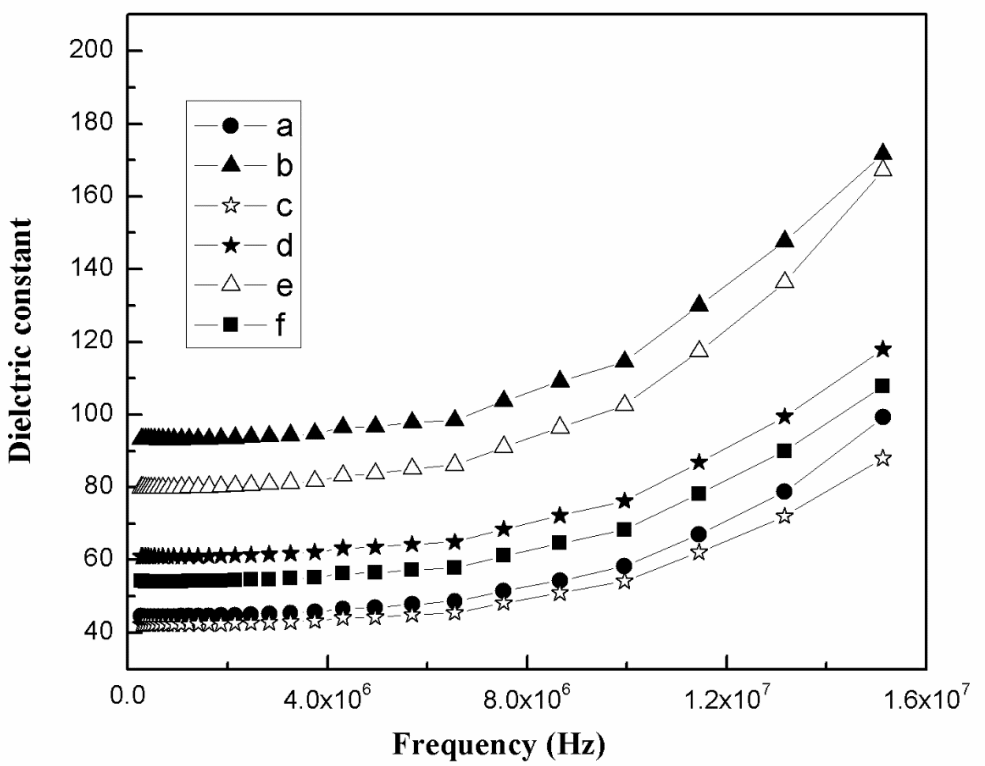


Fig. 4 Variation of dielectric constant of samples a-f with frequencies.

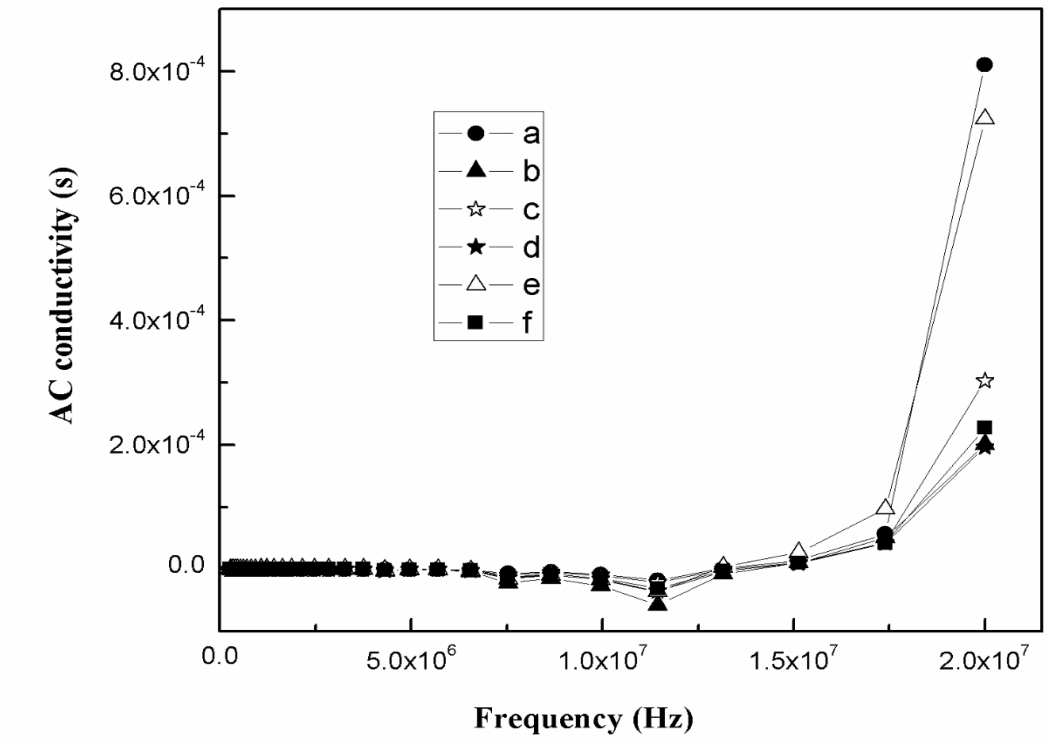


Fig. 5 AC conductivity of samples a-f plotted against frequencies.

Figure 5 shows ac conductivity of these aluminum oxide samples calculated using the following formula (Dridi et al. 2015):

$$AC\ conductivity = \omega C tan\delta \frac{d}{A}$$

The value of AC conductivity increases with increasing frequency in the same manner of dielectric constant. The mechanism of AC conductivity can be explained on the basis of hopping of electrons. The capacitance of the samples increase due to hopping of charges between different lattice sites at high frequency, which increases the AC conductivity of samples. At low frequency, reactance of the dielectric increased because of the reduction of its polarizability. It is assumed that the lattice deformation and reduced particle size due to the milling are the reasons for generation of additional carriers by traps.

## 4. Conclusions

Ball milling effect on structural, optical and dielectric properties of aluminium oxide ($Al_2O_3$) has been investigated. Aluminum oxide samples with different milling time were made by means of solid-state reaction method and were characterized using XRD, SEM and dielectric measurements for the study of structural, morphological and dielectric properties, respectively. The structural parameters of $Al_2O_3$ such as crystallite size and dislocation density were determined. Crystallite size and dislocation density exhibited different trends with milling time. With increased ball-milling time, high values of dielectric constant and AC conductivity indicated high frequency applications.

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