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Experimental Study on Synthesizing Methods of Low Cost Mullite – Zro$_2$ Glass Ceramics

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Abstract

Mullite has achieved outstanding importance as a material for both traditional and advanced ceramics because of its favorable thermal and mechanical properties. The low power transferred arc plasma (TAP) processing is found to have various key features like high temperatures ranges at low power and time which makes it a suitable mullite synthesizing technique when compared to conventional solid state reaction methods. In the present literature an effort has been made to compare the processing parameters like processing cost, purity and capacity of high temperature furnace (HTF) and TAP for low cost mullite synthesis. Zirconia is inexpensive and easily available, and this technique used in the current study is highly attractive to large scale production. Mullite – zro$_2$ (MZ) mixtures in different molecular ratios were ball milled for 4 hr. The ball milled samples were synthesized in HTF and TAP. The XRD and SEM patterns show that the single phase mullite obtained from TAP and HTF processes are crystalline. The TAP process requires low power input than HTF process [20].

Keywords: HTF – High Temperature Furnace, TAP- Transferred Arc Plasma, XRD – X-ray Diffraction, SEM – Scanning Electron Microscope.

Introduction

Recent advances in the processing of materials and the need for graded materials with tailored properties has recently fetched great attention towards glass ceramics system due to their attractive properties.

Mullite is the only aluminosilicate which is stable at high temperatures. Mullite occurs very rarely in nature because of its high temperature but low pressure formation conditions. Mullite was first spotted at the contact of superheated magma intrusions with Al_2O_3 – rich sediments, as on the Island of Mull (Scotland), where the name mullite originated. Mullite has been traced in high temperature metamorphosed rocks of the sanidinite facies [1].

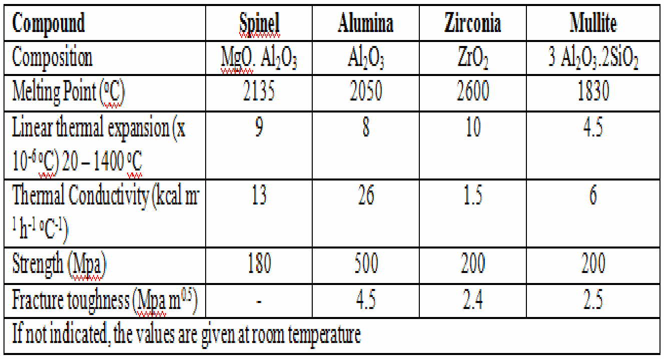
In spite of its rare occurrences, mullite is found to have gained an important phase in advanced ceramics. Its importance can be explained by:

a. Its high thermal stability up to melting point (2573K), low thermal expansion and conductivity of 1.56 $Wm^{-1}k^{-1}$ at 1273K, high creep resistance and corrosion stability together with suitable strength and fracture toughness (Table 1). [2]

b. Its ability to form glass ceramics in wide Al_2O_3/sio_2 molar ratio (ranging from 1.5 to 2) and its ability to incorporate a large variety of new cations into the structure.

c. Its ability to extend its structural principles to a large number of phases belonging to the family of mullite [3].

Table 1: Thermo – mechanical properties of mullite ceramics and other advanced oxide ceramics



Compound	Spinel	Alumina	Zirconia	Mullite
Composition	$MgO.\ Al_2O_3$	Al_2O_3	ZrO_2	$3\ Al_2O_3.2SiO_2$
Melting Point (°C)	2135	2050	2600	1830
Linear thermal expansion (x 10^{-6} °C) 20 – 1400 °C	9	8	10	4.5
Thermal Conductivity (kcal m^{-1} h^{-1} $°C^{-1}$)	13	26	1.5	6
Strength (Mpa)	180	500	200	200
Fracture toughness (Mpa $m^{0.5}$)	-	4.5	2.4	2.5
If not indicated, the values are given at room temperature				

A lot of works have been made to prepare mullite ceramics using various materials and methods, all of which follow different mullitization routes on heating. The most common methods are: 1. Use of HTF at 1200^0C and above for mullite formation. Here mullite is seen as a mixture of Kaolinite and alumina sol mixtures and diphasic gels. 2. Direct mullitization of Al rich mullite at about 900 - 1000^0C [4] observed as monophonic gels and glasses.

When Al_2O_3 and SiO_2 are mixed at different grains and on different molecular ratios, muttilization occurs by nucleation growth mechanisms at different routes. The low bending strength of mullite at room temperature has led to search for ways of improving the mechanical properties and thereby reducing the synthesis temperature. Some solution has been gained when ultrafine alumina, Zirconia and silica powders are used [5 - 6].

MZ composites are used in various applications due to its good mechanical properties like toughness, chemical stability and resistance to creep and spalling. MZ can be used in glass melting furnaces as glass contact materials [7].

The use of MZ ceramics is due to their relatively high corrosion resistance, attributed to the microstructure of Zirconia and slightly wetted by siliceous and metallic melts. Also, the solubility potential of Zirconia in silica is low, thus the chemical attack of the refractory is comparatively low [8]. Zirconia particles toughen the materials mainly because of fracture process and the tetragonal-monoclinic phase transformation that occur during the process as shown in Fig.1 [9, 10].

The stress induced phase transformation toughening mechanism activated during the fracture process is responsible for the increase in crack propagation energy [11, 12]. If the mullite crystal appears in needle shape, then an additional toughening mechanism is present. There are many ways to produce the

MZ composite i.e., chemical or use of conventional heating of alumina, zirconia and silica powders as well as sol-gel (aqueous solution of aluminumisopropoxide, aluminumnitrate and tetraethylorthosilicate) can be used [13]. The easiest and the most economical way is using sintering process where the complete mullitization occurs at temperatures near 1600°C [14]. The impurity added to the original material during manufacturing improves the sintering process but in turn, reduces the high temperature strength and shock resistance [15].

Experimental Work

The present investigation is undertaken to synthesize mullite through Zirconia powder by thermal processing. The newly tailored material is expected to combine the excellent properties of alumina (high hardness, wear resistance and refractoriness), mullite (excellent thermal shock resistance, high creep resistance, low thermal expansion coefficient and binging strength at high temperature) and Zirconia (high corrosion resistance, high fracture toughness and low thermal conductivity). In this investigation, mullite is prepared using HTF and TAP process at different temperatures and exposure time. The phase formation, microstructure, chemical compositions of the processed samples are analyzed using XRD, SEM respectively.

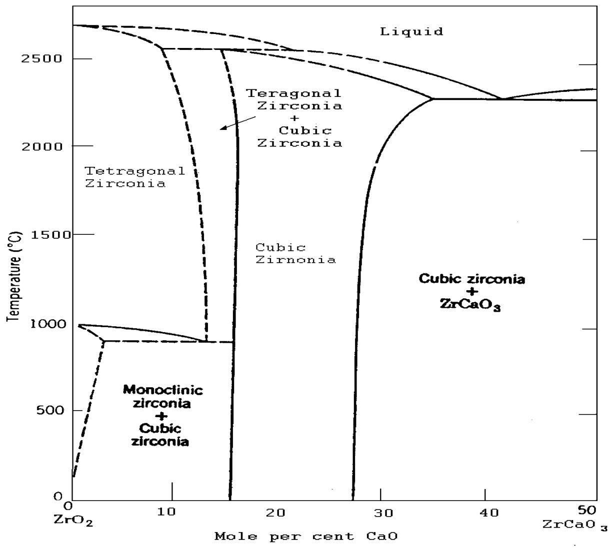


Fig.1. Phase transformation diagram for zro2 - cao

Material and Methods

In this work, commercially available lanthanum oxide -La_2O_3 (Sigma-Aldrich –99% purity), Al_2O_3 (Sigma-Aldrich– 99% purity) and SiO_2 (Sigma-Aldrich– 99% purity) were used to prepare MZ composite. The mixture of Al_2O_3 and SiO_2 at 3:2 molecular ratios were mixed in a slow rotating ball mill with corundum ball for 2h. Later, the obtained were mixed with La_2O_3 at different weight ratios (according to equation 1 and as listed in table 1) and ball milled for four hours with corundum ball mill using planetary ball mill (Insmart, India).

Table 1: Composition distribution model of MZ composite

Sample A - 90% 3 Al_2O_3+2SiO_2 / 10% ZrO_2
Sample B - 80% 3 Al_2O_3+2SiO_2 / 20% ZrO_2
Sample C - 70% 3 Al_2O_3+2SiO_2 / 30% ZrO_2

$$(Al_2O_3 + SiO_2) + ZrO_2 \rightarrow ZrSiO_4 + \quad 3\,Al_2O_3.2SiO_2 + Al_2O_3 \rightarrow \quad (1)$$

HTF process: The ball milled samples were placed in a graphite crucible and kept in a high temperature arc furnace for 1300° C and 1500° C for 4 hr. The 4 hr waiting time at the set temperature is expected to stabilize the mullitization growth.

TAP process: The ball milled samples were kept in graphite bowl (acts as an Anode in TAP process) 100 mm deep and 150 mm diameters. The graphite bowl also acts as the melting bed. The experimental setup consists of 12 kW plasma torch, power supply, gas (Argon) supply and water cooling system. The experimental system is shown in the schematic diagram (fig.2.).

The cathode (conical end) is made of a graphite rod 250 mm long and 50 mm diameter. The cathode is enclosed in a brass cylinder and the space between the brass cylinder and the cathode is filled with water. The cold water from the cooling unit is supplied (at 10 lpm) on the one end of the brass cylinder and the hot water after cooling the cathode is circulated back to the cooling unit from the other end of the brass cylinder. Provisions are also made for the argon gas flow through the brass cylinder. The sample is processed in the plasma (operating parameter as listed in the table 2).

Table 2: Operating parameters of Plasma

Description	**Parameter 1**
1. Input power	7.5kW
2. Argon gas flow rate	5 lpm
3. Plasma Processing time	5 minutes

The processed samples were allowed to cool in the atmosphere and were milled down to a few micrometer sized powders in an agate mortar prior to X- ray diffraction (XRD) analysis using a PW Philips Diffractometer with nickel filtered Cu-Kx radiation. For scanning electron microscope (SEM) investigation, the samples were polished using silicon carbide papers and with diamond paste. The chemical etching using 30 wt% HF solutions for 30 seconds was done on the sample. The microstructures of the sample were studied by the Philips XL40 SEM instrument.

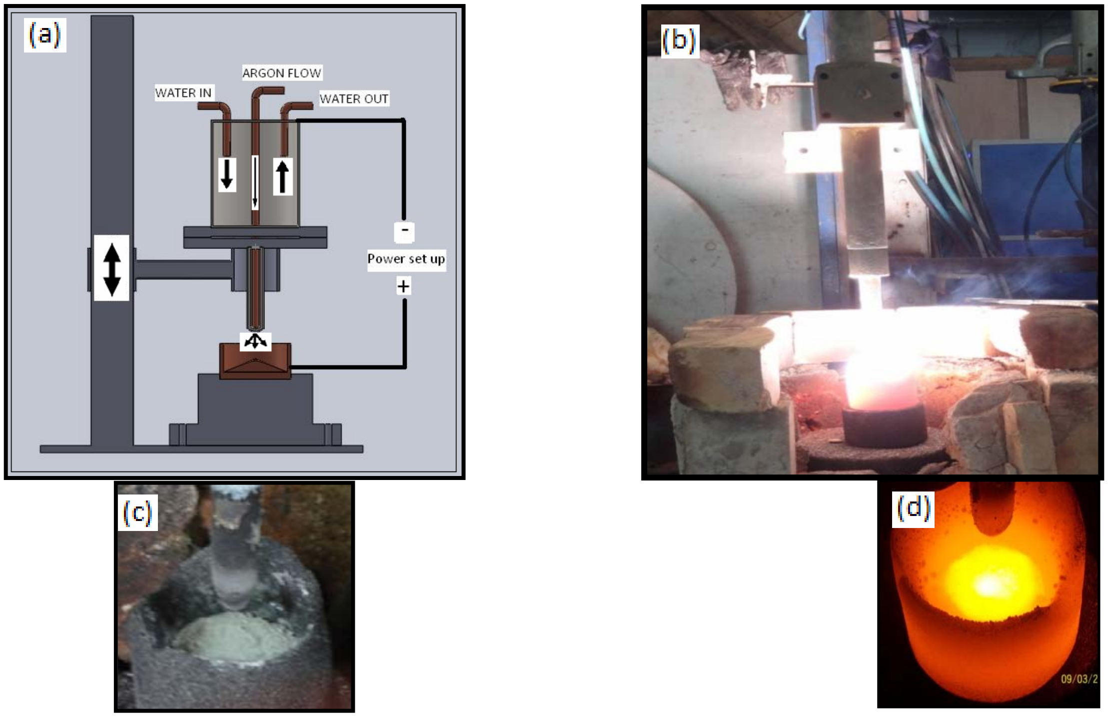


Fig.2. Experimental setup showing Transfer Arc Plasma

Results and Discussions

The synthesis of Al2O3, SiO2 and ZrO2 mixture involves two reactions. First involves composition of ZrSiO4 and latter, formation of Mullite. In accordance to the thermodynamic data from the literature [18], the free energy of the reaction in the range 1200 – 1400K can be described by the linear function of temperature, T:

$$\Delta G = 0.515\ T + 72.19[\mathrm{kJ/mol}] \rightarrow (2)$$

It is evident from equation (2) that the reaction should start at temperature T>1400 K (about 1127^{o}C).

The effect of processing temperature at 1300^{o}C and 1500^{o}C in the mullite formation was studied. The longer processing time subjects the molted pool of Al2O3, SiO2 and ZrO2 to a more extended heating. The extended heat causes the evaporation of ZrO2 [20] and causes deficiency in liquid phase concentration of ZrO2 system. The above tendency was slightly reflected in the XRD analysis in Fig.3; the peak shift at 1500^{o} C and 1300^{o} C at 25-28^{o}C interval of 2□ intensity.

The XRD result of overall formation of mullite – Zirconia composite can be studied in Fig.4. In this figure the mullitization starts appearing at 1300^{o}C, and the greater mullitization peaks was achieved at 1500^{o}C. Interestingly Zirconia exists in both tetragonal and monoclinic phases [23]. In comparison with the XRD pattern of sample processed at HTF - 1500^{o} C and 7.5 kW processed TAP sample as shown in

Fig.5, the mullitization is complete and the Zirconia peaks are greatly reduced due to complete mullitization process.

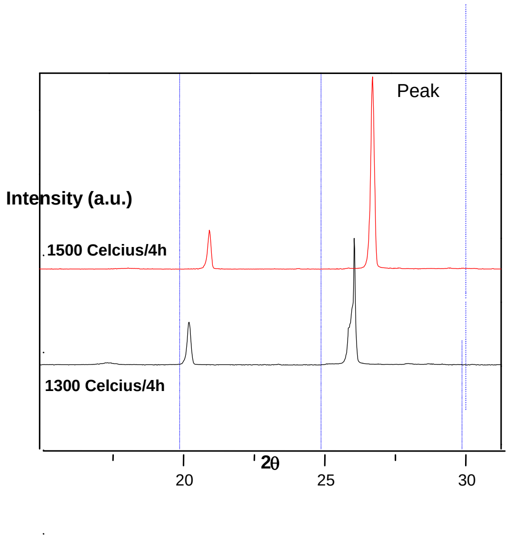


Fig. 3. XRD pattern of relative shift of peak with different processing temperature in HTF

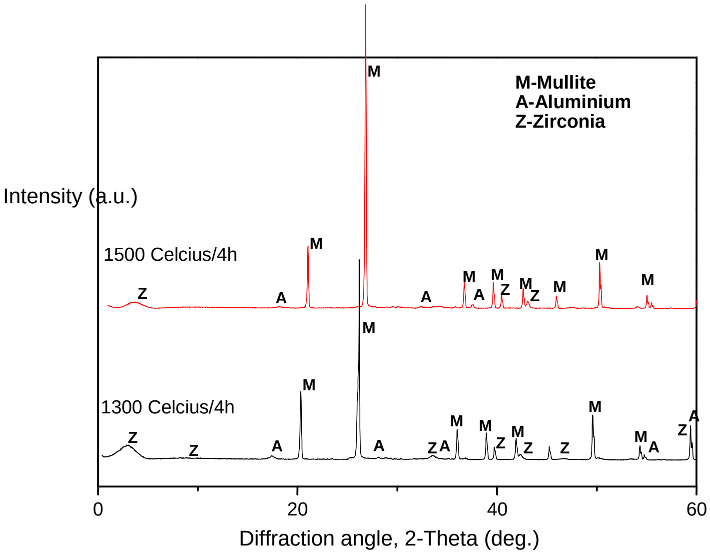


Fig. 4. XRD pattern of MZ sample processed at different processing temperature in HTF

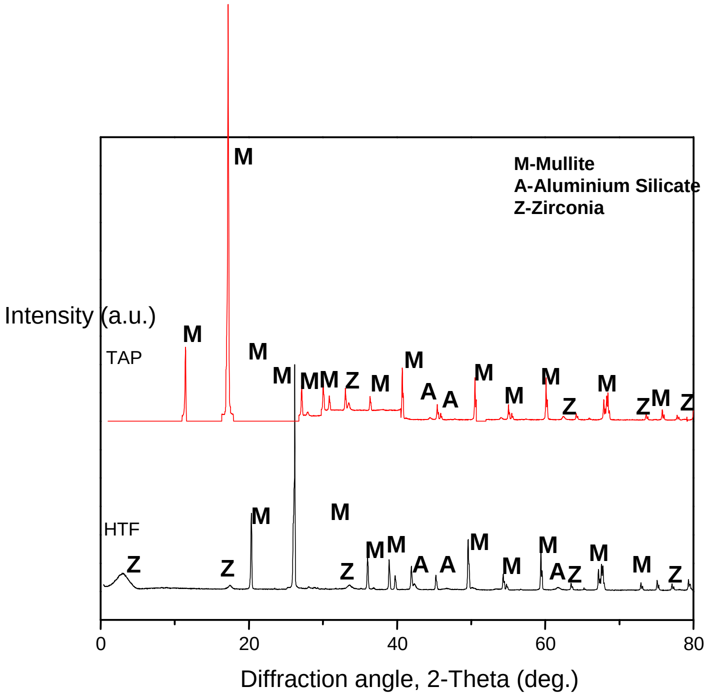


Fig. 5. XRD pattern of 5 min TAP processed MZ at 7.5 kW

The microstructure of the Mullite/Zirconia samples fired at 1300° C, 1500° C for 4 hr and TAP processed samples can be seen in SEM (Fig.6). The microstructure of mullite is very much dependant on the torch input power. The needle structure of mullite is disappearing (when compared to Fig.6.a- 6.b. and Fig.6.c.) at higher temperature, due to the presence of silica and alumina [21]. The reduction of silica ratio is because of the evaporation at high power in plasma and large number of pores is observed in TAP. Also, the Zirconia (white grains) is surrounded by the mullite (dark grains) [22]. From the SEM results, it is clearly evident that the mullitization process is more stabilized in samples formed from TAP process.

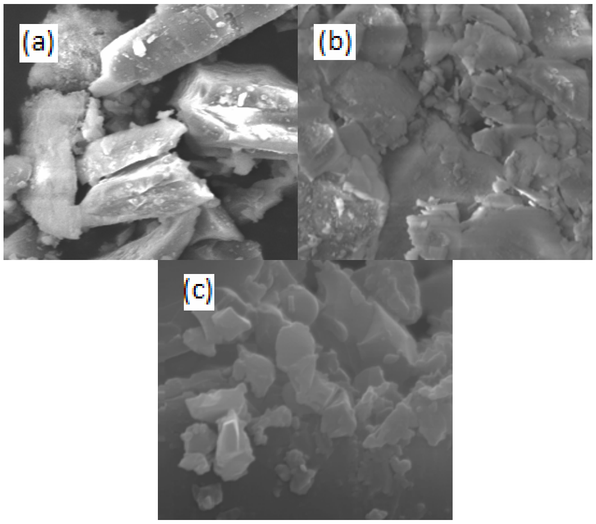


Fig. 6(a) SEM image of HTF processed sample @ 1300° C; (b) SEM image of HTF processed sample @ 1500° C; (c) SEM image of TAP processed sample at 5kW

Conclusions

The Mullite – Zirconia was successfully synthesized from Al_2O_3, SiO_2 and ZrO_2 powders by low power transferred arc plasma TAP and High temperature furnace – HTF melting. The processing parameters like, processing temperature, composition and processing method are directly influencing the Mullite-Zirconia formation. The obtained results confirm that the TAP processing at 7.5kW of torch input power, 5 min. of processing time are the appropriate conditions to give maximum mullite-zirconia composite formation. Hence the TAP process method is more effective for bulk production compared to the HTF synthesis process, due to its time and cost effectiveness.

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References

[1] Winkler, H. G. F., "Petrogenesis of Metamorphic Rocks (3rd ed.)" Springer, New York, 1974.

[2] X.Q. Cao,R. Vassen,D. Stoever, " Ceramic materials for thermal barrier coatings", J. Eur. Ceram. Soc. 24 (2004) 1e10.

[3] H.schneider, J.schreuer, B..hildmann, "Structure and properties of mullite—A review", Journal of European ceramic society 28 (2008) 329-344.

[4] K. Okada, N. Otsuka, S. Somiya, Japan, Am. Ceram. Soc. Bull., 70(10), 1633 (1991).

[5] Masuda Tatasuhiko, Yoshitom, Jyouki, Yamoshiro Hiroyaki, "Taikabutsu oversea", 20, 45 (2000).

[6] Aksel C., Konieczny F.: "Mechanical Properties and Thermal Shock Behaviour of PSR-333 Alumina-Mullite-Zirconia Refractory Material", Glass Int., 24, 1, (2001), 16-18.

[7] Manfredo L., McNallyt R.N.: "The corrosion resistance of high ZrO2 fusion-cast Al2O3-ZrO2-SiO2 glass refractories in soda lime glass", J. Mater. Sci., 4, (1984), 1272-1276.

[8] Jang H.M., Cho S.M., Kim K.T.: "Alumina-Mullite-Zirconia Composites : Part II, Microstructural Development and Toughening", J. Mater. Sci., 2, (1997), 503-511.

[9] Boch P., Chartier T., Giry J.P.: "Zirconia-toughened mullite/The role of zircon dissociated", Ceram. Trans., 6, (1990), 473-494.

[10] Claussen N., Rühle M.: "Design of transformation toughened ceramics", in Advances in Ceramics, Vol. 3, Science and Technology of Zirconia", A.H. Heuer and L.W. Hobbs (Eds.), The American Ceramic Society, Columbus, Ohio, (1981), 137-163.

[11] Evans G., Cannon R.M.: "Toughening of brittle solids by martenstinic transformations", Acta Metall., 34, (1986), 761.

[12] K Chang Song., Journal of Sol-Gel Science and Tech. 13, 1017 (1998).

[13] Koyama T., Hayashi S., Yasumori A., Okada K.: "Preparation and Characterization of Mullite-Zirconia Composities from Various Starting Materials", J. Eur. Ceram. Soc., 14, (1994), 295-302.

[14] A.I Natsenko, I.S. Kainarskii, "I.G Orlova, Neorg. Mater". 2, 1972.

[15] P. Pena, S. de Anza, "La Ceramica", 30 (1977) 1-6.

[16] P. Pena, S. de Anza, "La Ceramica", 12 (1983) 201-202.

[17] Zaho S-K, Wang Ch-A, Huang Y, Huang X-X, Guo J-K: "Mullite formation from Reaction sintering of ZrSiO4/_-Al2O3 mixtures", Mat. Let., 57, (2003), 1716-1722.

[18] N.A. Toropov and F.Ya.Galakhov, "Solid solution in the system Al2O3 – SiO2", IZV. Aka. NaukSSSR otd. Khim. Nauk 1958,8 (1958)

[19]. K. V. Kannan Nithin , N. Suriyanarayanan , DR Antonella Sola, "Mullite glass ceramics derived from sillimanite through TAP and HCP techniques", Journal of Non-Oxide Glasses Vol. 2, No 1, 2010, p. 23 - 34

[20] S Yugeswaran1, V Selvarajan1, P V Ananthapadmanabhan and L Lusvarghi "Twin step synthesis of lanthanum zirconate through transferred arc plasma processing", Journal of Physics: Conference Series 208 (2010) 012119

[21] Emad M.M. Ewais, Dina Hussien Amin Besisa, Zaki Ismail Zaki, Abd El Hakim Taha Kandil, "Tailoring of functionally graded zirconia–mullite/alumina", ceramics Journal of the European Ceramic Society 32 (2012) 1561–1573.

[22] Artur bradecki, Stanis, "Physical and Chemical Processes During Firing of ZrSiO4-Al2O3 Powders", Ceramic Materials, 63, 1, (2011), 22-26