

Study of the Structural Characteristics of α - Alumina Doped with Different Cations

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Three sets of α -alumina (α - Al_2O_3) doped with different cations namely, $\text{Al}_2\text{O}_3: x\text{MnO}$, $\text{Al}_2\text{O}_3: x\text{MoO}$ and $\text{Al}_2\text{O}_3: x\text{CdO}$ have been prepared with x ranges between 0.01 to 0.19 mol. The structure of the prepared samples was refined by applying the full pattern fitting of Rietveld method using FullProf program. It was found that the nonstoichiometric behaviour appeared from the refinable value of the occupancy of Al site, reflects the amount of lattice defects created in the samples. The amount of the dopant, incorporated into the host alumina, depends not only on the ionic radii but also on the dopant valency. The effect of dopant concentration on the unit cell parameters has been discussed on the basis of the amount of incorporated cations into the host alumina. It was found, that the more occupancy of the dopant at Al-site, the more the c/a ratio, the more is the distortion of the lattice.

1. Introduction:

Alumina is the most cost and widely used material in the family of engineering ceramics. The composition of the ceramic body can be changed to enhance particular desirable material characteristics. An example would be the addition of chrome oxide to improve hardness and change color. For this reason, the effect of cation additives on γ - Al_2O_3 -to- α - Al_2O_3 phase transition has been investigated by differential thermal analysis, X-ray diffractometry and surface area measurements⁽¹⁾. These additives were classified into three groups, according to their effect: i) with accelerating effect (Cu^{2+} and Mn^{2+}), ii) with little or no effect (Co^{2+} , Ni^{2+} and Mg^{2+}) and iii) with retarding effect (Ca^{2+} , Sr^{2+} and Ba^{2+}). Another several studies have demonstrated the sensitivity of the plastic behaviour of aluminum oxide to the presence of small amounts of dopants. If the interest has been focused on the reduction of the sintering

temperature and the improvement of the plastic behavior, the doping with equimolar amounts of CuO and TiO₂ has been demonstrated to achieve that goal ⁽²⁾. The X-ray diffraction study of such material shows one crystalline phase, giving an evidence of total dissolution of the Cu and Ti in the alumina and supporting that these species are present in the material as Cu²⁺ and Ti⁴⁺ and has been incorporated into alumina in the Cu:/ TiO₃ ratio and, thus not introducing vacancies into the oxygen sub-lattice.

Thus, the aim of this work has been directed to prepare α -alumina doped with different cations of different concentrations namely, MnO, MoO₃ and CdO, and to study the effect of these dopants on the structural characteristics of α -alumina.

2. Experimental Work:

Three sets of doped alumina were prepared using solid state reaction technique, namely, Al₂O₃: x MnO [x = 0.01, 0.05, 0.09, 0.14 and 0.19], Al₂O₃: x MoO₃ [x = 0.01, 0.04, 0.08, 0.12, 0.16 and 0.18], and Al₂O₃: x CdO [x = 0.02, 0.04, 0.08, 0.12 and 0.16]. All the investigated samples were prepared using highly pure materials of aluminum hydroxide, manganese nitrate Mn(NO₃)₂. 4H₂O, ammonium molybdate (NH₄) Mo₇ O₂₄. 4 H₂O and cadmium sulphate (3CdSO₄. 8H₂O). Weighted materials were mixed well in molar ratio and were ground to a very fine powder in agate mortar. The mixtures were pressed in the form of pellets and heated at 500°C for 4 hours in an electric furnace. Then all the heated samples were ground again, pressed into pellets and then heated in air with heating rate 4°C/min at different temperatures (1000, 1100 and 1200°C) for 4 hours. The sintered samples at each temperature were tested by X-ray diffraction to ensure the formation of single phase of corundum structure.

Among the prepared samples, only those sintered at 1200°C gave α -alumina phase for both aluminum manganese oxide and aluminum cadmium oxide systems, but those sintered at 1000°C gave the corundum structure for the aluminum molybdenum system. The X-ray diffractograms of these three sets are shown in Fig (1).

Powder X-ray diffraction data were collected on computer controlled X-ray diffractometer (Diano corporation, USA) using step scanning mode and filtered Co K α - radiation. The scanning range was 20-110 (2 θ) with step size = 0.05 (2 θ) and counting time = 5 sec. / step.

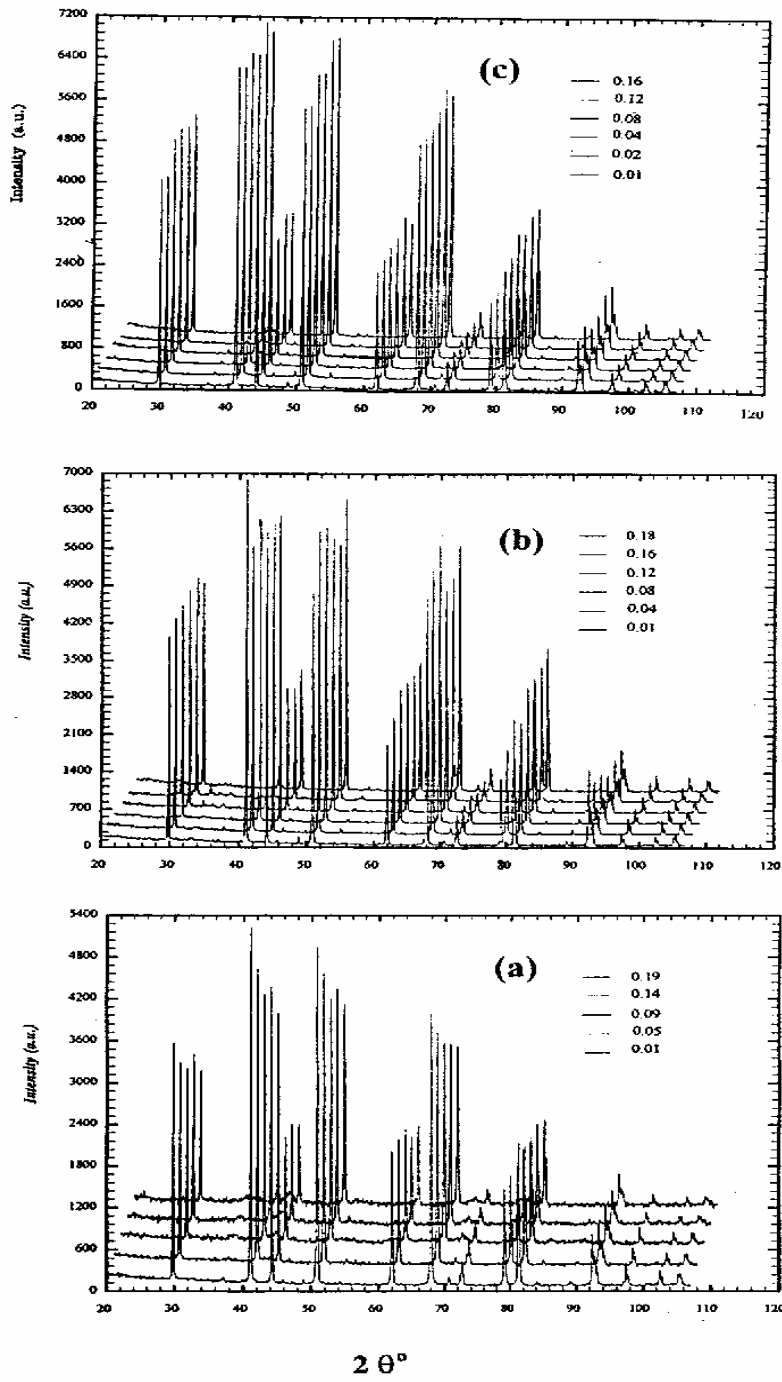


Fig (1): X-ray diffractograms of the three investigated sets (a) $\text{Al}_2\text{O}_3: x\text{MnO}$, (b) $\text{Al}_2\text{O}_3: x\text{MoO}_3$ and (c) $\text{Al}_2\text{O}_3: x\text{CdO}$

Using FullProf program [3], the refinement of the samples were achieved using a model [4], in which the space group is R3c. the dimensions of the corresponding hexamolecular cell referred to hexagonal axes, obtained during the indexing of the X-ray patterns using troer program for indexing. The experimental profile was fitted by modified Thompson Coxhasting Pesudo Voigt function [5,6], recommended by the international union of crystallography [7]. In the first step of the refinement the global parameters followed by the structure parameters were refined, taking into consideration that the site occupancy of Al ions and doping cations were constrained by the same code number because they have the same coordinates. In the last cycle, when the discrepancy factors have reached their minimum values, all the parameters were refined simultaneously giving goodness of fit as given.

3. Results and Discussion:

The refined values of atomic coordinates, occupancy, unit cell dimensions, Lorentzian isotropic crystallite size parameter Y, Gaussian isotropic microstrain parameter U, are given in Table (1), while Fig. (2) gives a representative diagrams of the relation between the observed and calculated X-ray patterns.

Table (1 a) The parameters of system MnO α - Al₂O₃Dopant concentration Parameter

Dopant concentration		0.01	0.05	0.09	0.14	0.19
Al	X	0.0	0.0	0.0	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0
	Z	0.352	0.352	0.352	0.353	0.352
O	X	0.306	0.306	0.304	0.306	0.305
	Y	0.0	0.0	0.0	0.0	0.0
	Z	0.26	0.25	0.25	0.25	0.25
Occupancy	Al	1.929	1.915	1.861	1.801	1.724
	Mn	0.0	0.015	0.041	0.081	0.104
	O	2.999	3.014	3.023	2.9910	3.005
a = b		4.7601	4.7608	4.7609	4.7613	4.7675
c		12.9972	12.9965	12.9969	12.9982	12.997
c /a		2.72910	2.7299	2.72910	2.72910	2.7303

Table (1 b) The parameters of the system $\text{Mo O}_3 - \alpha \text{Al}_2\text{O}_3$

Dopant Concentration		0.01	0.04	0.08	0.12	0.16	0.18
Al	X	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.352	0.352	0.352	0.352	0.352	0.352
O	X	0.303	0.303	0.304	0.305	0.304	0.304
	Y	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.25	0.25	0.25	0.25	0.25	0.25
Occupancy	Al	1.985	1.9262	1.8700	1.800	1.7326	1.7000
	Mo	0.0036	0.0062	0.0301	0.0405	0.0526	0.0600
	O	2.9419	3.0027	2.9701	2.9803	3.0059	2.7907
a = b		4.7601	4.7599	4.7603	4.7604	4.7601	4.7607
c		12.994	12.9946	12.9963	12.997	12.997	12.999
c / a		2.7298	2.7300	2.7301	2.7303	2.7303	2.7301

Table (1 c) The parameters of the system $\text{CdO} - \alpha \text{Al}_2\text{O}_3$

Dopant concentration		0.01	0.02	0.05	0.08	0.14	0.16
Al	X	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.35230	0.35221	0.35211	0.35221	0.35294	0.35226
O	X	0.30511	0.30473	0.30603	0.30521	0.30523	0.30607
	Y	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.25	0.25	0.25	0.25	0.25	0.25
Occupancy	Al	1.97490	1.96384	1.92696	1.86030	1.79959	1.73274
	Cd	0.0	0.00384	0.00696	0.02030	0.03959	0.05274
	O	3.0038	3.0015	2.9996	3.0128	2.9736	3.0045
a = b		4.759849	4.759889	4.7597	4.7601	4.7598	4.7595
c		12.9929	12.9934	12.9926	12.9937	12.9934	12.9923
c / a		2.7298	2.7298	2.7298	2.7297	2.7298	2.7298

The most interesting results, obtained from the structure refinement of the doped alumina, are the values of the occupancies of both Al^{3+} and dopants. These results are depicted in Fig. (3), showing an increase in dopants occupancy on the expense of Al occupancy with increasing the amount of dopants in the preparation process of each system. This means, that the dopants, which are incorporated into the host α - alumina, increase with increasing the dopant concentration creating lattice defects at the Al-site of the host compound. On other hand, the curves, relating the dopant occupancy with each dopant concentration, have different slopes, indicating that the degree of

dopants solubility into the α - alumina lattice depends mainly on the nature of the dopant itself, such as ionic radius and valancy.

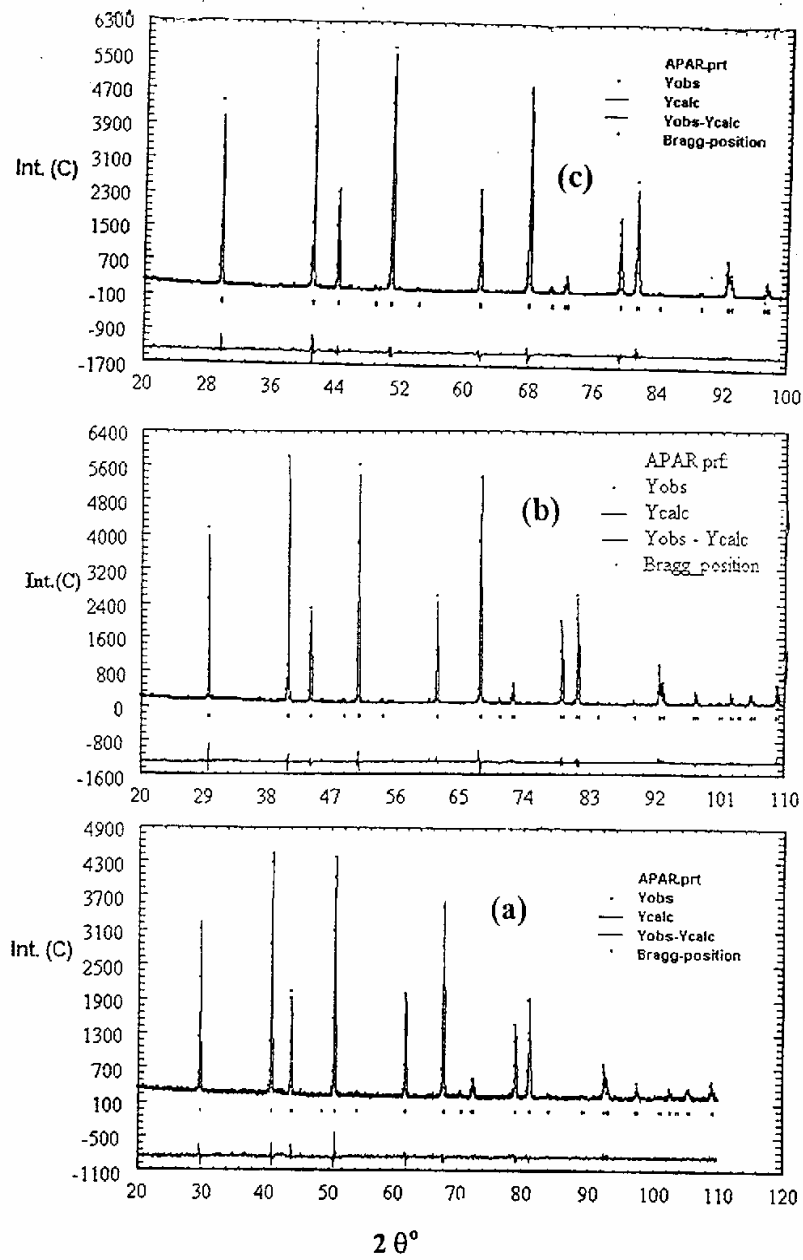


Fig (2): The relation between observed and calculated X-ray patterns (a) $\text{Al}_2\text{O}_3: 0.05 \text{ MnO}$, (b) $\text{Al}_2\text{O}_3: 0.08 \text{ MoO}_3$ and $\text{Al}_2\text{O}_3: 0.04 \text{ CdO}$ as representative patterns.

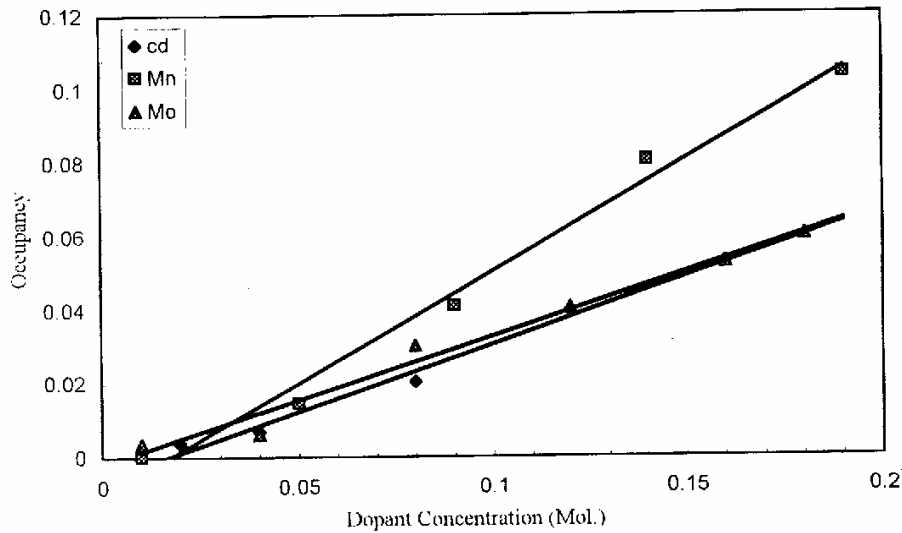


Fig (3): The variation of the dopant occupancy with the dopant concentration.

The deviation of the occupancy of the Al-site from its crystallographic value can be calculated on the basis of the ionic distribution of the constituents, which occurs at that site and their scattering power. So, the equivalent occupancy at Al- site, N_{eq} , can be defined as

$$N_{eq} = (N_{Al} Z_{Al} + N_{dop} Z_{dop}) / Z_{Al}$$

where N_{Al} and N_{dop} are the refined occupancy values; Z_{Al} and Z_{dop} are the atomic number of Al and dopant ion respectively.

The calculated values of N_{eq} corresponding to dopant concentration are given in Table (2). The values of N_{eq} , indicate that the occupancy at the Al- site of the three prepared systems, decreases with increasing dopant concentration. This decrease has high values for Mo dopant and the values decrease for Cd then become nearly constant for Mn dopant. Of course, the decrease in occupancy is always accompanied by lattice defect at the corresponding site. However, the percentage of the lattice defects at Al-site can be considered as

$$\text{Lattice defect percent (LD \%)} = (N_{\text{perfect}} - N_{eq} / N_{\text{perfect}}) \times 100$$

where N_{perfect} is the occupancy of Al-site in the perfect structures of $\alpha\text{-Al}_2\text{O}_3$ which is equal to two. The deduced LD % together with the corresponding dopant concentration is shown in Fig (4). From this figure, it is

obvious, that LD % at Al- site in all the investigated systems shows an increase trend with different rates, with increasing dopant concentration and according to the type of dopant. It is clear, that Mo doped-alumina has the highest LD %, while the Cd doped-alumina tends to increase with relatively high rate at low Cd content followed by low rate at high Cd content. On other hand, Mn- dopant induced approximately constant LD % values, around 3% over the whole range of Mn content.

Table (2): The variation of N_{equiv} and lattice defect (LD) with dopant concentration.

Mn Concentration	0.01	0.05	0.09	0.14	0.19	
N_{equiv}	1.92912	1.94156	1.9397	1.9554	1.9279	
Lattice defect	0.07088	0.05844	0.0603	0.0446	0.721	
LD %	3.54	2.92	3.02	2.23	3.61	
Mo concentration	0.01	0.04	0.08	0.12	0.16	0.18
N_{equiv}	1.9953	1.9460	1.9673	1.9314	1.9024	1.8939
Lattice defect	0.0047	0.05310	0.0327	0.0687	0.0976	0.1061
LD %	0.23	2.7	1.54	3.43	4.88	5.30
Cd concentration	0.01	0.02	0.05	0.08	0.14	0.16
N_{equiv}	1.9749	1.9780	1.9527	1.9353	1.9458	1.9275
Lattice defect	0.0251	0.02110	0.0473	0.0647	0.0542	0.0725
LD %	1.25	1.01	2.37	3.24	2.17	3.63

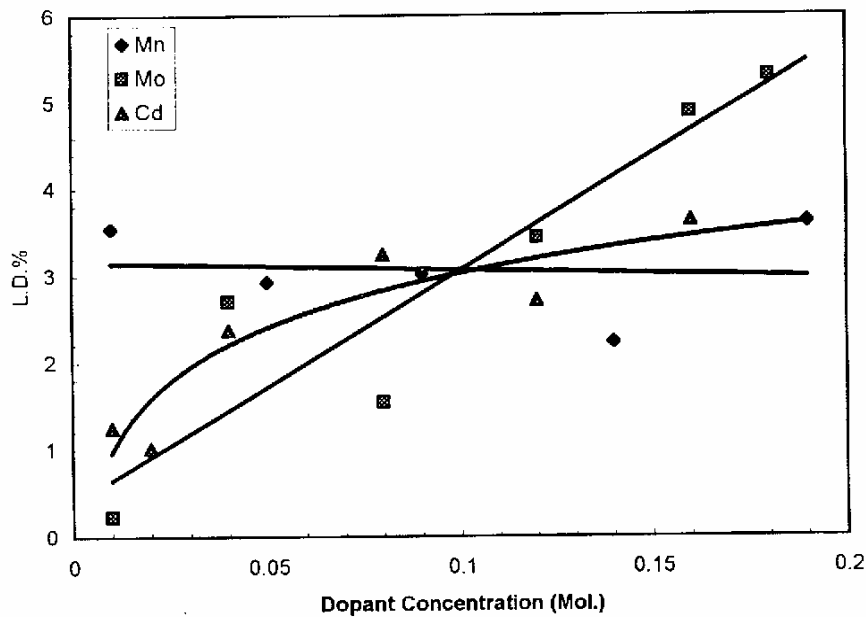


Fig (4): Variation of LD % with dopant concentration.

Taking into consideration the fact, that any impurities with a valence different from the host compound will create of some defects in the surrounding for charge compensation [8]. Therefore, one may conclude, that the nearly fixed value of the LD % in Mn- doped- alumina may be attributed to the fact that Mn^{2+} may enter into the lattice as Mn^{3+} which is the same valancy as Al^{3+} and their ionic radii do not differ so much. Hence, certain amount of Mn^{3+} dissolves in alumina lattice and at high concentration the excess Mn cation do not produce lattice defects but segregate at the grain boundaries as second amorphous phase. On other hand, although the ionic radius of Cd^{2+} is greater than that of Mo^{6+} , the lattice defect induced in the Mo doped alumina is greater than in Cd doped alumina. This observation may be explained by the fact, that Cd dopant introduced into alumina lattice as bivalent cation only. But Mo dopant may introduce into alumina lattice not only as Mo^{6+} but also as its reduced forms, which may be arise during the sintering process, giving rise to more lattice defects for charge compensation.

The unit cell parameters of the investigated three systems, listed in Table (2), show scattered small variations in their values. However, the values of the unit cell parameters versus the dopant concentration show some trends. It is clearly shown, that for $Al_2O_3: x MnO$ there are almost no variations in a-axis with increasing Mn content. But with respect to the c-axis, there is ascending trend with increasing Mn content, resulting in an increase in the ratio c/a, Fig. (5), which may be taken as a measure for the lattice distortion (unit cell volume variation). Thus, the lattice distortion increases with increasing Mn content. The increase of the lattice distortion by such way may be attributed to the continuous dissolution of Mn cations into the host alumina at the Al-site. Which, in turn suffers noticeable changes in its Z-coordinate due to the difference in ionic radii between Mn^{2+} and Al^{3+} and consequently reflects these changes to the c-axis.

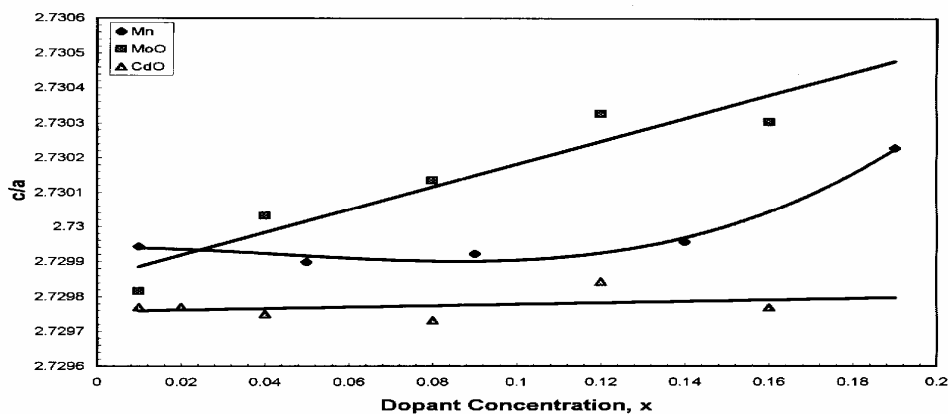


Fig (5): The relation between the c/a ratio and the dopant concentration.

The same trend has been observed in the system $\text{Al}_2\text{O}_3: x \text{MoO}_3$, but with less increment than that of Mn doped alumina. This is clearly indicated by the low slope of the trend line for the ratio c/a . This means that the Mo doped alumina is characterized by small distortion compared with that of Mn doped alumina. It is worth mentioning, although Mo dopant creates the highest LD % as premensioned before, it produces less lattice variation than Mn dopant. This may be attributed to the fact that the difference of valency in case of Mo is larger, while atomic radii of Mo^{6+} is much less than Mn^{2+} . Moreover, more Mn dopant are incorporated into the host alumina lattice than that of Mo as indicated from the occupancy values of both dopants. On other words, the more the occupancy of the dopant at Al- site the higher the ratio c/a the more is the distortion of the lattice.

The same reason can be given to explain the lowest value for the ratio c/a of the system $\text{Al}_2\text{O}_3: x \text{CdO}$, where Cd cation has the less occupancy value i.e. the less amounts that incorporated into the host alumina, and hence the less distortion could be attained, although the large difference between the ionic radii of both Cd^{2+} and Al^{3+}

Conclusion:

Three sets of α -alumina doped with different cations namely, $\text{Al}_2\text{O}_3: x\text{MnO}$, $\text{Al}_2\text{O}_3: x\text{MoO}$ and $\text{Al}_2\text{O}_3: x\text{CdO}$ have been prepared with x ranges between 0.01 to 0.19 mol. using solid-solid interaction. The doped sample with Mo was sintering at 1000°C , while the doped samples with Mn and Cd were sintered at 1200°C . The structure of the prepared samples was refined by applying the full pattern fitting of Rietveld method using FullProf program. It was found that: 1- The nonstoichiometric behaviour appeared from the refinable value of the occupancy of Al site, reflects the amount of lattice defects created in the samples. 2- The degree of dopants solubility into the α -alumina lattice depends mainly on the nature of the dopant its self, such as ionic radius and valency. 3- The more the difference between the valence of the dopant and the host alumina the more are the lattice defects. 4- The more the occupancy of the dopant at Al- site the more is the lattice distortion.

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