Study of dielectric properties of $\alpha$-alumina doped with MnO, CdO and MoO

I S Ahmed Farag, I K Battisha & M M El-Rafaay
National Research Center Solid State Department, Dokki, Cairo, Egypt
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The dielectric constant ($\varepsilon$), conductivity ($\sigma$) and activation energy ($E_g$) of $\alpha$-alumina doped with different molar ratios ranging from 0.01 to 0.19 of manganese oxide (MnO), and from 0.01 to 0.16 for both molybdenum oxide (MoO) and cadmium oxide (CdO) were studied. The XRD patterns reveal clearly that the prepared samples, consist of only single phase ($\alpha$-alumina phase). The crystallite size and micro-strain of the investigated samples were calculated. The crystallite size increases with increasing dopant concentration. But the rate of the crystallite growth differs from one system to another. The value of $\varepsilon$ has been measured in a frequency range 42 Hz-5 MHz as a function of temperature ranging from 100 to 450°C. The possible explanations and the role of some impurities (mainly Mn, Mo and Cd) are analyzed. The value $\varepsilon$ of pure sample increases from 9.4 to 10.63 as a function of temperature at constant frequency 1 MHz. In this material, the value of $\varepsilon$ increases with increase of temperature due to space charge polarization and crystal defects, while it decreases as a function of frequency due to the scattering of charge carriers at high frequencies. From the plots of log $\sigma$ as a function of the reciprocal of temperature at different frequencies, it has been shown that more than one straight line with different shapes are obtained, indicating different conduction mechanisms at 100 kHz and 1 MHz. An increase in the conductivity with increasing dopant concentration appeared and it could be related to the increase of the charge carriers, which are localized at ions or vacant sites. The activation energies for conduction in the high temperature region are calculated and found to be equal to 0.489, 0.457 and 0.459 eV for 0.01% of Mn, Mo and Cd, cations respectively at constant frequency of 100 kHz. The lower activation energy values for conduction in doped materials may be attributed to a larger charge carrier concentration in them compared to pure $\alpha$-alumina. The XRD was elucidating to confirm that the obtained phase is a single $\alpha$-alumina phase.

Keywords: Dielectric constant, Conductivity, Alumina, Micro-strain, Crystallite
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1 Introduction

Alumina is the most costly and widely used material in the family of engineering ceramics. The raw materials from which this high performance technical grade ceramics are made, are readily available and reasonably priced. Aluminium oxide, commonly referred to as alumina, possesses strong ionic interatomic bonding giving rise to its desirable material characteristics. It can exist in several crystalline phases, which revert to the most stable hexagonal alpha phase at elevated temperatures. This is the phase of particular interest for structural applications. Alpha phase alumina is the strongest and stiffest of the oxide ceramics. Its high hardness, excellent dielectric properties, refractoriness and good thermal properties make it the material of choice for a wide range of applications. Pure $\text{Al}_2\text{O}_3$ doped with different impurities had been extensively studied. Each technique produces $\text{Al}_2\text{O}_3$ with different properties, which should be optimized for particular applications, such as gas laser tubes, wear pads, seal rings, high temperature electrical insulators, high voltage insulators, electronic substrates etc. The conductivity of insulators and semiconductors increases with temperature, contrary to metals. A strong and rigid chemical bond in an oxide will cause a high resistivity and a small dielectric constant of the oxide. Accordingly, it can be expected that aluminium oxide will be a very good insulator.

The dielectric constant ($\varepsilon$), loss (tan $\delta$), and conductivity ($\sigma$) of single crystals of $\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3$: Cr (0.03 and 2 mol%) and $\text{Al}_2\text{O}_3$: V (2 mol%) have been measured as a function of frequency in the range $10^2$-$10^7$ Hz and in the temperature range 30-450°C as reported by Govinda and Rao. The value of $\varepsilon$ of $\text{Al}_2\text{O}_3$ at 30°C was found to be equal to 9.4 and frequency-independent.

The aim of the present paper is to prepare $\alpha$-alumina doped with different cations of different
concentrations, study the effect of these dopants on the structural characteristics of \( \alpha \)-alumina, and correlate between the obtained structure characteristics and electric properties of the doped alumina.

2 Experimental Details

Three sets of doped alumina, were prepared using solid state reaction technique, namely, \( \text{Al}_2\text{O}_3: x\text{MnO} \) \( [x = 0.01, 0.05, 0.09, 0.14 \text{ and } 0.19] \), \( \text{Al}_2\text{O}_3: x\text{MoO}_3 \) \( [x = 0.01, 0.04, 0.08, 0.12, 0.16 \text{ and } 0.18] \), and \( \text{Al}_2\text{O}_3: x\text{CdO} \) \( [x = 0.02, 0.04, 0.08, 0.12 \text{ and } 0.16] \). All the samples were prepared using highly pure materials of aluminium hydroxide, manganese nitrate \( \text{Mn(NO}_3)_2 \), 4\( \text{H}_2\text{O} \) to prepare aluminium manganese oxide system, ammonium molybdate \( (\text{NH}_4)\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} \) to prepare aluminium molybdenum oxide system and cadmium sulphate \( 3\text{CdSO}_4 \cdot 8\text{H}_2\text{O} \) to prepare aluminium cadmium oxide system. Weighted materials were mixed well in molar ratio and ground to a very fine powder in corundum mortar. The mixtures were pressed in the form of pellets and heated at 500°C for 4 hr in an electric furnace. Then all the heated samples were ground again, pressed into pellets and then heated in air at different temperatures 1000, 1100, 1200°C for 4 hr with heating rate 4°C/min. The sintered samples at each temperature were tested by X-ray diffraction to ensure the formation of single phase of corundum structure. The powders X-ray diffraction data were collected on computer controlled X-ray diffractometer (formally made by Diano Corporation, USA) using step scanning mode and filtered Co Kα-radiation. The scanning range was (20-110) 2θ with step size = 0.05 (2θ) and counting time = 5 sec/step.

The computerized LRC bridge (Hioki model 3531 Z Hi Tester) was used to measure the electrical properties of the samples. The bridge measures the capacitance from 19 pF to 370 mF, the resistance from 100 m\( \Omega \) to 200 M\( \Omega \) and the dielectric loss tan \( \delta \) from \( 10^{-5} \) to \( 10^4 \). The bridge is good earthed and all connected cables are good shielded and connected to earth, the accuracy of measurement is better than 1%. The ac resistivity as well as the dielectric constant \( \varepsilon \) of the samples was carried out from room temperature to 450°C at different frequencies ranging from 10 kHz to 5 MHz. The samples used in the measurement were in the form of pellets in the form of circular disk specimens of 2 cm diameter and 3 mm thickness, pressed using a pressure of 10 torr at room temperature. The surfaces of each pellet were carefully polished and then coated with silver paint (BDH). Before conducting the experiment, the surfaces were checked for good contact. The sample was located between two cell electrodes and then inserted into non-inductive furnace used for heating the samples with constant rate. The temperature of the sample connected to thermometer with junction in contact with the sample was measured. The accuracy of measuring temperature is ± 1°C.

The real part, \( \varepsilon \), of the dielectric constant, was calculated using the relations:

\[
\varepsilon = \frac{L}{Cs/A} \varepsilon_0 \tag{1}
\]

where \( L \) is the thickness in m, \( A \) is the area in m\(^2\), \( Cs \) is the capacity in F and \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2 \).

3 Results and Discussion

3.1 XRD analysis

Figure 1 (a, b and c) represents diffraction patterns of \( \alpha \)-alumina doped with different cations (Mn, Mo Cd) with different concentrations. Among these samples, only those sintered at 1200°C gave \( \alpha \)-alumina phase for both aluminium manganese oxide and aluminium cadmium oxide systems, but those sintered at 1000°C gave the corundum structure for the aluminium molybdenum system. These patterns reveal clearly, that the prepared samples consist of only single phase, where the diffraction lines are completely matched with the JCPDS card number (46-1212). The absence of the characteristic X-ray diffraction lines of dopants or any other phases confirms the existence of one phase \( \alpha \)-alumina. Therefore, the appearance of the prepared samples as single phase and the disappearance of the characteristic peaks of the dopant oxide may elucidate the mechanism of the reaction that occurred at the sintering temperature. The cations used in this study may be completely soluble in \( \alpha \)-alumina or completely adsorbed on its grain boundaries, forming spinel structure \( \text{MAl}_2\text{O}_4 \) (M is the cation under consideration) or finally one part adsorbed and the other incorporated in the crystal lattice itself. The absence of the secondary phase may be due to its very small concentration which is not detectable by X-ray diffraction or may constitute a considerable amount but in an amorphous phase. However, the incorporation of the cations in the crystal lattice of \( \alpha \)-alumina may be verified by two facts: First, the change of the sample colour from pale yellow at room
temperature to violet at sintering temperature and the latter become more dark with increase in dopant concentration in case of Mo doped alumina; second, the change of the relative intensity of the characteristic peak of doped alumina in comparison with the pure $\alpha$-alumina particularly, the diffraction peak corresponds to the plane 113, which undergoes considerable changes in its relative intensity from 66% (JCPDS card) up to 100% in many cases [see Fig. 1 (a, b and c)]. This behaviour can be explained by the fact that Al site (0,0,0.35) contributes mainly to the diffraction line (113), so any partial substitution of Al ions at this site with larger atomic scattering power (Mn, Mo, Cd) will enhance the intensity of this plane. This gives clear evidence that part of the dopants was incorporated in the crystal lattice at the vacancies of Al site. Moreover, the occupancy of the Al site shows quantitatively the explanation of this behaviour. The appearance of a hump between the reflection (104) and (110) at relatively high doping concentration of Mn$^{2+}$ reveals the existence of an amorphous phase. Accordingly, the third expectation predominates, which favour the presence of some segregation of one part on the grain boundaries of $\alpha$-alumina, not detectable by X-ray diffraction due to its amorphous state or due to its low content, and the other part incorporates in the crystal lattice.

Another evidence for the partial solubility of the dopants in the $\alpha$-alumina lattice is the lowering of the formation temperature of $\alpha$-alumina from 1250 to 1000$^\circ$C for doping with Mo and 1200$^\circ$C for doping with both Mn and Cd. This is consistent with the work of Kingery who reported the reduction of the sintering temperature and improvement of the plastic behaviour of $\alpha$-alumina doped with equi-molar amounts of Cu and Ti. Resulting from the total dissolution of the both cations and these have been incorporated into alumina lattice as Cu$^{2+}$ and Ti$^{4+}$. So one can conclude that the additions of dopant cations enabled the onset of the $\gamma$- to $\alpha$-alumina transformation at low temperatures depending on the nature of the dopants, which is the same as that observed with the seeding method.

The crystallite size and micro-strain of the investigated samples were calculated by the equations.

Strain (Gaussian) = $(\pi/1.8) (U-U_{ins})^{1/2}$

Size (Lorentzian) = $180 K\lambda/\left[\pi (Y-Y_{ins})\right]$
diffraction patterns are given previously. The calculated values of the crystallite size and microstrain of the investigated samples are given in Table 1. These values reveal large crystallite size and high micro-strain. But there is a noticeable difference between the three investigated systems. The largest crystallite size belongs to Mo-system, followed by Cd-system and the smallest one belongs to Mn-system. On the other hand, there are noticeable variations among each system. The general behaviour observed from the values of the crystallite size is its increase with increase in dopant concentration. But the rate of the crystallite growth differs from one system to another. Fig. 2 (a, b and c) shows diagrammatically these differences. It is obvious that the increase of the crystallite size is always accompanied by a decrease in the micro-strain as shown in Fig. 3 (a, b and c). Basically, it has been reported by Dorre et al., that additives to α-alumina can either promote or impede both densification and grain growth. Others concluded, that the growth kinetics of the nano-sized alumina doped with Cr₂O₃ was unaffected by the presence of dopant, but distinct inhibition of grain growth was observed as a result of the presence of dopant. However, increased growth rates have been attributed to increased material transport as a result of strain in the alumina lattice, the presence of a glassy phase, and increased grain boundaries or surface diffusion. Accordingly, our speculations may explain the increase of the crystallite size and the decrease of micro-strain in α-alumina lattice with increase in the dopant concentration. But the rate of the crystallite growth differs from one system to another.

### 3.2 Dielectric properties

#### 3.2.1 Dielectric constant

The dependence of the real part of ε on temperature, as a function of the applied different frequencies, 10 kHz, 1 MHz and 4 MHz, for pure α-alumina (Al₂O₃) crystal and α-alumina doped with different cations Mn, Mo and Cd, with molar ratios 0.09, 0.08 and 0.08, respectively, is shown in Fig. 4 (a-d). It is clearly shown that the general trend at the applied selected frequencies is the increase of ε with increasing temperature but with different rates according to the type of the dopant and the applied frequency. The general feature of the curves in Fig. 4(a-d) is that these consist of two distinct regions. The first region for pure alumina, which is defined by the temperature range from room temperature to 100°C, is nearly temperature and frequency independent. Meanwhile, the first region for doped alumina, which is defined by the temperature range from room temperature to 300°C, is characterized by small increment in ε value. Beyond 300°C the values of ε show rather fast rise. This result is in agreement with the previously reported study in literature. The changes in values of ε as a function of temperature for pure alumina and the three doped samples at 10 kHz, 1 MHz and 4 MHz are presented in Table 2. i.e., ε of pure alumina was found to be equal to 9.4 at 9.4 at frequency 1 MHz. While ε of alumina doped with molar ratios 0.09 for MnO, 0.08 both for MoO and CdO at the same temperature and frequency were found to be equal to 9.4, 9.8 and 9.7 respectively.

The decrease of value of ε with increasing frequency as shown in Fig. 4 (a-d). This behaviour is
a general trend for the dielectric materials due to the scattering of charge carriers at high frequencies as well as the fast variation of the electric field accompanied with the frequency. This process leads to random orientation of the dipole moments and accordingly decreases the value of $\varepsilon$. The increase of $\varepsilon$ with temperature for the investigated samples can be ascribed to the contribution of more than one type of polarization, electronic, ionic, dipolar and space charge polarization. In fact the nature of the variation of the dielectric constant as a function of temperature and frequency indicates which contributions are present. Beginning from room temperature to $300^\circ$C (first region), the electronic polarization may be the most predominant one, where it needs very small thermal energy and small electric field to take place in the polarization process. Obviously, the electronic

Fig. 2—Crystallite size versus the dopant concentration the three investigated sets (a) $\text{Al}_2\text{O}_3$: $x\text{MnO}$, (b) $\text{Al}_2\text{O}_3$: $x\text{MoO}_3$ and (c) $\text{Al}_2\text{O}_3$: $x\text{CdO}$

Fig. 3—Micro-strain versus the dopant concentration the three investigated sets (a) $\text{Al}_2\text{O}_3$: $x\text{MnO}$, (b) $\text{Al}_2\text{O}_3$: $x\text{MoO}_3$ and (c) $\text{Al}_2\text{O}_3$: $x\text{CdO}$
polarization is nearly field independent in this temperature region except for small electric field, as shown in Fig. 4 (a-d). The increment of $\varepsilon$ values after the first region means, that the participation of another type of polarization has taken place. The space charge contribution, which depends on the purity and imperfections, may be started to take role in the polarization process in this high temperature region. This means that Maxwell Wagner polarization and orientational one start to appear in the intergranular regions.

Taking into consideration the findings that obtained during the structure refinement in which it has been indicated that the ability of Mn$^{2+}$ cation to incorporate into $\alpha$-alumina lattice is greater than that of both Mo$^{6+}$ and Cd$^{2+}$ cations. This means that the amount of the dopant cations that segregate on the grain boundaries is greater for Cd$^{2+}$ and Mo$^{6+}$ than that for Mn$^{2+}$ cations. This may explain why the $\varepsilon$ values for Mn doped alumina is smaller than that for both Mo- and Cd-doped alumina. Moreover, this may elucidate that Maxwell Wagner and orientational polarization

<table>
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<tr>
<th>Sample names</th>
<th>Temperature range $^\circ$C</th>
<th>10 kHz</th>
<th>1 MHz</th>
<th>4 MHz</th>
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<tr>
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<td>RT $\rightarrow$ 300$^\circ$C</td>
<td>9.4 $\rightarrow$ 9.85</td>
<td>9.4 $\rightarrow$ 9.65</td>
<td>9.4 $\rightarrow$ 9.525</td>
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<td></td>
<td>300$^\circ$C $\rightarrow$ 450$^\circ$C</td>
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<td>9.525 $\rightarrow$ 10</td>
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<td>9.9 $\rightarrow$ 10.65</td>
<td>9.4 $\rightarrow$ 10</td>
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<tr>
<td></td>
<td>300$^\circ$C $\rightarrow$ 450$^\circ$C</td>
<td>12 $\rightarrow$ 17</td>
<td>10.65 $\rightarrow$ 13</td>
<td>10 $\rightarrow$ 11.5</td>
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<td>9.8 $\rightarrow$ 11</td>
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<tr>
<td></td>
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<td>15 $\rightarrow$ 21</td>
<td>11 $\rightarrow$ 14</td>
<td>10.7 $\rightarrow$ 12</td>
</tr>
<tr>
<td>Alumina:CdO</td>
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<td>9.7 $\rightarrow$ 11.6</td>
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<td>300$^\circ$C $\rightarrow$ 450$^\circ$C</td>
<td>15.5 $\rightarrow$ 21</td>
<td>11.6 $\rightarrow$ 13.6</td>
<td>10.4 $\rightarrow$ 12</td>
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predominates in the polarization process. In order to highlight on the behaviour of the dopants concentration on the dielectric constant, a plot between the dielectric constant versus temperature at constant frequency 10 kHz for the different cation concentrations of the prepared samples, has been drawn and shown in Fig. 5 (a-c). The general trend for all the doped samples is the increase of $\varepsilon$ by higher relative values compared with pure alumina, depending on the type of dopant. In other words, the increase of $\varepsilon$ due to the dopant concentration is minimum for Mn$^{2+}$ dopant and has maximum values for both Cd$^{2+}$ and Mo$^{6+}$ doped alumina. But the increase in $\varepsilon$ for Mo$^{6+}$ cation is more relevant than that of Cd$^{2+}$ cation doped alumina for the high concentrations namely, 0.12 and 0.16 mol. ratio, as shown in Fig. 4 (a-c). This situation can be explained by the findings that obtained from X-ray analysis that, Mn$^{2+}$ cation may enter into the alumina lattice as Mn$^{3+}$ which is the same valency as Al$^{3+}$ and their ionic radii do not differ so much. Hence, certain amount of Mn$^{3+}$ dissolves in Al$_2$O$_3$ lattice and at high concentration excess Mn cation does not produce point defects but segregates at the grain boundaries as second amorphous phase. In case of Cd and Mo dopants, it has been indicated that Cd dopant introduced into alumina lattice as bivalent cation only. While Mo dopant may be introduced into the host lattice not only as Mo$^{6+}$ but also as its reduced form, which may arise during sintering process, giving rise to more points defects. Therefore, the high $\varepsilon$ values for Mo doped alumina samples followed by Cd doped alumina may be attributed to the lattice defects introduced by the applied dopants. This behaviour is obviously consistent with the X-ray findings, where the Mn doped samples have minimum lattice defects followed by Cd doped samples and the highest one is that attained for Mo-doped samples. However, the effect of the dopant concentration on the dielectric constant can be summarized by the statement that, the higher the dielectric constant value the higher the lattice defects introduced to the host lattice by the dopant. In other words, the type of the dopant and its concentration is one of the main factors affecting the dielectric constant value. This behaviour is in good agreement with that published in literature, which reported that the increase in the dielectric constant of $\alpha$-alumina and doped one being frequency dependent beyond 200°C. This may be attributed to the space charge polarization due to the lattice defects and the

Fig. 5—Variation of dielectric constant of pure alumina, and alumina doped with different molar ratios ranging from 0.01 to 0.19 of MnO (a), from 0.01 to 0.16 for MoO$_3$ (b) and CdO (c) as a function of temperature at constant frequency; 10 kHz.
large changes in $\varepsilon$ and tan $\delta$ (with temperature) in doped alumina indicate larger space charge polarization effects and hence a larger concentration of lattice defects in doped samples as compared to pure alumina.

The reaction that occurred at the sintering temperature of the prepared doped alumina samples, is verified by X-ray diffraction analysis. That one part of cations Mn, Mo and Cd, used in this study, incorporates into the $\alpha$-alumina lattice and the other part segregates on the grain boundaries. This findings may explain the type of polarization, which may be expected to be Maxwell Wagner polarization, where it usually takes place in the high resistivity regions separating the conducting grains. It has been reported by some researchers, that the size of the conducting grains increases with temperature i.e. the intergranular spacing decreases, accordingly Maxwell Wagner polarization is efficiently working in this area. From a closer look to Figs 4 and 5 one can observe, that $\varepsilon$ decreases with increasing frequency. In other words, at high frequency the dipoles cannot follow up the field variation accompanied with the applied frequency, resulting in a decrease in the dielectric constant.

The presence of number of vacancies due to the introduction of different dopants at the Al-site of the host alumina, which in turn, increase the crystallite size according to the type of dopant (ionic radius and valency) as indicated by X-ray analysis. The crystallite size of Mn-doped alumina is smaller than that of Cd-doped alumina, while Mo-doped alumina is the largest one. The increase of the crystallite size will decrease the intergranular spacing of the non-conducting regions. So, the result of this process is the increase in the values of $\varepsilon$ according to the increase of the crystallite size of each doped sample. This would be happened, particularly, at the high temperature region, which is clearly shown in Figs. 4 and 5.

3.2.2 Conductivity

In $(\sigma)$ versus the reciprocal of temperature as a function of some selected frequencies 100 kHz, 1 MHz and 4 MHz of the pure sample and the samples doped with the three different cations (Mn, Mo and CdO), are shown in Figs (6-8). It has been shown, that more than one straight line with different shapes are obtained, indicating different conduction mechanisms, except the curves, that obtained using the frequency 4 MHz, which are characterized by straight lines with nearly one slope. Another

Fig. 6—Conductivity of pure alumina and alumina doped with different molar ratios ranging from 0.01 to 0.19 of MnO as a function of 1000/T, at different frequencies; 100 kHz, 1 MHz and 5 MHz
Fig. 7—Conductivity of pure alumina, and alumina doped with different molar ratios ranging from 0.01 to 0.16 of MoO as a function of 1000/T, at different frequencies; 100 kHz, 1 MHz and 5 MHz.

Fig. 8—Conductivity of pure alumina, and alumina doped with different molar ratios ranging from 0.01 to 0.16 of CdO as a function of 1000/T, at different frequencies; 100 kHz, 1 MHz and 5 MHz.
lattice, which leads to the increase in \( \ln (\sigma) \) of the investigated samples with increasing dopant concentration. Also, this may explain the occurrence of two slopes in the plot \( \ln (\sigma) \) versus \( 1/T \), where \( E_I \) and \( E_{II} \) are the activation energies for the two temperature regions. The values of activation energy in the low temperature region \( E_I \) is always less than that in the high temperature region \( E_{II} \) because the material passes from one conduction mechanism to another. In the low temperature region, the increase in conductivity is due to the mobility of charge carrier, which is dependent on the impurity concentrations. So, the conduction mechanism is usually called the region of low temperature or impurity conduction. In this region the activation energy decreases as the frequency increases, because a small thermal energy is quite sufficient for the activation of the charge carriers to take part in the conduction process. In other words, the impurities and vacancies weakly attached in the lattice and formed due to the presence of ions of other valence can easily migrate within an external electric field since the activation energy required for their drift is rather low. Consequently the activation energy decreases as the dopant concentration increases. In this case, more charge carriers, created from the increase of the dopant concentration, are responsible for the increase in conductivity. Hence, the increase in conductivity in this region can be attributed not only to the increase of the charge carrier mobility but also the increase of the charge carrier concentration, that induced by the increase of the dopant concentration.

The high temperature region, defined by the second slope of the curves relating \( \ln (\sigma) \) versus \( 1/T \), where the activation energy is higher than that of the low temperature region, seems to be frequency-independent in comparison with low temperature region. In this region, the electrical conductivity is mainly determined by the intrinsic defects and hence, is called high temperature or intrinsic conduction. The high values of the activation energy obtained for this region may be attributed, to the fact, that the energy needed to form defect is much larger than the energy required for its drift. For this reason, the intrinsic defects caused by the thermal fluctuations determine the electrical conductance of the samples only at elevated temperature.

The increase in dopant concentration is always associated with an increase in the electrical conductivity. This behaviour can be attributed to the presence of impurities and vacancies at low – temperature region and the intrinsic defects at the high temperature region. But, the occurrence of the secondary phase segregates on the grain boundaries of the \( \alpha \)-alumina, and this segregation increases with the increase of dopant concentration, as indicated from X-ray analysis. This will give the possibility of another reason in the electrical conduction mechanism. This expectation is based on the fact that in some glasses it has been demonstrated that the presence of an insoluble second dispersed phases, in general, enhances the ionic conductivity. Basically, an enhanced conductivity in these systems has been caused by the formation of a highly disordered diffused space charge layer along the interface facilitating the ionic conduction.

The formation of a space charge layer at the interface due to surface interaction and consequently desirable enhancement in ionic transport along coherent interface was originally proposed by Jow and Wagner based on the theory of Kliewer and Koehler. Later, Maier elaborated and gave a quantitative treatment of such systems. The suggested theory points out that the surface charge density and surface activity of the dispersoid are the fundamental parameters governing the extent of the space charge layer. This may explain clearly the situation that observed in the \( \ln (\sigma) \) versus \( 1/T \) plots for the three investigated alumina systems using the
Fig. 9—Activation energy of pure alumina and alumina doped with different molar ratios ranging from 0.01 to 0.19 of MnO as a function of molar ratio at two different frequencies; (a & c) 100 kHz, (b & d) 1 MHz and 5 MHz. For the high temperature region (a & b) and for the low temperature region (c & d).

Fig. 10—Activation energy of pure alumina and alumina doped with different molar ratios ranging from 0.01 to 0.1 of MnO as a function of molar ratio at two different frequencies; (a & c) 100 kHz, (b & d) 1 MHz and 5 MHz. For the high temperature region (a & b) and for the low temperature region (c & d).
frequency 5 MHz. Where each curve in the plot has only one slope, indicating one conduction mechanism, which could be related to space charge interaction through the interface of grains. It is worth mentioning that the application of high ac electric field together with the increase of second insoluble phase that segregates on the grain boundaries with the increase of the dopant content enhances the heterojunction conduction in addition to the homojunction conduction. In this case the surface interaction at the Al2O3 un-dissolved phase is described as analogous to that at the moderately ion conductor insulator interface giving rise to a space charge layer.

4 Conclusion

Three sets of α-alumina doped with different cations namely, Al2O3: xMnO, Al2O3: xMoO and Al2O3: xCdO (where x ranging from 0.01 to 0.2 mol) have been prepared. The value of ε, σ and the activation energy of α-alumina doped with different molar ratios from 0.01 to 0.19 of manganese oxide MnO, and from 0.01 to 0.16 for both molybdenum oxide MoO and cadmium oxide CdO were studied. One single (α-alumina phase) is obtained as revealed from the XRD patterns. The crystallite size increases, while the micro-strain in α-alumina lattice decreases with increasing the dopant concentration of the different cations. But the rate of the crystallite growth differs from one system to another.

The increase in ε of both α-alumina and doped samples are frequency dependent beyond 200°C. This may be attributed to the space charge polarization due to the lattice defects and the large changes in ε (with temperature) in doped alumina indicate larger space charge polarization effects and hence a larger concentration of lattice defects in doped samples compared to pure alumina. Another behaviour can be shown, which is the decrease of ε with increasing frequency. ε of pure alumina was found to be equal to 9.4 at frequency 1 MHz. While ε of alumina doped with molar ratios 0.09 for MnO, 0.08 for MoO and CdO at the same temperature and frequency were found to be equal to 9.4, 9.8 and 9.7 respectively.

The electrical conductivity increases as the dopant concentration of the three sets increases, due to the presence of impurities and vacancies at low-temperature region and the intrinsic defects at the high temperature region. While the activation energy decreases as the dopant concentration increases, where, more charge carriers, created from the increase of the dopant concentration.
References