

Synthesis with Variation of Some Basic Properties of Si-Al-O-N- Based Ceramic Materials

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ABSTRACT

Sialon is an excellent material belonging to the oxynitride ceramics. It has high strength, wear resistance, and other mechanical and chemical properties. β -sialon has the general formula of $\text{Si}_6\text{Al}_z\text{O}_z\text{N}_{8-z}$, where $z=0$ to 2.1. In the present work in total nine different Sialon samples with different compositions were sintered at 7 different temperatures viz., 1575 to 1840°C. Green density, fired density, % linear shrinkage at different temperatures and compositions were reported. Theoretical density of 3.2 gm/cc. was almost reached. The properties were compared and various parameters were corroborated in terms of at % N.

Keywords: Sintering, linear shrinkage, β -SiAlON, cold isostatic pressing, attrition milling, refractories, fabrication, oxynitride, sieving, mesh, green density, fired density, linear shrinkage.

INTRODUCTION

Silicon nitride and oxynitride ceramics have attracted interest for high-temperature engineering and are termed as engineering ceramics. Its application is based on their properties such as: (1) high strength; (2) wear resistance; (3) high decomposition temperature; (4) oxidation resistance; (5) thermal shock resistance; (6) low coefficient of friction; (7) resistance to corrosive environments^{1,2}. Al^{3+} can enter the silicon nitride crystal without changing the structure by replacing Si^{4+} , if at the same time N^{3-} is replaced by O^{2-} , similar to the compound N_2O_3 , as well. Such a solution was named "SiAlON". SiAlON -ceramics are a specialised class of high temperature refractory materials, with high strength (including at high temperature), good thermal shock resistance by molten non-ferrous metals, compared to other refractory materials such as alumina. A typical use is with handling of molten

aluminium. They also are exceptionally corrosion resistant, low thermal expansion and oxidation resistance up to above 1000°C³. Sialons are ceramic alloys based on the element silicon (Si), aluminium (Al), oxygen (O) and nitrogen (N). Sialons exist in three basic forms. Each form is iso-structural with one of the two common forms of Si_3N_4 , β and α and with silicon oxynitride. SiAlON is based upon the atomic arrangement existing in β - Si_3N_4 . In this material, Si is substituted by Al with corresponding replacement of N by O. The second form of Si_3N_4 with which sialon is iso-structural is β - Si_3N_4 . The stacking structure in β - Si_3N_4 is different from β - Si_3N_4 in that the long 'channels' which run through the α structure are blocked at intervals. This gives rise to a series of interstitial holes. In each $\text{Si}_{12}\text{N}_{16}$ unit cell there are two interstitial holes⁴. In β -sialons, Si in the tetrahedral structure is replaced by Al with limited substitution of N by O. Valency requirements are satisfied by modifying cations occupying the

interstitial holes. In this way cations of yttrium (Y), calcium (Ca), lithium (Li) and neodymium (Nd) for example can be incorporated into the structure. The final form of sialon, O-sialon, is iso-structural with silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$). The structure of $\text{Si}_2\text{N}_2\text{O}$ consists of layers of Si_3N_4 rings joined by Si-O-Si bonds. In O-sialon, Al and O are replaced by some Si and N atoms.

In liquid phase sintering of Sialon some metal oxides like Y_2O_3 or MgO is added to promote

their sintering which ultimately go to the grain-boundary of such ceramics. This is called the oxynitride glass^{4,6}. The drawback is that during working condition of these ceramic materials, different foreign elements depending on the substrate make a way through the grain-boundary phase and lead to the their deterioration⁵.

Sialon has the applications in engineering ceramics viz., cutting tool, bearing balls, bearing casing, turbine materials etc².

Table 1: for sample Y1

Sample	Temp. (°C)	Soaking Time (hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y1	1575	2	1.91	3.34	18.25
Y1	1620	2	1.82	3.46	18.42
Y1	1625	2	1.82	3.47	17.83
Y1	1675	2	1.96	3.66	17.74
Y1	1725	2	1.95	3.34	14.38
Y1	1780	2	1.86	3.38	16.7
Y1	1840	2	1.94	3.36	14.35

Table 2: For Sample Y2

Sample	Temp. (°C)	Soaking Time (hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y2	1575	2	1.86	3.38	17.55
Y2	1620	2	1.9	4.04	17.01
Y2	1625	2	1.86	3.38	18.36
Y2	1675	2	1.88	3.36	18.28
Y2	1725	2	1.91	3.27	13.88
Y2	1780	2	1.92	3.35	17.02
Y2	1840	2	1.93	3.23	12.55

Table 3: For Sample Y3

Sample	Temp. (°C)	Soaking Time(hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y3	1575	2	1.84	3.33	17.69
Y3	1620	2	1.82	3.34	18.99
Y3	1625	2	1.84	3.36	17.18
Y3	1675	2	1.89	3.31	17.87
Y3	1725	2	1.78	3.22	16.88
Y3	1780	2	1.88	3.35	11.35
Y3	1840	2	1.8	3.26	18.06

Table 4: For Sample Y4

Sample	Temp. (°C)	Soaking Time (hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y4	1575	2	1.76	3.26	18.4
Y4	1620	2	1.7	2.91	20.2
Y4	1625	2	1.83	3.28	17.59
Y4	1675	2	1.83	3.27	17.4
Y4	1725	2	1.81	3.09	13.59
Y4	1780	2	1.86	3.32	15.56
Y4	1840	2	1.84	3.12	13.73

Table 5: For Sample Y5

Sample	Temp. (°C)	Soaking Time (hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y5	1575	2	1.79	2.97	14.72
Y5	1620	2	1.69	2.98	17.01
Y5	1625	2	1.42	3.91	17.22
Y5	1675	2	1.82	3.19	17.69
Y5	1725	2	1.81	3.26	18
Y5	1780	2	1.74	3.31	17.99
Y5	1840	2	1.93	3.25	18.34

Table 6: For Sample Y6

Sample	Temp. (°C)	Soaking Time (hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y6	1575	2	1.75		
Y6	1620	2	1.72	2.93	13.3
Y6	1625	2	1.75	3.04	10.7
Y6	1675	2	1.73	3.02	11.94
Y6	1725	2	1.79	2.88	16.34
Y6	1780	2	1.77	3.22	14.2
Y6	1840	2	1.71	2.99	15.56

Table 7: For Sample Y7

Sample	Temp. (°C)	Soaking Time (hr)	Green density	Fired Density gm/cc	% Linear Shrinkage
Y7	1575	2	1.99	3.6	17.31
Y7	1620	2	2.05	3.55	19.31
Y7	1625	2	1.98	3.48	17.92
Y7	1675	2	1.98	6.61	17.96
Y7	1725	2	1.99	3.54	17.94
Y7	1780	2	1.98	3.21	17.13
Y7	1840	2	1.97	3.43	15.01

Composition wise these β -Sialons can be considered as a solid solution between Si_3N_4 and $\text{Al}_2\text{O}_3\text{N}$ ⁷. Self propagating high temperature synthesis (SHS) of Sialon is another beautiful method involving high temperature processing⁸.

In another work a unique method was developed⁹ in the pressureless densification of a ceramic with composition in the Sialon region.

In a separate approach sialon was synthesised under a low n-pressure by gel mixture⁸. Effect of alumino silicate son the pressure less densification of a ceramic with composition in the Sialon region was studied⁷. Self-propagating high temperature synthesis (SHS) was adopted and outstanding characterisation was achieved⁸.

The density of such hard materials with high fired density can be compared to that of diamond¹⁰.

Table 8: For Sample Y8

Sample	Temp. (°C)	Soaking Time (hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y8	1575	2	2.11	3.42	11.35
Y8	1620	2	2.11	3.6	19.6
Y8	1625	2	2.12	3.67	11.22
Y8	1675	2	2.07	3.76	18.27
Y8	1725	2	2.07	3.75	18.44
Y8	1780	2	2.06	3.28	19.28
Y8	1840	2	2.07	3.74	17.85

Table 9: For Sample Y9

Sample	Temp. (°C)	Soaking Time (hr)	Green density gm/cc	Fired Density gm/cc	% Linear Shrinkage
Y9	1575	2	2.47	3.19	8.91
Y9	1620	2	2.21	3.91	18.39
Y9	1625	2	2.32	3.29	10.32
Y9	1675	2	2.39	3.54	12.27
Y9	1725	2	2.37	4.09	16.54
Y9	1780	2	2.43	3.26	16.79
Y9	1840	2	2.35	4.23	17.33

Table 10: Sample No. With varying N (Atom%) concentration

Sample	Composition	Temperature	green density	fired density	N (Atom %)
Y1	SiAlO_2N	1575	1.91	3.34	13.86
Y2	$\text{Si}_6\text{Al}_6\text{O}_9\text{N}_8$	1575	1.86	3.38	22.24
Y3	$\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_2$	1575	1.84	3.33	6
Y4	$\text{Si}_7\text{Al}_9\text{O}_{23}\text{N}_3$	1575	1.76	3.26	7.4
Y5	$\text{Si}_4\text{Al}_4\text{O}_{11}\text{N}_2$	1575	1.79	2.97	6.61
Y6	$\text{Si}_{10}\text{Al}_{15}\text{O}_{32}\text{N}_7$	1575	1.75	2.91	7.56
Y7	$\text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8$	1575	1.99	3.6	7.12
Y8	$\text{Si}_{12}\text{Al}_{18}\text{O}_{36}\text{N}_{10}$	1575	2.11	3.42	9.1
Y9	$\text{Si}_{16.4}\text{Al}_{23.6}\text{O}_{48.8}\text{N}_{11.2}$	1575	2.47	4.23	7.5

Table 11: Variation of parameters with N content (Atom %) at different Temp.

Variation of parameters with N content (Atom%) at Firing Temperature 1575°C			
Sample no.	at.% N	Fired density (g/cc)	% linear shrinkage
Y1	13.86	3.34	18.42
Y2	22.24	3.45	17.01
Y3	6	3.4	17.18
Y4	7.4	3.26	20.2
Y5	6.61	2.97	17.01
Y6	7.56	2.91	10.7
Y7	7.12	3.42	19.31
Y8	9.1	3.6	19.6
Y9	7.5	3.19	18.39

Variation of parameters with N content (Atom%) at Firing Temperature 16750C			
Sample no.	at.% N	Fired density (g/cc)	% linear shrinkage
Y1	13.86	3.34	14.38
Y2	22.24	3.27	13.88
Y3	6	3.22	16.88
Y4	7.4	3.09	13.59
Y5	6.61	3.26	18
Y6	7.56	2.88	16.34
Y7	7.12	3.54	17.94
Y8	9.1	3.75	18.44
Y9	7.5	4.09	16.54

Variation of parameters with N content (Atom %) at Firing Temperature 17800C			
Sample no.	at.% N	Fired density (g/cc)	% linear shrinkage
Y1	13.86	3.38	16.7
Y2	22.24	3.35	17.02
Y3	6	3.35	11.35
Y4	7.4	3.32	15.56
Y5	6.61	3.31	17.99
Y6	7.56	3.22	14.2
Y7	7.12	3.21	17.13
Y8	9.1	3.28	19.18
Y9	7.5	3.26	16.79

(3.51 g/cc). Various methods have been discussed in the synthesis of β -Sialon based ceramic materials and on their net shape consolidation into radome

Variation of parameters with N content (Atom %) at Firing Temperature 16200C

Sample no.	at.% N	Fired density (g/cc)	% linear shrinkage
Y1	13.86	3.34	19.25
Y2	22.24	3.45	17.55
Y3	6	3.4	17.69
Y4	7.4	3.26	18.4
Y5	6.61	2.97	14.72
Y6	7.56	2.91	10.7
Y7	7.12	3.42	17.31
Y8	9.1	3.6	19.6
Y9	7.5	3.19	8.91

Variation of parameters with N content (Atom%) at Firing Temperature 17250C			
Sample no.	at.% N	Fired density (g/cc)	% linear shrinkage
Y1	13.86	3.34	19.25
Y2	22.24	3.45	17.55
Y3	6	3.4	17.69
Y4	7.4	3.26	18.4
Y5	6.61	2.97	14.72
Y6	7.56	2.91	10.7
Y7	7.12	3.42	17.31
Y8	9.1	3.6	19.6
Y9	7.5	3.19	8.91

Variation of parameters with N content (Atom%) at Firing Temperature 18400C			
Sample no.	at.% N	Fired density (g/cc)	% linear shrinkage
Y1	13.86	3.36	14.35
Y2	22.24	3.23	12.55
Y3	6.0	3.26	18.06
Y4	7.4	3.12	13.73
Y5	6.61	3.25	18.34
Y6	7.56	2.99	15.56
Y7	7.12	3.43	15.01
Y8	9.1	3.74	17.85
Y9	7.5	4.23	17.33

structure was done¹¹. Reaction sintering of Sialon from Si_3N_4 , AlN and Al_2O_3 without externally added sintering aids was done by several workers¹²⁻¹⁵. Out of different methods in our case we had adopted the high temperature sintering procedure.

MATERIALS AND METHODS

Reaction sintering of SiAlON from the system Si_3N_4 -AlN- Al_2O_3 (Sarabhai M. Chemicals, India), SiO_2 (Quartz, Optical Grade) without externally adding aids were done. From the batch materials for e.g., Si_3N_4 , AlN, Al_2O_3 of specific particle size, the powder with some pre-determined composition was chosen (Table 10). These were mixed and fired at high temperature for a period of time and under nitrogen atmosphere. The batches of 100g of materials were attrition milled with 700g of Al_2O_3 ball of size of about 2mm for 3-4 hour in pure acetone. The milled powder was then air-dried and sintered through a 150 mesh sieve. Cold pressed pellets of cylindrical were prepared by uniaxial pressing followed by isostatic pressing at around 300 MPa pressure. Green density of the samples were measured from their dimension. The pressed pellets were taken in BN-coated graphite crucible and were sintered in a controlled atmosphere furnace. The firing temperature was varied in the range 1575 to 1840 °C for a time period of 2h. Linear shrinkage, weight loss and green and fired density were measured using conventional methods. Phase identification was done by XRD analyses using $\text{CuK}\alpha$ radiation (Philips PW 1730). % linear shrinkage was measure from dimension of the final product. All the firings here were done in a Hot Press, Vacuum Industries Inc, U.S.A., under nitrogen atmosphere.

RESULT AND DISCUSSION

Composition wise these β -Sialon can be considered as a solid solution between Si_3N_4 and $\text{Al}_3\text{O}_3\text{N}_7$. Out of different methods, in our case we had adopted the high temperature sintering procedure^{2,3}.

The followings are the tables (Table 1) through (Table 9) of sample no., temperature, time etc. vs. time and density values. The changes in properties follow regular pattern in some sense with variation in temperature of firing and at % N in the concentration. Sialon materials which can be considered as a solid solution based on the Si_3N_4 structure. Based on a composition and viewpoint these materials can be regarded as solid solution between Si_3N_4 and $\text{Al}_3\text{O}_3\text{N}_7$.] Self

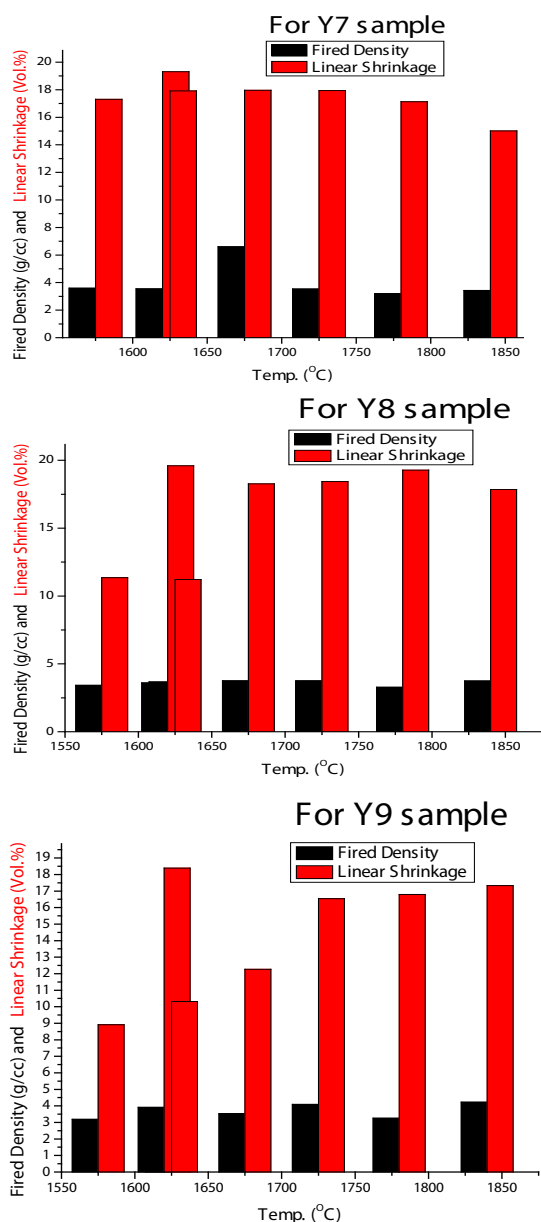


Fig. 1: Bar Diagram of Temperature vs. Fired Density (g/cc in all cases) and % Linear Shrinkage for different samples

propagating high temperature synthesis of Sialon is another beautiful method involving high temperature processing¹¹. Sintering Parameters of different samples

In the following tables Table1 through Table 9, Sample Temperature, Time, Green density (gm/cc), Fired Density (gm/cc) and % Linear Shrinkage of different samples are tabulated the present work:

The density of such hard materials with high fired density is compared to that of diamond⁸. Here only temperature 1575^o C was taken since it is the lowest temp. of study as in the present work .

As is evidenced from Table 10, for the samples Y1 and Y2 show a lowering of % Linear shrinkage. The table also shows no regular pattern with change of N (at %). On the contrary for samples

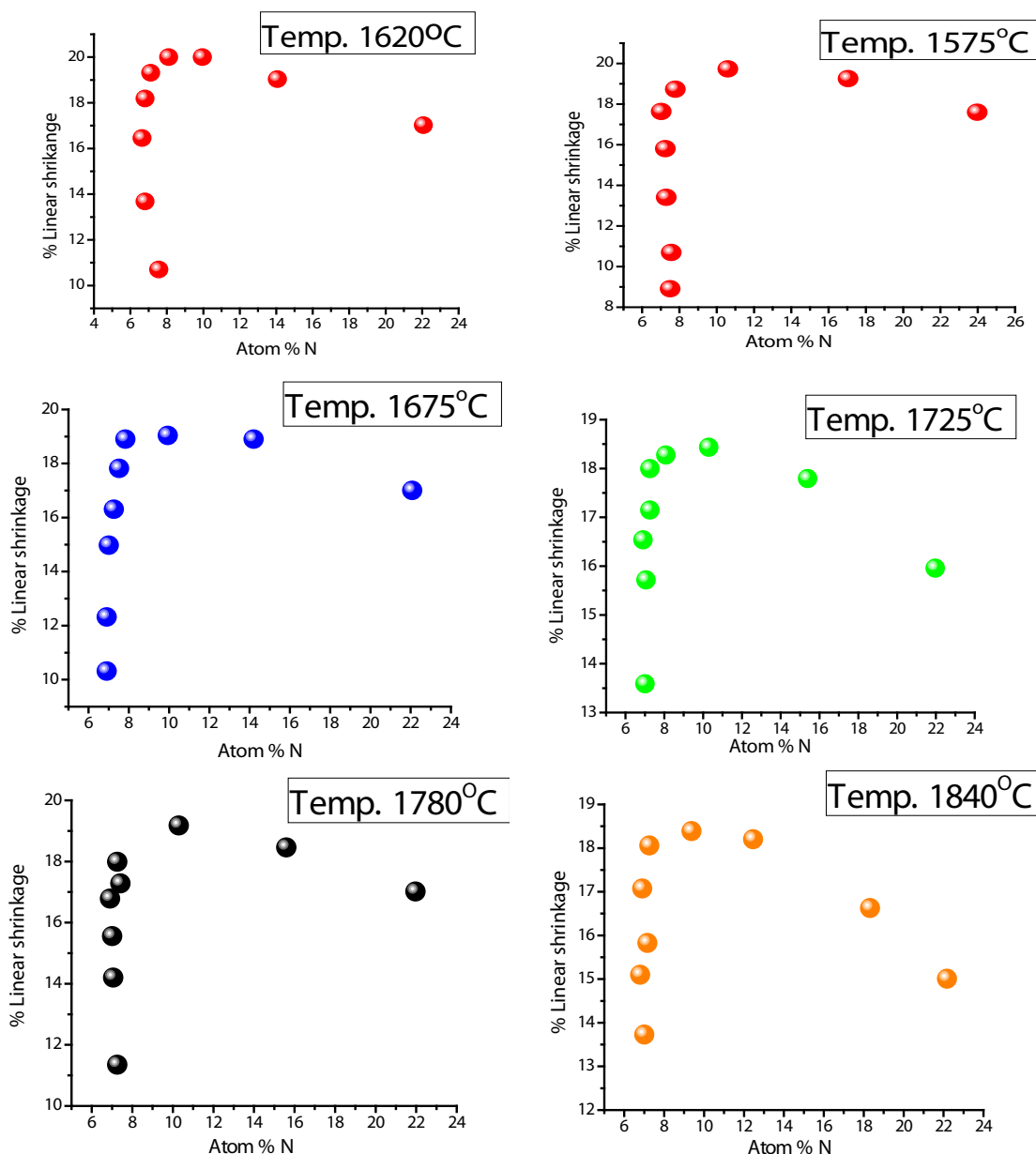


Fig. 2: % Linear Shrinkage vs. at % N at different Temperatures

Y_1, Y_2 show as lowering of %Linear shrinkage with temperature while the other show reverse.

In a unique method Sialon was synthesised under a low N-pressure by gel mixture⁸. These materials can be regarded as solid solution between Si_3N_4 and Al_3O_3N ⁷.

In case of Y9 with higher N (atom %) of 7.5 the fired density is the highest of 4.23. Interestingly the linear shrinkage value is lower here compared to others. For Y2 with highest at% N 22.24% fired density is the highest at 1575°C among all other samples. Thus increase in N at% is not the only criterion in the study.

The fired density observed by other authors¹⁵ is also in the range that of ours around 3.0 gm/cc.

As shown in the plots [Figs 1 and 2] both the fired density and the % linear shrinkage show some pattern when plotted against at % N. This is a regular feature in all the plots. The plots initially show a steep rise and then get levelled off or decrease to a little extent. In all cases it is obvious that the fired density was twice than the green one as observed. [Table 1 through Table 9].

Variation in % linear shrinkage values

The % linear shrinkage vs atom % N is synonymous to tightening and compactness. As found in the Fig.2 at low at% N shrinkage is low so also at high at % N while intermediate at the intermediate concentration of N. A good shrinkage implies a better binding.

This might be explained in the light of as we are going from oxide system to oxynitride system the O is slowly being replaced by N. Now O is dibridging (-O-) while N is tribridging (>N-) leading to higher compactness in the structure of Sialon. Now ultimately it may so happen that when O concentration leads to a limiting low lowering of the % linear shrinkage at high N value or remains almost the same due to saturation N uptake capacity. Structural aspects of Sialon have been well discussed⁷.

This reflects that with increased tribridging N (in place of dibridging O, in the structure) the fired density gets up a steep rise. After reaching a maximum value it gets saturation and sometimes a lowering in value though it cannot be explained [Figs 1 and 2].

The % linear shrinkage also follows a steep rise with increase in N and becomes levels off at the end a slow decrease. Thus the enhanced amount of N does not play any role in altering the effect.

The theoretical density of sialon being 3.2 g/cc, the remaining of the highest value for any sample is significant.

Variation of % linear shrinkage was at per with some earlier workers¹⁵, that is, in between 16-19 % and that of ours.

With temperature, however, there is shown no regular trend with change in at% N. On the other hand some irregular phenomenon is shown.

Asis evidenced from Fig1 that the Fired Density remaining the same with some exception. But % linear shrinkage shows some variation for different samples as the temperature is varied.

Among all samples the fired density is found to be highest for Y9 at 1840°C, ie. 4.23 g/cc with an at. % N of 9.1. (Table 11) From the figure 3 it is evident that with increasing at % N initially fired density show a steep rise and then levels off after a sharp fall.

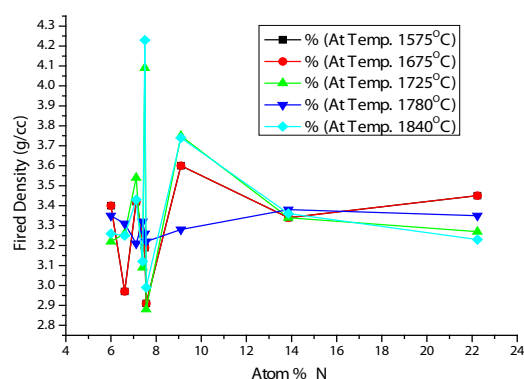


Fig. 3: Atom % N vs. Fired Density at different Temperatures

In case of Y7 with higher N (at. % of 7.12) the fired density is the highest of 3.6. Actually it is Y3 with 6 at. % N which has the highest fired density of 3.4 with a firing temperature of 1575 °C. Interestingly the linear shrinkage value is lower here compared to others. For Y2 with highest at. % N (22.24) fired density is highest at 1575 °C among all other samples.

The % linear shrinkage is on the other hand is with a highest value for Y8 i.e., 19.28 and then value remains at the top at 18 for any of the sample, Overall at soaking temp. of 1575°C the value of fired density reaches a maximum of 4.23 though it does not contain the the highest nitrogen content. It is again due to the fact that as the O is replaced by N a saturation is reached even after that N is increased in some cases it shows a decreasing value. The peculiarity here is that % linear shrinkage viz., 19.25, is also having the highest value for sample Y1. In case of Y1 the % linear shrinkage is found to be highest (18.20 %) at the lowest temp of study while the lowest value is observed (14.35%) at the highest temperature of 1840°C studied so far. A saturation value is observed in both cases of fired density and % linear shrinkage with atom % N value. Change of fired density and % linear shrinkage both observed to depend upon the sintering temperature and at % N.

CONCLUSION

Synthesis of Sialon of various compositions with the help of excess silica with nitrogen rich liquid shows expected property dependence. On the average for all sintered samples the theoretical density was almost reached. The properties like fired density and their variation with N-content and % linear shrinkage are well in accordance which has been properly explained. Change of fired density and % linear shrinkage both depend on the sintering temperature and at % N which is the essence of this study. Thus it can be considered as the simultaneous effect of soaking temperature and presence of nitrogen which are responsible for their variation in our studied properties.

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