MATERIALE CERAMICE POROASE OBŢINUTE PE CALE GEOPOLIMERICĂ
CERAMIC POROUS MATERIALS OBTAINED BY THE GEOPOLYMER ROUTE

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In this paper, the synthesis and physico-chemical characterization of some porous ceramic materials were studied using the geopolymer processing route. Samples were synthesized to contain as mineralogical component the mullite. For the synthesis, metacaolin and a NaOH solution were used. The samples were heat treated at temperatures between 1100 and 1200°C. It resulted that in this temperature range samples with low density are obtained, this decreasing with increasing temperature and at 1200^{0}C the density is below 1 g/cm^3. The mineralogical composition of the samples was examined by X-ray diffraction and the presence of mullite, cordierite, α-quartz and nepheline as crystalline phases was found. Also, the presence of the vitreous phase was observed, which increases with the increase of the heat treatment temperature. Through scanning electron microscopy studies it was observed that the samples contain pores of different shapes, closed and non-communicating, which explains the low density of the samples.

În această lucrare, s-au studiat sinteza și caracterizarea fizico-chimică a unor materiale ceramice poroase folosind ruta de procesare geopolimerică. S-au sintetizat probe care să conțină teoretic drept component mineralogic mulitul. Pentru sinteză s-a folosit metacaolinul și o soluție de NaOH. Probele au fost tratate termic la temperaturi cuprinse între 1100 și 1200^{0}C. A rezultat că, în acest interval de temperatură se obțin materiale cu densitate mică, aceasta scăzând odată cu creșterea temperaturii, iar la 1200^{0}C densitatea este sub 1 g/cm^3. Compoziția mineralogică a probelor s-a examinat prin difracție de raze X, constatându-se prezența mulitului, cordieritului, α-cuartului și a nefelinului ca faze cristaline. De asemenea, s-a observat prezența fazei vitroase, care crește odată cu creșterea temperaturii de tratament termic. Prin studii de microscopie electronică de baleiaj s-a observat că, probele conțin pori de diferite forme și dimensiuni, închiși și necomunicanți, ceea ce explică densitatea mică a probelor.

Keywords: *geopolymer route, metakaolin, alkaline solution, XRD, SEM*

1. Introduction

Inorganic polymers are hard, non-flammable materials which can resist at high temperatures. They result by the reaction between reactive aluminosilicate materials and alkaline solutions [1,2]. The geopolymers obtained at temperatures below 1000°C are amorphous or semi-crystalline, but through high-temperature heat treatment it was observed a development of some crystalline phases. For this reason they have studied as thermal insulation materials [3], refractory materials [4,5], technical ceramics [6,7] and so on.

High porosity ceramic materials can be obtained through many processes that influence their specific properties such as porosity, pore size and distribution, mechanical strengths and so on. Thus, granules with their own open porosity, mixtures with an appropriate granular composition, additives that produce gas in the initial mixture, the introduction of gas into suspensions or in melts, etc. can be used. Recently, some papers were presented in which such materials can be obtained starting from raw materials such as kaolin, metakaolin, metallurgical slags, fly ash by an alkaline or acid activation technology [8-11].

The production of ceramic materials by a geopolymeric route involves two stages: one of preparation and the other of sintering. The preparation of the mixture can be made from clay raw materials (natural or calcined) and alkaline solutions capable of reacting with them. Sintering must leads to the formation of such compounds, which to ensure a behavior of the obtained products, comparable to the manufactured products by traditional technologies, but in more economical conditions and in balance with nature.

In this paper, porous ceramic materials were synthesized starting from metakaolin and a sodium hydroxide solution, so that after the heat treatment, the samples to contain the mullite.

2.Experimental

For the synthesis of the samples, the metakaolin obtained by calcining the Harghita kaolin at temperature of 750^{0}C with two hours plateau was used. The heat treatment of kaolin at this temperature has the leads to chemically active metastructure. This is because by removing the hydroxyl ions from the kaolinite network it is create point defects and unsatisfied valences that give chemical instability [12]. The oxide composition of the used metakaolin, determined by X-ray

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fluorescence, is given in Table 1. The sodium hydroxide was dosed as a solution of 12 M concentration. The water amount was supplemented so that the final mixture to contain 25% liquid and to presente itself as a paste of normal consistency. The cylindrical shaped samples, with a diameter of 20 mm and a height of 40 mm were obtained from paste, and after removal from the mold, were kept for 24 hours at room temperature. Afterwards, the samples were treated for 10 hours at 80°C for the curing process. Then, they were thermally treated, in an electrical furnace, at temperatures of 1100, 1150 and 1200°C with a two hour plateau at maximum temperature. On the heat treated samples, water absorption, apparent density and apparent porosity were determined by the Archimedes method [13]. By X-ray diffraction, using the Shimadzu 6100 diffractometer, the mineralogical composition of the heat treated samples was determined, which was compared with theoretical mineralogical composition calculated starting from the oxide composition [12]. The microstructure of the samples was determined by scanning electron microscopy with the SEM Quanta FEG microscope.

Table 1

Oxide composition of heat treated kaoline at 750°C
Compoziția oxidică a caolinului calcinat la 750 °C

Oxides *Oxizi*	Weight % *% masice*
MgO	3.29
Al_2O_3	31.24
SiO_2	60.79
K_2O	1.26
CaO	0.75
TiO_2	1.00
Fe_2O_3	1.63

3.Results and discussions

The recipes of the synthesized samples are given in Table 2, and in Table 3 the oxide composition of the samples reduced to the main oxides is presented. The same table shows the mineralogical composition, theoretically calculated on the basis of the oxide composition. The used oxides in a proportion greater than 1.5% were considered, because only they may influence the composition of the crystalline phases formed during thermal treatment.

Table 2

The recipes of the studied samples / *Rețetele probelor studiate*

Sample no. *Nr. probă*	Metakaolin, % *Metacaolinit, %*	Na_2O, %	NaOH solution 12 M, ml *Soluţie NaOH12 M, ml*
1	97.50	2.50	6.70
2	95.00	5.00	13.43
3	90.00	10.00	26.87

Table 3

The oxide and mineralogical composition of the synthesized samples
Compoziția oxidică și mineralogică a probelor sintetizate

Sample no. *Nr. probă*	Oxide composition of the synthesized samples (%weight) / *Compoziția oxidică a probelor sintetizate (% masice)*				Theoretical mineralogical composition (%weight) *Compoziția mineralogică teoretică (% masice)*			
	Al_2O_3	SiO_2	MgO	Na_2O	mullite	cordierite	nepheline	α-quartz
1	31.96	62.18	3.36	2.50	26.86	24.52	11.46	37.16
2	31.13	60.60	3.27	5.00	20.30	23.94	22.93	32.93
3	29.50	57.40	3.10	10.00	7.15	22.60	45.85	24.40

Table 4

The properties of heat treated synthesized samples / *Proprietățile probelor sintetizate tratate termic*

Sample no. *Nr. probă*	Temperature *Temperatura, °C*	Water absorption *Absorbția apei, %*	Apparent density *Densitatea aparentă* g/cm^3	Apparent porosity *Porozitatea aparentă*, %
1	1100	0.57	2.35	1.34
	1150	3.53	1.58	5.58
	1200	6.95	< 1	-
2	1100	3.09	1.88	5.81
	1150	4.87	1.27	6.18
	1200	9.01	< 1	-
3	1100	1.67	1.15	1.92
	1150	5.20	1.05	5.46
	1200	13.05	< 1	-

3.1.Sintering behaviour

On the synthesized samples were determined: the water absorption, the apparent density and the apparent porosity, the obtained results being presented in Table 4. Thus, for all samples an increase of water absorption and a decrease of the apparent density with the increase of the temperature are observed . The small values of the apparent density are explained by the fact that the samples contain a very large amount of pores. At the same time, the water absorption has low values because the pores are closed and non-communicating, was showed by scanning electron microscopy.

At 1200˚C an increasing of volume of the samples is observed, so that their density decreased below 1 g/cm^3 (Figure 1).

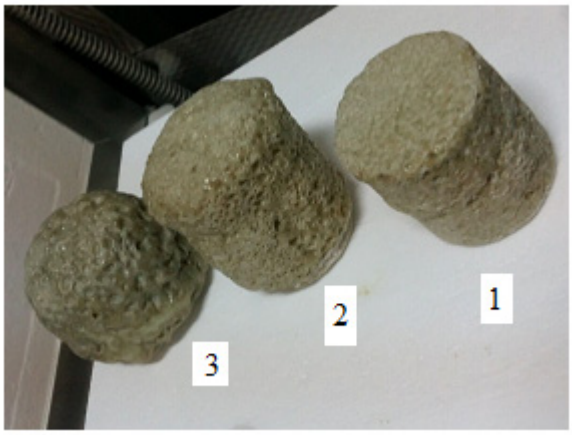


Fig.1 - Image of heat treated samples at 1200˚C / *Imaginea probelor tratate termic la 1200˚C.*

3.2.Mineralogical composition

The mineralogical composition was analysed on the heat treated samples at temperatures between 1100 and 1200°C. The X-ray diffraction patterns for sample 1, depending on the firing temperature, are shown in Figure 2. Thus it is observed that the mullite is well crystallized regardless of firing temperature. The lines of the α-quartz continuously decrease in intensity from 1100 to 1200°C, because it is solubilize in the melt. Cordierite, although is formed starting from temperatures of 1100°C, has lines barely visible regardless of firing temperature. In the case of sample 2 (Figure 3), we observe the presence of three phases, mullite, α-quartz and cordierite. As the temperature increases, the intensities specific to quartz and cordierite lines decrease, so at 1200°C the mullite is the main component, because both the quartz and the cordierite are dissolved in the melt. Regarding the sample 3 (Figure 4), at 1100°C, the most intense lines are found for cordierite and α-quartz and weaker lines for mullite. At temperature of 1150°C, practically the same phases are observed, but at 1200°C only the mullite remains and next to it the nepheline specific lines appear. Sample 3 is the only one in which the presence of nepheline is observed, which means that for the first two samples, sodium oxide contributed mainly to the formation of the liquid phase which favored the chemical reactions.

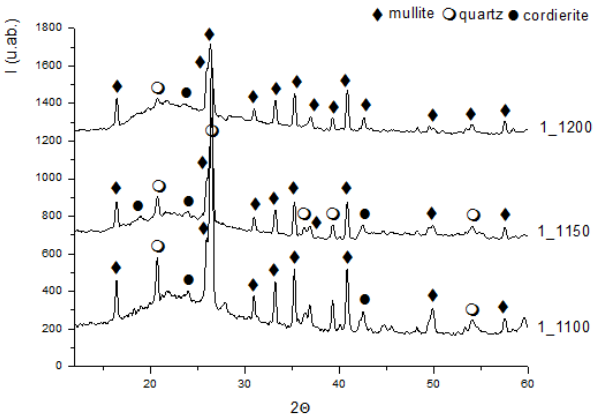


Fig.2 - X-ray diffraction patterns for sample 1 thermally treated at temperatures between 1100 and 1200˚C / *Difractogramele pentru proba 1 tratată termic la temperaturi cuprinse între 1100 și 1200˚C.*

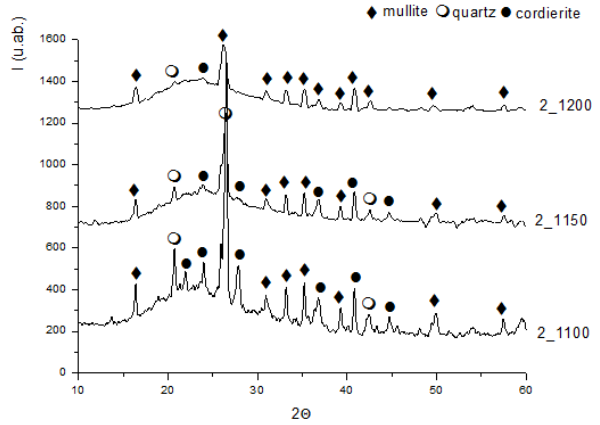


Fig.3 - X-ray diffraction pattern for sample 2 thermally treated at temperatures between 1100 and 1200˚C / *Difractogramele pentru proba 2 tratată termic la temperaturi cuprinse între 1100 și 1200˚C (mullite-06-0258; α-quartz-83-0539; cordierite-84-1221).*

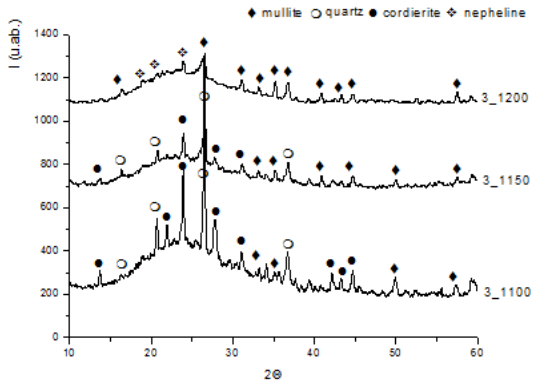


Fig.4 - X-ray diffraction pattern for sample 1 thermally treated at temperatures between 1100 and 1200˚C / *Difractogramele pentru proba 3 tratată termic la temperaturi cuprinse între 1100 și 1200˚C (mullite-06-0258; α-quartz-83-0539; cordierite-84-1221; nepheline-81-2081).*

By the deviation of the baseline from the linearity, it is observed in all samples thermally treated at temperature of 1200°C, the presence of vitreous phase. This leads to volume increase of samples, so that their density decreased below 1 g/cm^3 (Table 4). Also, all heat treated samples at 1200°C are self-glazed, sample 3 also being strongly deformed under their own weight (Figure 1). A similar deviation from the linearity is observed in the case of the samples thermally treated at 1100°C, but this is due to the non-crystallized amorphous phases due to the reduced temperature.

If we analyze the theoretical mineralogical composition (Table 3) it is found that proportion of cordierite in the three samples is almost constant. This is explained by the fact that MgO, which comes from kaolin, varies within very closely limits. The amount of mullite varies a lot from sample 1 to 3 in latter specimen, being only 7%, due to the fact that aluminum trioxide introduced by kaolin is not only consumed when the mullite is formed, but also in the reactions that lead to the appearance of the other phases. An important variation is also observed for nepheline that increases from sample 1 to 3, parallel to the increase of sodium oxide content.

From the realised experiments it is noticed that starting from 1100°C, in all samples a melt is noticed which contributes to the formation of compounds by chemical reaction.

3.3. Reactions occurring at thermal treatment

Taking into account the mineralogical composition, determined by X-ray diffraction, the following chemical reactions, can take place on the heat treatment of the samples:

$$2(Al_2O_3 \cdot 2SiO_2) + 2MgO + \\ + SiO_2 \rightarrow 2MgO \cdot 2Al_2O_3 \cdot 5SiO_2 \quad (1)$$

reaction that starts at temperature of 1100°C and leads to the formation of cordierite. The second reaction leads to the formation of mullite:

$$3(Al_2O_3 \cdot 2SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 \quad (2)$$

Metakaolin is also the basis of nepheline formation according to reaction:

$$Al_2O_3 \cdot 2SiO_2 + Na_2O \rightarrow Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \quad (3)$$

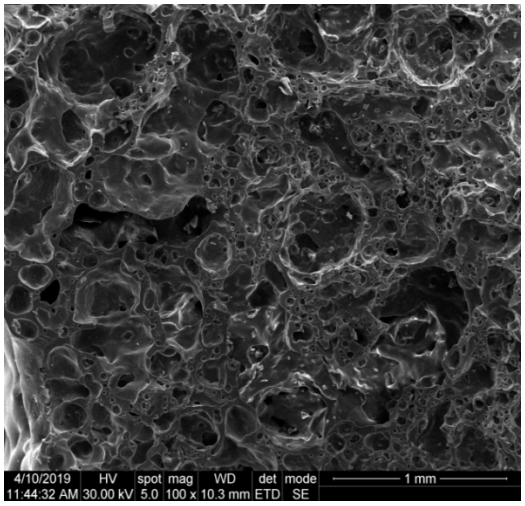
Of these three compounds, cordierite is incongruent in the presence of the liquid phase when it dissociates into mullite and a melt in accordance with the reaction:

$$2MgO \cdot 2Al_2O_3 \cdot 2SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + liq \quad (4)$$

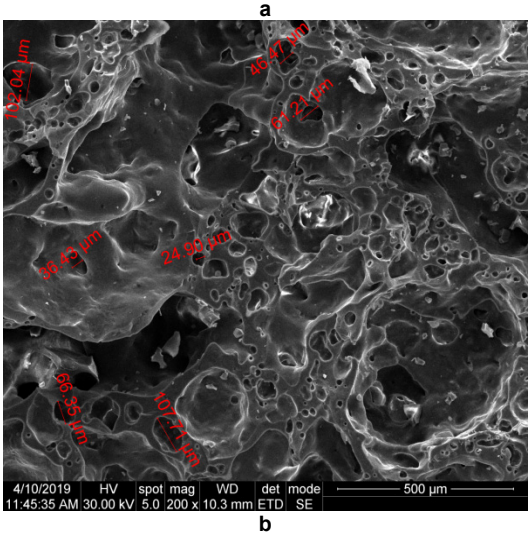
Due to this reaction, the quantity of mullite can increase especially in the sample 3 thermally treated at 1200°C, where the cordierite has totally entered in the melt.

3.4.Microstructure

The microstructure of the samples was studied by scanning electron microscopy.

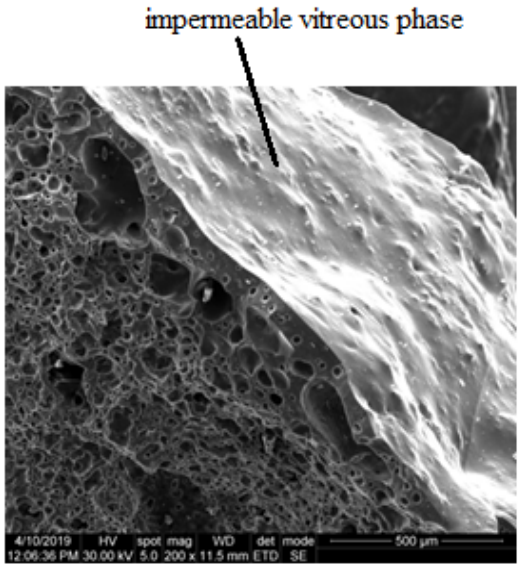


a



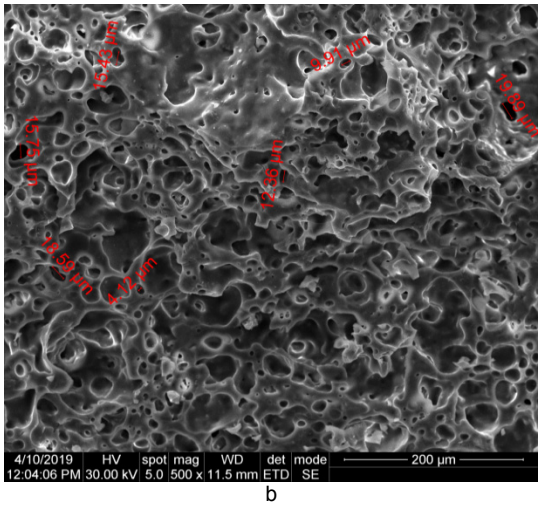
b

Fig.5 - SEM image of sample 1 thermally treated at 1200°C / *Imaginea SEM a probei 1 tratată termic la 1200°C* a)x100; b) x200.



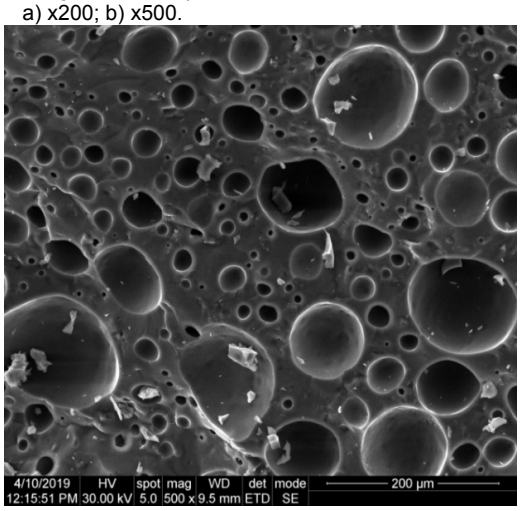
a

Fig. 6 - continues on next page



b

Fig.6 - SEM image of sample 2 thermally treated at 1150°C / *Imaginea SEM a probei 2 tratată termic la 1150°C.*
a) x200; b) x500.



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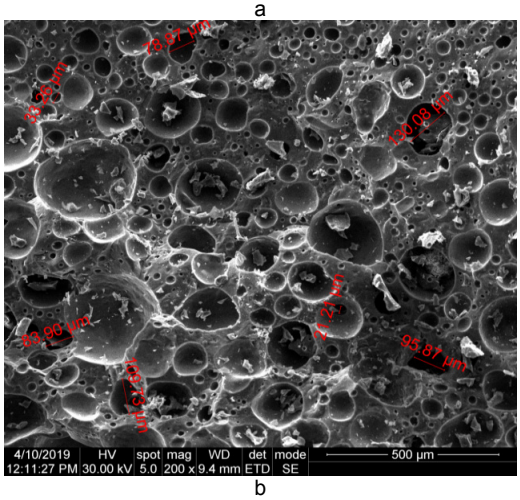

b

Fig. 7 - SEM image of sample 3 thermally treated at 1100°C / *Imaginea SEM a probei 3 tratată termic la 1100°C*
a) x500 b) x200.

For sample 1 (Figure 5), the presence of pores with different shapes and sizes but non-communicating was noticed. In the case of sample 2 (Figure 6) the most pores are small, but there are also very large pores, especially near the surface of the samples.

The SEM image of sample 3 shown in Figure 7 presents pores of different sizes, non-communicating and a spherical shape, which shows that the sample contains a large amount of liquid phase. All samples have a dense vitreous layer on the surface, which prevented the release of gases. The Figures 5b, 6b and 7b show the pore sizes for the three samples.

4.Conclusions

The obtained results in this paper showed that, by geopolymer route synthesis, the mullite can be synthesized, starting from metakaolin by alkaline activation at low temperatures (1100-1200°C). Beside to it, α-quartz, cordierite and even nepheline are as crystalline phases. The used sodium oxide is either in the form of a vitreous phase or in the nepheline compound. The obtained samples have low densities, which shows that they have a high pore content. At the 1200°C the samples are self-glazed and their density is less than 1g/cm^3. The contained pores in the samples have sizes approximately between 10 and 150 µm, different shapes, and on their surface was developed an impermeable vitreous phase.

REFERENCES

[1].Z.H. Zhang, H.Z.Zhu, C.H.Zhou and H.Wang, Geopolymer from kaolin in China : An overwiew, Appplied Clay Science, 2016, **119**, 31-41

[2].P.N.Lemougna, K.Wang, Q. Tang, U.Chinje Melo and X.Cui, Recent developments on inorganic polymers synthesis and applications, Ceramics International, 2016, **42,** 15142-15159

[3].N. A. Jaya, M. M. .Abdullah, C.M.R. Ghazali, M. Hussain, K. Hussin and R.Ahmad, Kaolin Geopolymer as Precursor to Ceramic Formation, MATEC Web of Conferences, 2016, **78** (01061), 1-8

[4].D.S. Perera and R.L.Trautman, Geopolymers with the Potential for Use as Refractory Castables, Azo Materials, online Doi10.2240/azojomo0173, 2006

[5]. A. Melinescu, M. Eftimie , A. Nicoară, R. Truscă, M. Preda, Synthesis of the Ceramics with Nepheline from Geopolymeric Precursors, Romanian Journal of Materials 2018**, 48** (3), 285 - 289

[6]. J. L. Bell, P. E. Driemeyer and W. M. Kriven, Formation of Ceramics from Metakaolin-Based Geopolymers: Part I -Cs-Based Geopolymer, J. Am. Ceram. Soc., 2009, **92** (1) 1–8

[7]. N. Xie, J. L. Bell, W. M. Kriven, Fabrication of Structural Leucite Glass–Ceramics from Potassium-Based Geopolymer Precursors, J. Am. Ceram. Soc., 2010, **93** (9) 2644-2649

[8].A. A. Reka, B. Pavlovski, P. Makreski, New optimized method for low-temperature hydrothermal production of porous ceramics using diatomaceous earth, Ceramics International, 2017, **43**, 12572–12578

[9].R. Ahmad, M. M. Abdullah, K. Hussin, A. V. Sandu, M. Binhussain and N. A. Jaya, Processing and properties of polymer filled geopolymer ceramics fabricated via powder metallurgy method: a review, Rev. Adv. Mater. Sci., 2016, **44** 26-32

[10]. N. A.Jaya, M. M. Abdullah, C. M. R. Ghazali, M. Binhussain, K. Hussin, R.Ahmad and M. V. Tran, Fabrication and Microstructure of Clay-based Geopolymer Ceramic using Powder Metallurgy Method, Applied Mechanics and Materials, 2015, **754-755,** 145-151

[11]. A. Romisuhani, A.M. Al Bakri, J.N.Ain, Review on Development of Clay based Geopolymer Ceramic Composites, Materials Science Forum, Trans Tech Publications, Switzerland, 2015, **803**, 37-43.

[12]. M.Preda, Ceramics and Refractory, Editura PRINTECH, Bucuresti, 2001

[13]. M.Preda, A.Ianculescu, A.Melinescu, Methods of analysis and control in ceramics, Editura MATRIX ROM, București, 2004

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