Effect of Nd_2O_3 doping on sintering Silica using L^2- regression modeling technique

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Abstract

In this research the effect of Nd_2O_3 doping on densification rate for the initial and intermediate stages of sintering were studied .The experimental results for α – cristobilite powder are modeled using date analysis (L^2-Regression) technique in study the effect of Nd_2O_3 doping using three particles size (6.12, 8.92, 13.6) µm, with undoped initial powder and with Nd_2O_3 doping . The mathematical simulation shows slight impact for doping in initial stages of sintering on densification rates for three initial particles sizes , so that the minutes additive Nd_2O_3 affect the grain boundaries movement when a grain growth-limiting the speed of the grain growth of intermediate stage of sinter process ,those seen on the densification rates of intermediate stage where the doping enhances the densification rates date for three initial particles sizes due to that , the dopants acts against the grain boundaries movement causing discourage closing of porosity and encourage escaping of voids enhances the densification rates .

Key Words **grain size, sintering, densification rate, mathematical simulation**

تأثير التطعيم بمادة Nd_2O_3 في تلبيد السيليكا باستعمال تقنية L^2- regression

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الخلاصة

تم دراسة تأثير التطعيم بأوكسيد النيديميوم Nd_2O_3 على معدلات التكاثف في المر حلة الابتدائية والوسطية من عملية التلبيد ،حيث نمذجت النتائج التجريبية لمسحوق السليكا(ألفا– كرستوبلايت) باستعمال تقنية(Regression) في دراسة تأثير التطعيم باستعمال ثلاثة أحجام حبيبية µm (٦,١٢ ، ٨,٩٢ ، ١٣,٦) ، ولحالتين(عدم التطعيم والتطعيم بمادة Nd_2O_3)، وقد بينت نتائج المحاكاة الحسابية التأثير الطفيف لحبيبات التطعيم في المرحلة الابتدائية من عملية التلبيد على معدلات التكاثف للأحجام الحبيبية الثلاثة ،حيث أن دقائق المادة المضافة Nd_2O_3 تؤثر على حركة الحدود الحبيبية عند حدوث النمو الحبيبي فتحد من سرعة النمو الحبيبي المرافق للمرحلة الوسطية من عملية التلبيد وهذا ما يلاحظ على معدلات التكاثف في المرحلة الوسطية حيث أن حبيبات التطعيم ترفع معدلات التكاثف للأحجام الحبيبية الثلاثة والسبب هو أن Nd_2O_3 تعرقل حركة الحدود الحبيبية مسببة تأخير عملية غلق المسامات موفرة بذلك فرصة أفضل لهروب الفجوات وحصول التكاثف .

الكلمات المفتاحية الحجم الحبيبي ، التلبيد ، معدل التكاثف ،التمثيل الحسابي

introduction

Sintering is an important step in the fabrication process of ceramic bodies, which can significantly affect the microstructure and properties of material [1]. Synthesis of nanocrystalline materials powders has paid much attention due to their promising properties. The sintering of nanocrystalline materials is an important step in the fabrication process that significantly affects their final microstructure and properties [2-4]. Sintering of silica (SiO_2) is usually understood as the sintering of vitreous silica . The tetragonal form of silica (α – cristobilite ,theoretical density = 2.334 $g.cm^{-3}$) ,the α – β transformation takes place with a relatively low volumetric expansion of 3.7 % , the cristobilite is chosen for sintering experiments because it is promising high density of crystalline silica ceramics [5].

The intension of this study is to study the densification rate of doped silica (α – cristobilite) using L^2- regression modeling technique utilizing Nd_2O_3 additives .

Theoretical part

The sintering behavior and microstructural evolution of a powder compact is influenced strongly by initial properties, such as the relative density, the particle and pore size distribution, and the powder packing. While the influence of the former parameters on the
microstructural evolution has been investigated in some detail, the impact of the initial packing of the powder has been mostly overlooked [6] . .

Sintering has long been recognized as a very complicated process, involving the evolution of microstructure through the action of several different transport mechanisms [7]. The sintering phenomena progress with the reduction of the total surface area of the powder particles ,therefore, the total surface energy is reduced , the reduction of the excess surface energy of a compact is the driving force for sintering .One or combination of three-process achieves the reduction of the surface area [5]

1-Replacement of the gas/solid interfaces by lower energy solid /solid interfaces (densification)

2-Conversion of many small particles into fewer large ones (grain growth).

3- Reduction of the amount of grain boundary area by grain growth .

In the initial stage of sintering, the inter particle contact area of the powder compact increases and the grain boundaries are formed on the expense of surface area ,therefore,
surface area decrease then the free surfaces energy decrease . The intermediate stage begins at the start of the grain growth and shrinkage of the volume of the pore network. The densification continues with pore shrinkage and reaches a stage where pore phase transforms into individual closed pores assigning the final stage of sintering [8-9].

As described by Brook [10,11] ,the reduction of the grain growth rate in intermediate stage may naturally enhance the densification rate , the grain growth inhibition due to impedance to the grain boundary motion by dopant particles .

The shrinkage is a result of mass transport process ,these processes have two steps [9] .

Step (1) is the movement of material along the particle- particle contacts (the grain boundary) to the neck regions .

Step (2) the movement is from the neck to free surface regions .

In this study, utilized the experimental data for the controlling movement in step (1)for initial and intermediate stages [5].

The densification equation is conveniently expressed in terms of the fractional porosity P

P = 1 – ρ .....(1)

Where ρ is the fractional density between density of the sintered compact and theortical density of the material .
The densification ,is represented by the rate of change of porosity as follows [9] :

$$\left[\frac{1}{p^{1/2}\left(0.60+0.17\,p^{1/2}-0.12\mathrm{P}\right)}\right]\frac{dp}{dt}=-C_1N^4\ldots\ldots\ldots(2)$$

Where C_1 is constant at constant temperature , N is the number of inter connected pores per unit volume which is inversely proportional to the grain size ,and t is the sintering time .
Utilizing integrated formula

$$\int\frac{dx}{a^2-x^2}=\frac{1}{a}\tanh^{-1}\frac{x}{a}+cons\tan t\ldots\ldots\ldots\ldots\ldots(3)$$

For the initial stage of sintering N remains essentially constant , equation (2) can be integrated by using integrated formula above to give :

$$\left[\tanh^{-1}\left(-0.43p^{1/2}+0.3\right)-\tanh^{-1}\left(-0.43p_0^{1/2}+0.3\right)\right]=\mathrm{K}_1(t-t_0)..(4)$$

Where P_0 and t_0 is the porosity and time at which the compact reaches the test temperature and K_1 is a constant including N^4 and represents coefficient of densification equation for the initial stage

In the intermediate stag , the grain growth is accompanied by the reduction of the number of pores per unit volume N [9], that the reducing of the number of pores follows a cubic law of time dependence as :

$$N^3=\frac{1}{m_0t}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Where m_0 is a time independent coefficient .

Substituting t for N in equation (2) and integrate gives :

$$\left[\tanh^{-1}\left(-0.43p^{1/2}+0.3\right)-\tanh^{-1}\left(0.43p_0^{1/2}+0.3\right)\right]=\mathrm{K}_2\left[\frac{1}{t^{1/3}}-\frac{1}{t_0^{1/3}}\right].....(6)$$

Where K_2 is aconstant represents coefficient of densification equation for the intermediate stage.The numerical values (0.3 and –0.43)in equation (4)and (6) are based on adihedral angle of 140^o and unfired fractional porosity of 0.54 (fractional green density 0.46),other values for these parameters will not change the shape of the function but only change the numerical values in the equation with shifting the position of the function , therefore; it is more convenient for calculation purposes to rewrite equation (4) and (6) as follows:

$$\left[\tanh^{-1}(a+bp^{1/2})-\tanh^{-1}(a+bp_0^{1/2})\right]=K_1(t-t_0).....(7)$$

Equation (7) for initial stage of sintering

$$\left[\tanh^{-1}\left(a+b\mathrm{P}^{1/2}\right)-\tanh^{-1}\left(a+bp_0^{1/2}\right)\right]=\mathrm{K}_2\left[\frac{1}{t^{1/3}}-\frac{1}{t_0^{1/3}}\right].....(8)$$

Equation (8) for intermediate stag of sintering ,**a** and **b** are constants depending on the dihedral angle and the green density .

Regression modeling technique

The equation of L^2_ regression which used in this study can be express as follow [12]

$X=(A^TA)^{-1}A^Tb$ ……..…(9)

where A is the matrix , A^T is the transpose of matrix A , b is random abservation and X the fixed part of equation but unknown
it is more convenient for calculation purposes to rewrite equation (7) as follows:

$X_1 = K_1t + h_1$……..(10)

Where h_1 is a constant represents densification equation parameter for the initial stage and equals to

$$h_1 = \tanh^{-1}(a + bp_0^{1/2}) - K_1 t_0 \ldots\ldots\ldots\ldots(11)$$

Equation (10) can be utilized in modeling L^2_ regression equation where K_1 and h_1 are coefficient and parameter in modeling equation ,by using value of a and b where equal (0.3) and (-0.43) respectively , we can find value of θ then can be find value of X_1 based on the experimental results [5] obtained for the density and time values .

For intermediate stag, it is more convenient for calculation purposes to rewrite equation (8) as follows:

$$X_2 = K_2 T + h_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Where T is equals to

$$T = t^{-1/3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

And h_2 is a constant represents densification equation parameter for the intermediate stage and equals to

$$h_2 = \tanh^{-1}\left(a + bp_0^{1/2}\right) - K_2 t_0^{-1/3} \ldots\ldots\ldots\ldots(14)$$

From equation (12) we can find value of K_2 ,h_2 where equation (12) is asuitable form of L^2_ regression equation and K_2 ,h_2 are the coefficient and parameter in modeling equation, by using value of a and b we can find value of X_2 based on the experimental results [5] obtained for the density and time values .

By using L^2- regression modeling technique as described in [13] we can find density calculate value .

The doping material (Neodymium oxide Nd_2O_3) was achieved by adding (0.0125g) of the dopant to the appropriate amount of α – cristobilite giving a total of 5g sample ,this gives 0.25% doped powders .sintering processes were perform with heating rate of 10°C/min and cooling rate of 15°C/min ,the compacts of green densities 29.2% was sintered at 1500 °C for different sintering times [5]

Results and discussion

Figures (1), (2) and (3) are show the densification curves of undoped and Nd_2O_3 doping for α – cristobilite compacts for three particles size (6.12, 8.92, 13.6) µm respectively , in fig (1) when grain size (6.12 µm) we can see in the

initial stage the densification rates are almost the same for undoped and doping sample where the density value reached to (61.7 % $gm.cm^{-3}$) for Nd_2O_3 doping sample , and the undoped sample have approximates the same value where reached to (61.7 % $gm.cm^{-3}$) for sintering time 10 min ,this is show the additive Nd_2O_3 have slight impact on the densification

rate in the initial stage of sintering because of, in the initial stage the grain boundaries are formed on the expense of surface area and the additive particle have effect on grain boundaries movement when grain growth happening accordingly effect on grain growth speed and that was association to the intermediate stage as described by [10,11] , we can recognize the same thing in fig (2) and (3) for initial stag there are no significant change in density value for undoped and doping samples were the density value was reached to (62.2 % $gm.cm^{-3}$) and to (63.9 % $gm.cm^{-3}$) for doping samples when grain size 8.92 µm and 13.6 µm respectively ,the last value were approximates the same value for undoped sample because of the same resin above .

In table (1) we can see no effect have done in the coefficient of densification K_1 for the initial stage of sintering when additive Nd_2O_3 because of the same resin above where the additive particle have effect on grain boundaries movement when grain growth happening accordingly effect on grain growth speed and that can recognize on the intermediate stage , for doping sample on the intermediate stage the densification rate enhance with increase grain size , we can see in fig (1) when grain size (6.12 µm) the density value reached to (76.4 % $gm.cm^{-3}$) and reached to (76.5 % ,78.32 %) $gm.cm^{-3}$ when grain size (8.92 ,13.6) µm respectively for sintering time 30 min ,the value for additive Nd_2O_3 are more than density value for undoped simple because of additive Nd_2O_3 acts against the grain boundaries movement discourage closing of porosity and encourage escaping of voids and densification .

In table (1) we can see the effect of doping on the coefficient of densification
K_2 for the intermediate stage of sintering where the value of porosity drop with decrease the grain size ,the value of K_2 reached to (0.274 ,0.543 ,0.592) when
grain size (6.12 ,8.92 ,13.6) µm respectively , when grain size was small we can see small porosity and big speed of densification .

Table (2) show the parameter value associate to the densification equation on initial and intermediate stage for undoped and Nd_2O_3 doping sample .

Conclusion

1. Demonstrate the possibility of mathematical simulation in initial and intermediate stage of sintering where the calculated results using L^2_Regression technique agrees with experimental results .
2. In the initial stage the additive Nd_2O_3 have no effect on densification rates for three particles size (6.12, 8.92, 13.6) µm due to the Nd_2O_3

particle have effect on grain boundaries movement associate the intermediate stage .

3. The Nd_2O_3 doping enhances the densification rates in the intermediate stage due to , the additive particles acts against the grain boundaries movement discourage closing of porosity and encourage escaping of voids and densification for three particles size (6.12, 8.92, 13.6) µm .

References

1- Wang1,Q.B.;Wang2,Q.G. and Wan2*,C.X.(2010) ,Effect of Sintering Time on the Microstructure and Propertiesof Inorganic Polyphosphate Bioceramics . Science of Sintering, 42 ,337-343 .

2- Ebrahimi F. (2012), Nanocomposites - New Trends and Developments, InTech, Croatia .

3- Neralla S. (2012), Nanocrystals - Synthesis Characterization and Applications, InTech, Croatia .

4- Hashim A. A. (2012), Smart Nanoparticles Technology, InTech, Croatia .

5- Faridy ,S. B. H , A .(1999), Sintering and microstructure development of α- cristobalite ,D.Sc, physics, College of Science ,University of Baghdad.

6- Bjørk, R.; Tikare , V.; Frandsen, H. L. and Pryds, N. (2012) , The sintering behavior of close-packed spheres . Scripta Materialia 67 ,81–84 .

7- Li[1, 2] ,D.; Chen[2,*] , S.; Jing[2] ,Y.; Shao[2] ,W.; Zhang[2] ,Y and Luan[2] ,W.(2007) ,
The Master Sintering Curve for Pressureless Sintering of TiO_2 . Science of Sintering, 39, 103-110 .

8- Zhao, J. and Harmer, M.P. (1988), Effect of pore distribution on microstructure development: I, Matrix pores, J. Am. Ceram. Soc. 71, 2,113-20.

9- Wong, B. and Pask, J. A. (1979), Models for Kinetics of Solid State Sintering, J. Amer.
Ceram. Soc.; 62,138 .

10- Brook, R.J.; Gilbart, E.;Shaw, N.J. and Eisele, U. (1985), Powder Metallurgy .28,105 .

11- Brook, R.J.;Howlett ,S.P.and Suxingwu . (1982), The use of solid solution additives in sintering .Material science monographs .14 ,135 .

12- Robert.J.V.b,(2001),Linear programming .Foundations and extensions ,second edition ,Copy right C. U.S.A .

13- . Malyaly, H.K. (2005),Analysis the three stage of sintering using linear programming .M.Sc,physics . College of Education IbnAl-Haitham ,University of Baghdad.

Table (1) densification rate coefficient for undoped and Nd_2O_3 doping on initial and intermediate stage .

densification rate coefficient	Grain size 6.12 µm	8.92 µm	13.6 µm
Initial stage K_1 (undoped)	0.027	0.0311	0.037
Intermediate stage K_2 (undoped)	0.2401	0.481	0.516
Initial stage K_1 (Nd_2O_3 doping)	0.027	0.0311	0.037
Intermediate stage K_2 (Nd_2O_3 doping)	0.280	0.562	0.651

Table (2) densification rate parameter for undoped and Nd_2O_3 doping on initial and intermediate stage .

densification rate parameter	Grain size 6.12 µm	8.92 µm	13.6 µm
Initial stage h_1 (undoped)	0.0011	0.0010	0.0004
Intermediate stage h_2 (undoped)	0.485	1.281	1.336
Initial stage h_1 (Nd_2O_3 doping)	0.0011	0.0010	0.0004
Intermediate stage h_2 (Nd_2O_3 doping)	0.587	1.518	1.743

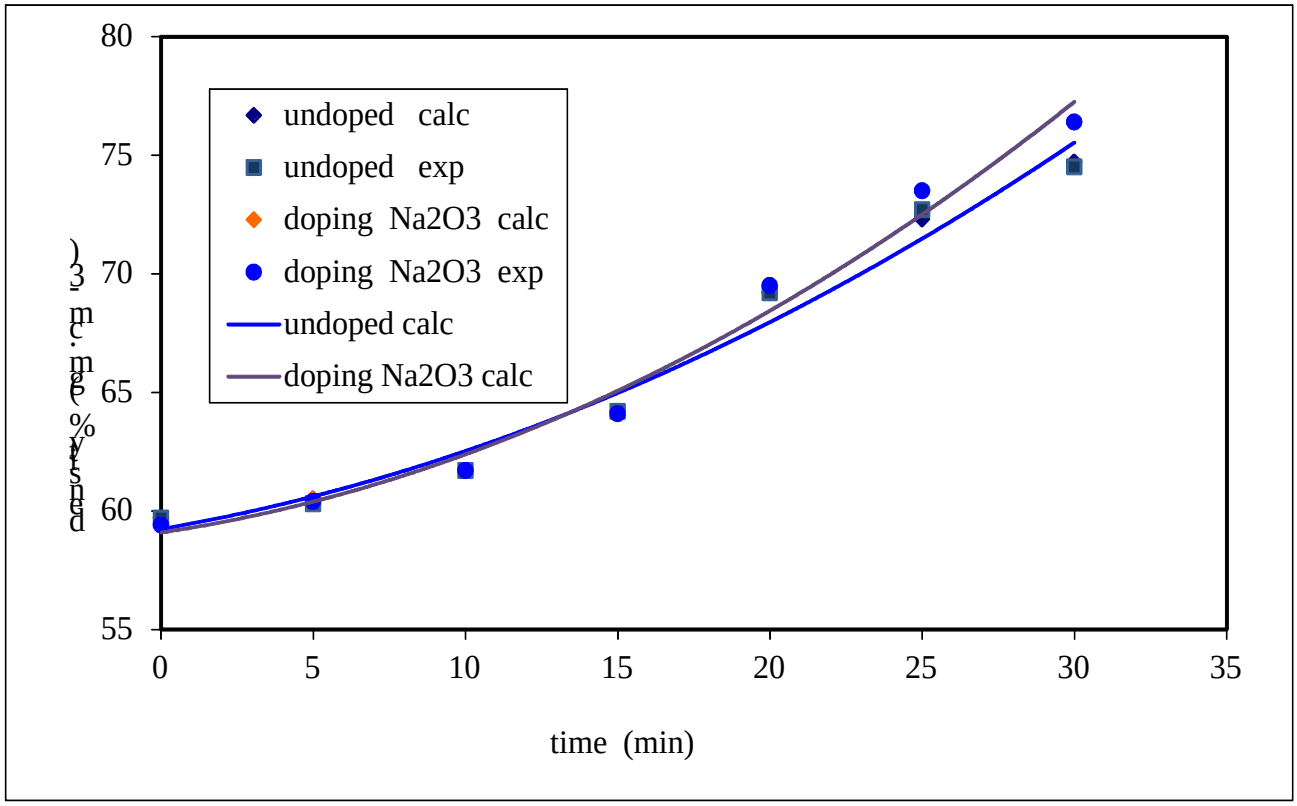

fig (1) density date as a function of time on grain size (6.12 µm) for undoped and Nd_2O_3 doping on initial and intermediate stage .

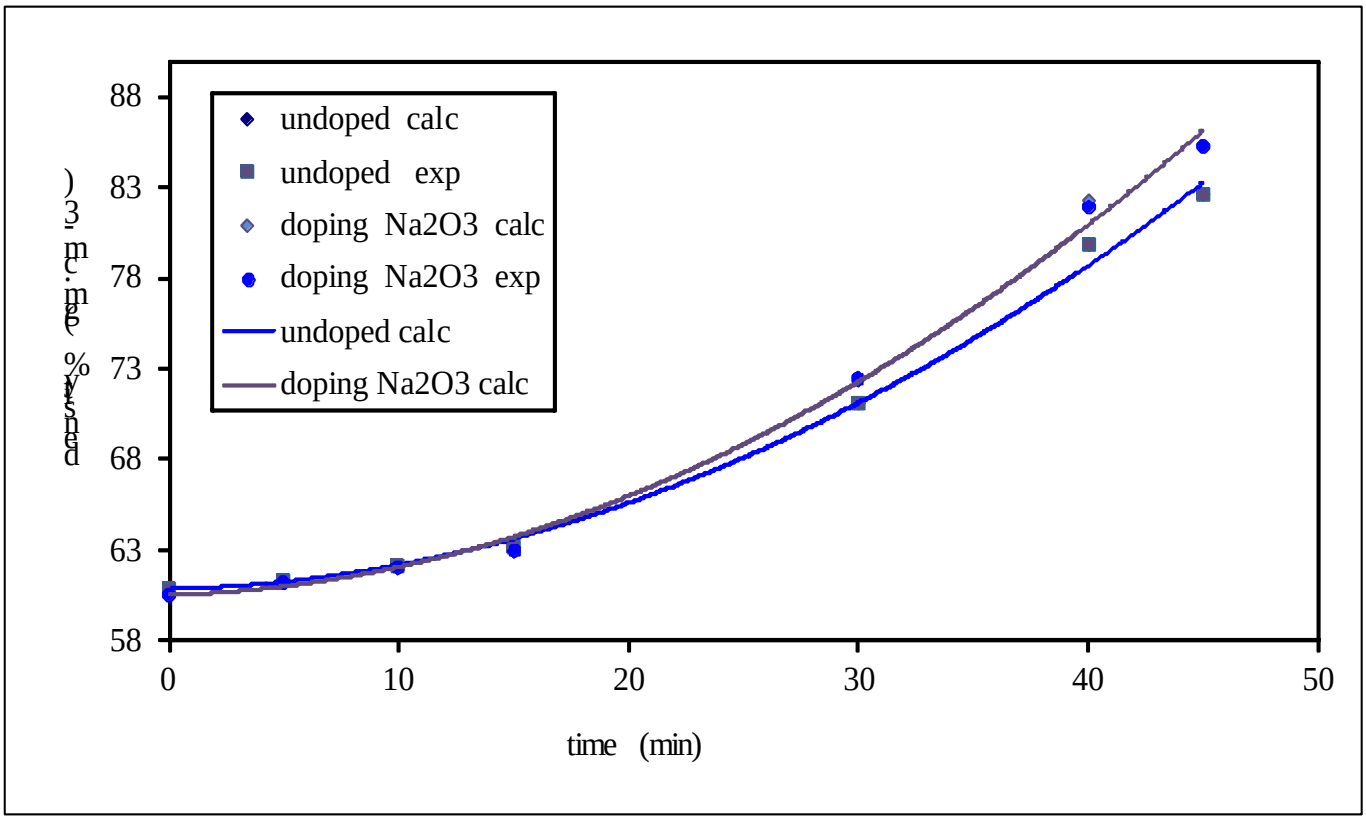

fig (2) density date as a function of time on grain size (8.92 µm) for undoped and Nd_2O_3 doping on initial and intermediate stage .

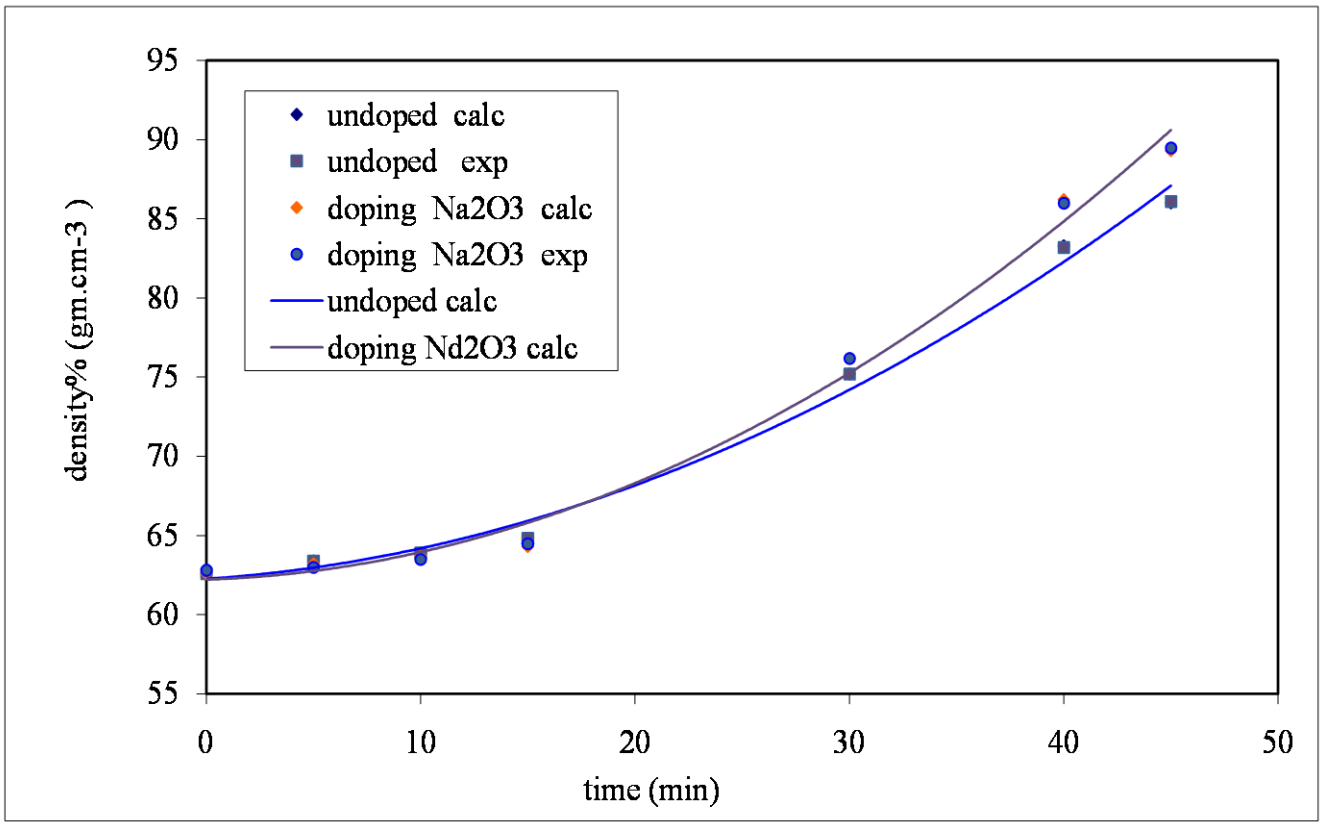

fig (3) density date as a function of time on grain size (13.6 µm) for undoped and Nd_2O_3 doping on initial and intermediate stage .