

# Investigations of Porous Mullitic Materials Based on Greek Raw Materials for High Temperature Applications

S. Thomaidis, G. Kostakis, Chr. G. Aneziris

Mixtures of bauxite and kaolin in various proportions were heated at temperatures up to 1500 °C in order to create porous ceramic materials for possible use in refractory applications. The physical properties of technological interest related to the possibility of using them in refractory applications are investigated. On this way the production of an open-porous mullitic material of an interesting combination of properties such as sufficient compressive strength as well as refractoriness under load is achieved.

S. Thomaidis, G. Kostakis  
Al. A. Eminov, B.K. Matyakubov  
Technical University of Crete,  
Dept. of Mineral Resources Engineering,  
73100 Chania  
Greece

Chr. G. Aneziris  
TU Bergakademie Freiberg  
09599 Freiberg  
Germany

Corresponding author: G. Kostakis  
E-mail: kostakis@mred.tuc.gr

Keywords: open porous mullitic material,  
bauxite, kaolin, fly ash

## 1 Introduction

Due to its excellent properties for high temperature applications a lot of investigations have been attempt in the last decades to produce mullite in ceramic materials. The reaction between pure alumina and pure quartz is taking place at temperatures in the range of 1600 °C. In order to produce a low cost mullitic containing ceramics in several contributions kaolin, sillimanite, alumina hydrates in combination with fly ashes have been used as raw materials [1–4].

In Greece exist considerable deposits of bauxite and some smaller deposits of kaolin. The mean quantities of bauxite mined out is used for metallurgical applications, while the kaolines are chemically and mineralogically not very pure. In this contribution an attempt to extend the uses of Greek bauxite and kaolin for the production of refractory materials will be explored. Three bauxites of the Parnass mining region, two kaolins from the Milos island as well one from Drama and one fly ash sample of the Achlada-Meliti lignite power plant (West Macedonia/GR) are investigated regarding to the possibility to produce ceramic materials for refractory applications. Specimens of diverse mixtures from the materials above were fired at various temperatures and mainly examined according to their phase generation, porosity and deformation behaviour at temperatures up to 1500 °C.

## 2 Experimental techniques

The chemical analysis of the bauxite, kaolin and fly ash raw material has taken place with the aid of XRF-spectrometer (EDS, Bruker S2 - Ranger). Measurements were carried out at 40 kV with an Al filter (500 µm) for the heavier elements (Fe, Mn, Ti, Ca, K) and at 20 kV for the lighter elements (P, Si, Al, Mg, Na) without the use of filter. For the mineralogical study of the samples X-ray diffraction (Bruker Advance D8 diffractometer system, Bragg-Brentano geometry) was used. For the collection of the

X-ray data, the diffractometer was operated with a copper X-ray tube at 35 kV/35 mA, Ni-filter and LinxEye detector. Data were collected over a range from 7° to 70° 2θ. The X-ray powder data collected for the quanti-

Tab. 1 Chemical composition of the raw materials [%]

	Bauxite A	Bauxite B	Bauxite C	Kaolin A	Kaolin B	Kaolin C	Fly Ash
SiO <sub>2</sub>	6,67	2,43	6,80	63,39	67,90	55,19	51,49
Al <sub>2</sub> O <sub>3</sub>	55,16	46,17	51,68	21,19	12,70	29,07	23,07
Fe <sub>2</sub> O <sub>3</sub>	18,07	23,39	20,61	0,14	0,07	0,01	8,60
CaO	1,67	5,62	0,02	0,05	0,02	0,22	4,51
MgO	0,00	–	–	–	–	0,07	5,43
SO <sub>3</sub>	0,53	0,05	0,21	0,20	1,63	–	0,58
Na <sub>2</sub> O	n.a.	–	–	–	–	–	0,26
K <sub>2</sub> O	0,00	–	0,01	–	0,03	2,25	2,79
TiO <sub>2</sub>	3,24	4,64	2,60	0,43	0,32	0,48	0,77
MnO	0,00	0,02	0,01	0,01	0,01	-	0,09
P <sub>2</sub> O <sub>5</sub>	n.a.	0,08	0,11	0,09	0,08	0,01	0,18
Lol	13,86	17,65	17,94	14,51	17,19	11,25	2,28
Total	99,20	100,05	99,99	100,01	99,95	98,54	100,05

# Stretch Hood Wrapping

Innovative energy saving packaging technology



## Lachenmeier Stretch Hood

Replacing costly packaging with cardboard and/or strapping together with shrinking.

- Robust packaging suitable for railway transport and transport on pure roads
- Proven stability for combined freight transport (accelerations of up to 1.0G) and for pure rail transport (accelerations moving up to 4.0G)
- Eliminates the need for cardboard and strapping
- Eliminates problems with cardboard absorbing moisture
- Eliminates the use of gaz



**Tab. 2 Mineralogical composition of the raw materials [mass-%]**

	Bauxite A	Bauxite B	Bauxite C	Kaolin A	Kaolin B	Kaolin C	Fly Ash
Quartz	–	–	1	2	3	38	6
Rutile	tr	–	tr	–	–	–	–
Gibbsite	–	–	63	–	–	–	–
Goethite	3	–	9	–	–	–	–
Hematite	11	11	3	–	–	–	tr
Calcite	2	6	–	–	–	–	–
Anhydrite	–	–	–	–	–	–	1
Lime	–	–	–	–	–	–	tr
Feldspars	–	–	–	–	–	1	9
Muscovite	–	–	–	–	–	18	–
Magnetite	–	–	–	–	–	–	tr
Hercynite	–	–	–	–	–	–	3
Anatase	2	2	tr	–	–	–	–
Boehmite	13	2	–	–	–	–	–
Chlorite	2	–	–	–	–	–	–
Mullite	–	–	–	–	–	–	7
Diaspore	64	71	–	–	–	–	–
Kaolinite	–	–	11	42	34	43	–
Alunite	–	–	–	1	3	–	–
Tridymite	–	–	–	5	6	–	–
Cristobalite	–	–	–	23	22	–	–
Amorphous	3	8	13	27	32	–	74
Sum	100	100	100	100	100	100	100

**Tab. 3 Composition [mass-%] of the test specimens**

No.	Bauxite A	Bauxite B	Bauxite C	Kaolin A	Kaolin B	Kaolin C	Fly Ash
M1	–	–	72,5	–	–	–	27,5
M2	76	–	–	24	–	–	–
M3	–	72,5	–	–	–	27,5	–
M4	–	–	80	20	–	–	–
M5	–	–	82,5	–	17,5	–	–
M6	–	–	76	–	–	24	–
M7	–	–	76	9	–	–	15
M8	–	–	74	–	–	11	15
M9	–	–	81,5	–	–	–	18,5
M10	–	–	84	6	–	–	10
M11	–	–	85	–	5	–	10
M12	–	–	83	–	–	7	10
M13	–	–	86,5	13,5	–	–	–
M14	–	–	88	–	12	–	–
M15	–	–	84	–	–	16	–
M16	–	–	57,5	–	–	–	42,5
M17	55	–	–	–	–	10	35
M18	–	–	61	9	–	–	30
M19	65	–	–	35	–	–	–
M20	69,5	–	–	–	30,5	–	–
M21	58	–	–	–	–	42	–
M22	–	–	61	–	–	39	–
M23	–	–	22	63	–	–	15
M24	12	–	–	–	–	73	15
M25	–	18	–	–	–	67	15
M26	35	–	–	–	65	–	–
M27	40	–	–	–	60	–	–
M28	75	–	–	–	25	–	–
M29	50	–	–	–	50	–	–

tative estimation of the crystalline phases were refined by the *Rietveld* method [5], [6] using the *Rayflex Autoquan* program [7]. In order to include the *Roentgen*-amorphous in the quantitative phase analysis a crystalline internal standard (corundum, 15–20 %) was added to the specimens. The homogenisation of the samples was performed by hand in a mortar. After the chemical and the mineralogical analysis of the bauxite, kaolin and fly ash mixtures were prepared by pressing test specimens in the shape of tablets of 40 mm diameter and 10 mm thickness by uniaxial pressing at 100 MPa. The maximum grain size of the bauxite and the kaolin was less than 150 µm. After forming the samples were fired in several steps up to 1500 °C in an electrical furnace. The phase evolution was carried out with the same approach as the mineralogical determination of the raw materials. The microstructure of the material produced after firing was investigated due to a scanning microscope (*Philips XL 30*) and the porosity by the *Archimedes* method. To define the compressive strength by room temperature uniaxial compression according to ASTM C109 was carried out and additionally refractoriness under load was measured according to ASTM C583.

## 3. Results

### 3.1 Chemical and mineralogical analysis

The chemical composition of the bauxites, kaolines and fly ash samples is shown in Tab. 1 and the mineralogical composition in Tab. 2. As shown in these tables all three bauxite samples were very rich in iron contained in hematite or goethite and rich in titan, mainly contained in anatase.

The bauxite C was of the gibbsite type, while in the bauxite A and B the aluminium bearing mineral was diaspore. Essential differences between these bauxites are established also in the SiO<sub>2</sub>- and the calcium-content. The bauxites A and B had high content in amorphous and remarkable contents in crystalline SiO<sub>2</sub>-modifications (quartz and cristobalite). In the kaolin samples the content in kaolinite varied between 34 (sample B) and 43 % (sample C) and in SiO<sub>2</sub> content from 55,19 up to 67,90 mass-%. One of the kaolines (C) had a remarkable K<sub>2</sub>O-content owed mainly to the presence of muscovite and, in a lesser degree, of feldspars. The fly ash

was very rich in glass and rich in  $Al_2O_3$ , contained in mullite, feldspars, hercynite and in the glass phases, as well rich in  $SiO_2$ , and  $Fe_2O_3$  contained also mainly in the glass.

### 3.2. Firing

The compositions of the test specimens from the mixtures fired at various temperatures are included in Tab. 3. The resulted ceramics after one hour firing at 1350, 1400, 1450, and 1500 °C are presented in Fig. 1. From the 29 mixtures included in Tab. 3 the last seven (M23–M29) have shown progressive melting after firing at temperatures of 1200 or 1250 °C leading to softening of the test specimens and therefore they are not included in Fig. 1.

According to Fig. 1, specimens from eighteen mixtures could be fired up to 1450 °C and four up to 1500 °C without to be melted.

### 3.3. Shrinkage, porosity, and density

As listed in Tab. 4, the shrinkage of the most mixtures after firing at 1350 °C was relative moderate and increased limited by firing at the higher temperatures. Nevertheless the mixture M21 (58 % bauxite A + 42 % kaolin C) has shown a peculiar behaviour. After an initial minimal swelling (0,2 %) at 1350 °C shrank extremely limited (0,3 % at 1400, 0,8 % at 1400 and 1,3 % at 1500 °C).

The open porosity of the test specimens (Tab. 5), on the contrary, varied in a higher extent, arising values between 6,3 % (specimen M20) up to 34,1 % (specimen M8) at 1350 and 0,2 (specimens M19 and M20) up to 10,7 % (specimen M21) at 1500 °C. Their density varied between 1,87 g/cm<sup>3</sup> (specimen M8) up to 2,31 g/cm<sup>3</sup> (specimen M16) at 1350 and 2,41 (specimens M20) up to 3,01 % g/cm<sup>3</sup> (specimen M15) at 1500 °C.

### 3.4. Compressive strength, refractoriness under load

After the evaluation of the consistence, the porosity and the shrinkage after firing at temperatures above 1450 °C, the samples which did not show satisfactory values were excluded for farther investigation.

The compressive strength of the most interesting samples evaluated after burning

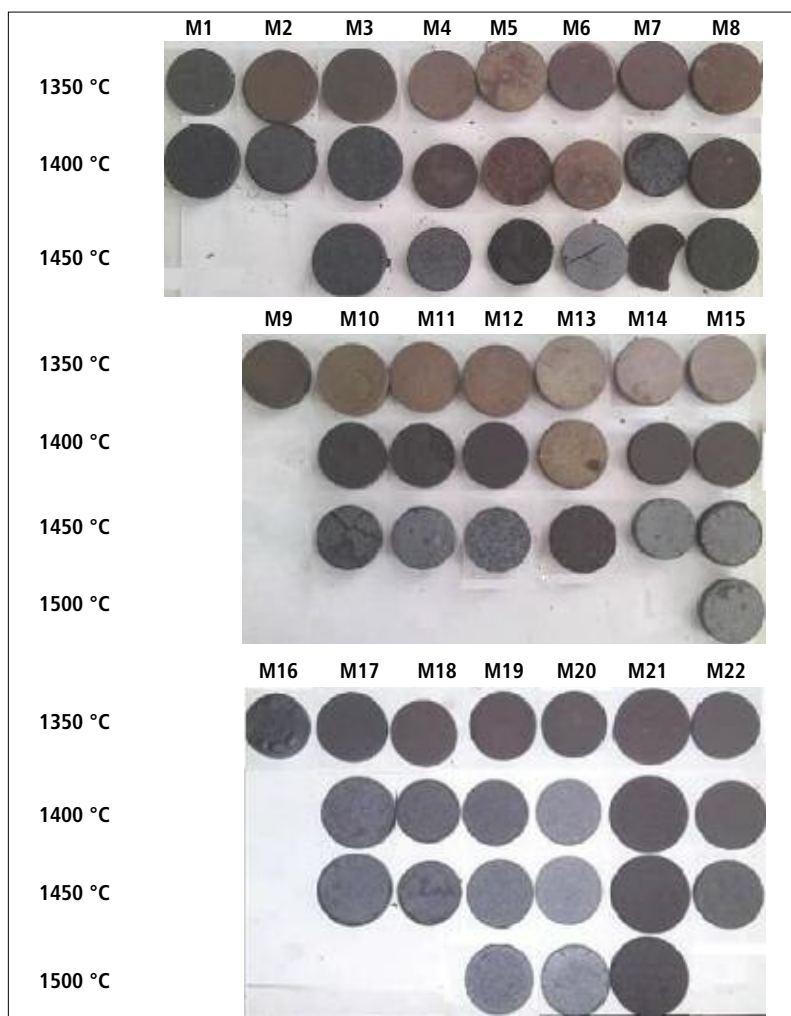


Fig. 1 a Specimens after firing at various temperatures

Tab. 4 Shrinkage after burning at various temperatures

No.	Temperature [°C]			
	1350	1400	1450	1500
M1	11,9	12,5	–	–
M2	8,1	10,1	–	–
M3	7,6	9,1	13,2	–
M4	7,1	10,1	12,9	–
M5	11,7	12,4	12,9	–
M6	9,0	12,7	14,4	–
M7	8,0	9,3	9,6	–
M8	6,2	7,8	10,1	–
M9	10,5	–	–	–
M10	7,3	9,9	13,1	–
M11	12,3	14,3	15,8	–
M12	11,8	14,7	15,1	–
M13	7,9	11,6	12,2	–
M14	13,4	17,2	17,4	–
M15	14,1	16,8	17,0	17,1
M16	partially melted	–	–	–
M17	10,9	12,1	12,7	–
M18	13,4	16,1	16,3	–
M19	11,2	12,9	13	13,1
M20	11,2	13,6	13,8	13,9
M21	–0,2	0,3	0,8	1,3
M22	9,3	12,1	12,6	–

**Tab. 5** Open porosity [%] and density [g/cm<sup>3</sup>] after burning at various temperatures [°C]

Temp. [°C]	1350		1400		1450		1500	
	No.	Porosity	Density	Porosity	Density	Porosity	Density	Porosity
M1	15,2	2,01	8,1	2,70	–	–	–	–
M2	23,7	1,98	12,5	2,51	–	–	–	–
M3	20,7	1,95	16,4	2,42	8,8	2,72	–	–
M4	30,9	1,77	25,1	1,99	10,5	2,21	–	–
M5	26,0	1,79	6,9	2,80	6,2	2,83	–	–
M6	29,0	2,01	12,4	2,49	9,5	2,62	–	–
M7	22,1	2,09	14,3	2,49	12,0	2,54	–	–
M8	34,1	1,87	23,8	2,36	11,6	2,61	–	–
M9	17,1	2,22	–	–	–	–	–	–
M10	29,3	2,09	16,8	2,65	6,1	2,97	–	–
M11	25,3	2,14	13,4	2,71	2,0	3,08	–	–
M12	26,4	2,11	12,1	2,65	2,8	2,99	–	–
M13	31,0	2,04	22,1	2,34	12,4	2,61	–	–
M14	28,0	2,11	10,1	2,99	7,3	3,05	–	–
M15	25,1	2,19	6,3	2,83	6,2	2,87	6,0	3,01
M16	7,5	2,31	–	–	–	–	–	–
M17	15,2	2,12	8,9	2,35	2,3	2,62	–	–
M18	13,0	2,30	0,9	2,79	0,8	2,80	–	–
M19	14,6	2,28	0,6	2,78	0,3	2,81	0,2	2,81
M20	6,3	2,68	0,3	2,78	0,2	2,75	0,2	2,75
M21	30,0	2,01	21,7	2,11	17,3	2,20	10,7	2,41
M22	18,2	2,14	9,6	2,69	5,3	2,81	–	–

**Tab. 6** Compressive strength P in [N/mm<sup>2</sup>] of the mixtures after burning

Mixture	M14 *	M15**	M18 *	M19**	M20**	M21**
Comp. strength	83	82	92	40	44	54

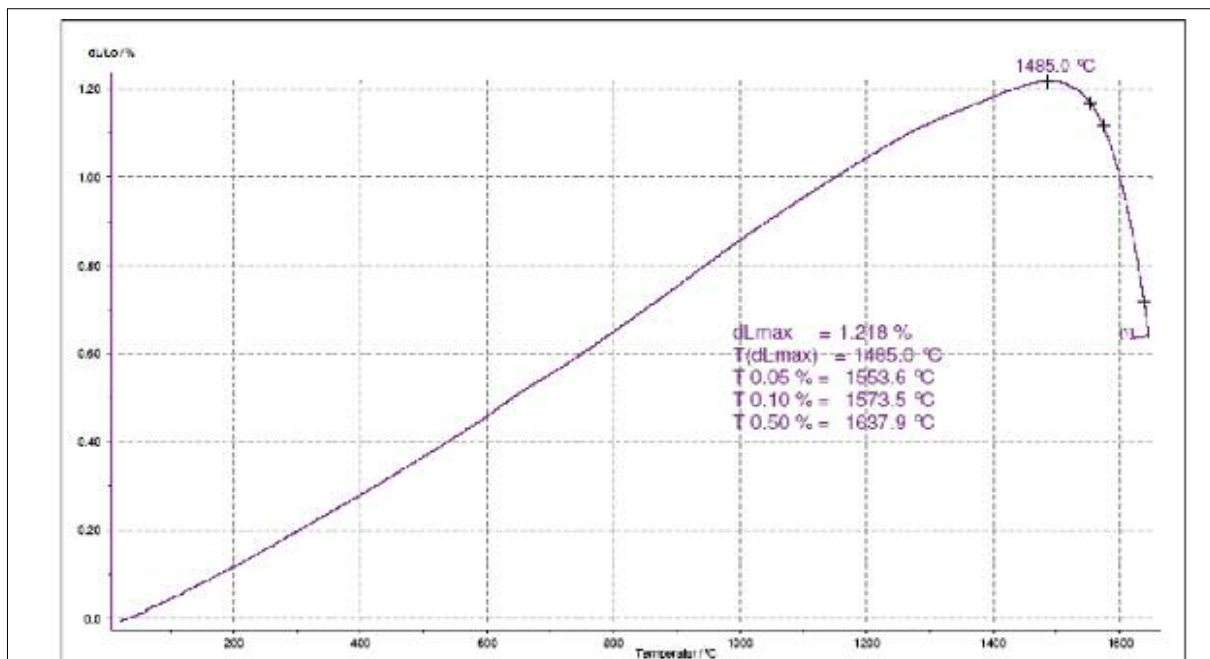
\* after firing at 1450 °C; \*\* after firing at 1500 °C

at 1450 and 1500 °C, respectively, is shown in Tab. 6, where the mean values of the results of the determination on five specimens of each mixture are included. As it is shown in this table the compressive strength of the samples varied between 40 and 92 N/mm<sup>2</sup>.

Because of the exceptional combination of the values of the shrinkage with the porosity and compressive strength by the mixture M21, the refractoriness under load was determined.

### 3.5. Phase composition and microstructure

The phases formed after firing of mixture M21 at 1500 °C are listed in Tab. 7. The mean constituents of M21 were mullite (43 %), and amorphous (43 %), accompanied by smaller amounts of corundum and hematite and traces of tridymite and anatase. According to SEM micrographs of M21 in Fig. 3 a, pores of irregular shape reaching up to a size of at least 300 μm, formed in a very compact matrix are identified. The mass formed a very compact body constituted mainly of stake shaped mullite crystals (Fig. 3 c), hematite (Fig. 3 d) corundum and the rest of the crystalline phases, bounded together by the glass, mainly, or sintered.



**Fig. 2** Refractoriness under load of sample M21. The T<sub>05</sub> temperature is lying at 1553,6 °C

# Expertise

is developing system solutions for each individual application.



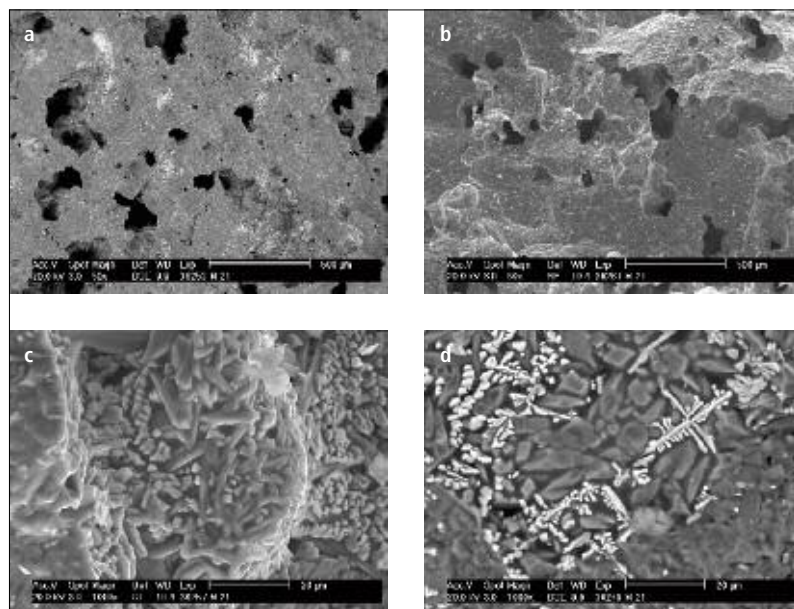
**ZSCHIMMER & SCHWARZ**  
GmbH & Co KG  
**CHEMISCHE FABRIKEN**

Max-Schwarz-Straße 3-5 · 56112 LAHNSTEIN / GERMANY · Tel. +49 2621 12-485 · Fax +49 2621 12-403  
keramik@zschimmer-schwarz.com · www.zschimmer-schwarz.com

**Tab. 7** Phase composition of M21 after burning at 1500 °C

Phase	Hematite	Mullite	Tridymite	Anatase	Corundum	Amorphous	Sum
[%]	6	43	1	tr	7	43	100

tr = traces



**Fig. 3** Mixture M21 (58 % bauxite A + 42 % kaoline C) after firing at 1500 °C (SEM); surface of the sample (a), and surface of a fracture (b); mullite and molten phase (c), and hematite (d, white fields)

## 4 Conclusion

The raw material used were, as mentioned, three karst bauxites, two of them of diasporic (samples A and B) and one of gibbsitic type, three kaolines, two of them free of mica (sample A and B) and one rich in muscovite (sample C), as well one fly ash rich in aluminium oxide and silicon dioxide. The high content of the iron oxide in the bauxites as well the very high content of glass and the relatively high content of iron oxide of the fly ash did not give hope to produce high refractive ceramics using these raw materials. Nevertheless their combination with the

kaolines seemed to lead probably to the production of ceramic masses of interesting technical properties. From these raw materials 29 different mixtures were investigated. From the 29 mixtures included in Tab. 3 the mixtures of bauxite with Kaolin and the fly ash (M23–M29) have shown progressive softening or melting by firing at temperatures below 1200 or 1250 °C, while other mixtures (Fig. 1 M9, M16) were melted at 1350 °C or at 1400 °C (M1, M2). Other samples (M3–M8, M10–M14, M17, M18, M22) were stable up to 1450 °C or 1500 °C (M15, M19–M21) up to 1500 °C but they

have shown a relatively high shrinkage. Some mixtures from the gibbsitic bauxite (bauxite C) with kaolines after firing at 1450 °C (M14, M18) and at 1500 °C (M15, M19–M21) were satisfactory sintered and gave high values of compressive strength related to their porosity. However the most interesting mixture (M21) was the mixture of one of the diasporic bauxites (bauxite A) with the muscovite rich kaolin (kaoline C) because it gave after firing at 1500 °C a ceramic structure with a  $T_{05}$  of 1553,6 °C. The mean constituents of this material were stake shaped mullite crystals and amorphous forming together a very compact matrix.

## References

- [1] Yingchao Dong; et al.: Preparation of low-cost mullite ceramics from natural bauxite and industrial waste fly ash. *J. Alloys and Compounds* 460 (2008) 599–606
- [2] Chen, C.Y.; Lan, G.S.; Tuan, W.H.: Preparation of mullite by the reaction sintering of kaolinite and alumina. *J. Eur. Ceram. Soc.* 20 (2000) 2519–2525
- [3] Temujin, J.; et al.: Phase evolution in mechanically treated mixtures of kaolinite and alumina hydrates (gibbsite and boehmite). *J. Eur. Ceram. Soc.* 20 (2000) 413–421
- [4] Sainz, M.A.; et al.: XRD microstructural analysis of mullites obtained from kaolinite-alumina mixtures. *J. Eur. Ceram. Soc.* 20 (2000) 403–412
- [5] Bish, D.L.; Howard, S.A.: Quantitative phase analysis using the Rietveld method. *J. Appl. Crystallogr.* 21 (1988) 86–91
- [6] Windburn, R.S.; et al.: Rietveld x-ray quantitative analysis of NIST fly ash standard reference materials. *Powder Diffr.* 15 (2000) [3] 163–172
- [7] Kleeberg, G.R.; Bergmann, J.: Quantitative Röntgenphasenanalyse mit den Rietveld-Programmen BGMN und AUTOQUAN in der täglichen Laborpraxis. *Ber. DTTG* 6 (1998) 237–250