SINTEZA MULLITULUI PRIN METODE NECONVENȚIONALE▲
MULLITE SYNTHESIS BY UNCONVENTIONAL METHODS

SILVANA BORCĂNESCU∗, IOAN LAZĂU, CORNELIA PĂCURARIU, ALEXANDRA JURCA

Universitatea Politehnica Timişoara, Bd V. Pârvan nr. 6, 300223, Timişoara, România

The paper presents the results obtained in the mullite synthesis using the sol –gel method, starting from $Si(OC_2H_5)_4$ (TEOS) and aluminum nitrate, respectively the sol-gel method combined with the combustion method. The combination of the two methods was achieved by addition urea, corresponding to the reaction with aluminum nitrate. The initiation of the combustion process was made by introducing the mixtures in the oven pre-heated at 500°C. The mullite formation requires further annealing at 1200°C, so in the case of the sol-gel method and in the combined version. The major difference between the two methods consist in avoiding the NO_x release by using the combined version.

Lucrarea prezintă rezultatele obținute în sinteza mullitului utilizând metoda sol-gel pornind de la $Si(OC_2H_5)_4$ (TEOS) și azotat de aluminiu, respectiv metoda sol-gel combinată cu metoda combustiei. Combinarea celor doua metode s-a realizat prin adaosul de uree corespunzător reacției cu azotatul de aluminiu urmată de inițierea procesului de combustie prin introducerea amestecurilor în cuptorul preîncălzit la 500°C. Formarea mullitului necesită calcinarea ulterioară la 1200°C atât în cazul metodei sol-gel cât şi în varianta combinată. Diferența majoră între cele două metode constă în evitarea emisiilor de NO_x prin aplicarea variantei combinate.

Keywords: sol-gel, combustion synthesis, X-ray method, mullite

1. Introduction

The usual formula attributed to mullite is $3Al_2O \cdot 2SiO_2$ (A_3S_2). Mullite forms solid solutions for higher proportion of Al_2O_3 until the limit composition corresponding to the $2Al_2O_3 \cdot SiO_2$ (A_2S) formula. Due to its properties: high refractivity, thermal shock resistance, very good chemical stability, high mechanical resistance, low thermal expansion coefficient, low thermal conductivity [1-4], mullite represents a ceramic material of great practical interest.

The mullite obtaining from the classical raw materials such as clay materials (aluminum hydrosilicates) or natural aluminosilicates (silimanite, andalusite, kyanite) and alumina (Al_2O_3) as powders micrometer-sized granules, requires high temperatures (above 1500°C) [5, 6]. The presence of a liquid phase decreases the mullite temperature formation around 1350-1400°C, but in this case results only masses containing dispersed mullite, eventually in a vitreous matrix, as for example porcelain.

The difficult synthesis of the mullite by classical method, associated with its practical importance, justifies the interest for using the unconventional synthesis methods and in particularly the sol-gel method. There are many papers for mullite synthesis by sol-gel method, which differs by the nature of the used precursors, work conditions and the characteristics of the obtained mullite.

Lee et al. [7] studied the mullite formation by the annealing of a gel resulted from colloidal silica and $Al(NO_3)_3 \cdot 9H_2O$. The mullite formation starts at 1200°C, in parallel with cristobalite crystallization, but the complete resorption of cristobalite with mullite formation as unique phase takes place only at 1500°C.

The big influence of the synthesis conditions on the mullite formation was studied by Wang and Saks [8], showing that:
- starting from microcomposite mixtures resulted from α-Al_2O_3 cover (with 14 m^2/g specific surface area, respectively the average particles size diameter 18 μm) with SiO_2 resulted from TEOS precipitation with ammoniacal water, mullite formation is accompanied by an endothermic effect with maximum at 1499°C;
- starting from a diphasic gel obtained from colloidal boehmite (specific surface area

- 156 m^2/g) and alcoholic TEOS solution, at pH~3.5, dried at 60°C two days, mullite formation is accompanied by a weak exothermic effect with maximum at 1332°C;
- starting from a monophasic gel obtained from an alcoholic TEOS solution and Al(NO$_3$)$_3$ alcoholic solution, mullite formation is accompanied by a strong exothermic effect with maximum at 987°C.

Mullite formation by sol-gel method, after annealing at 1000°C is noticed also by Leivo and et al. [9]; the gels were obtained starting from Si(OC$_2$H$_5$)$_4$, Al(O^{i}C$_3$H$_7$)$_3$ and Al(NO$_3$)$_3$ · 9H$_2$O.

For avoiding some segregation processes of the two Al^{3+} and Si^{4+} cationic species during the hydrolysis/condensation processes, it was studied the mullite formation starting from aluminosiloxane precursors – containing the two cations [10, 11]. Starting from di-(secbutoxy)aluminoxytrietoxysilane (sec-C$_4$H$_9$O)$_2$Al-O-Si(OC$_2$H$_5$)$_3$ and ethyl 3-oxobutanoatodiisopropoxyaluminum, (iso-C$_3$H$_7$O)$_2$Al(CH$_3$COCHCO$_2$C$_2$H$_5$) Yago and Aksay [10] obtained mullite fibers with diameter between 20 and 100 µm (by extrusion) and annealing at 1000°C.

The exothermic effect due to the mullite crystallization presents a maximum at 980°C under 10°C/min heating rate.

Mullite synthesis by the sol-gel method can be realized also from silica sols and alumina [12-14]. The sol of silica was obtained by passing the sodium metasilicate aqueous solution (Na$_2$SiO$_3$) through an ion exchange resin column. Alumina sol was obtained from an aqueous solution of Al(NO$_3$)3·9H2O and urea at pH=2. The mixture of silica and alumina sols was heated at 50°C, to obtain a gel that was dried and then annealed. The mullite crystallization in these samples was realized at 1250°C.

An interesting perspective for mullite synthesis is represented by combustion synthesis [15-17]. The oxide compounds synthesis by combustion is based on the strong exothermic redox reactions that take place between the oxidizing agents (mostly the desired metal nitrates) and a reducing agent or fuel (mostly urea, amino acids, amides etc.). Initiation of the combustion process is performed at relatively low temperatures, most times below 500°C and maximum temperature of the reaction mixture during the combustion can reach 1600°C [18, 19].

Combustion synthesis success is conditioned by the rational choice of the reducing agent depending on the nature of oxidizing agent. For example, tricalcium aluminate (3CaO·Al$_2$O$_3$) can be obtained directly from the combustion synthesis using calcium and aluminum nitrates (3/2 molar ratio) and a mixture of β-alanine and urea [20].

In case of the mullite synthesis, a major difficulty occurs because silica nitrate or other silica compound to function like an oxidant agent is not available. In these conditions it was attempted a combustion process between aluminum nitrate and urea, taking place in the presence of a precursor for SiO$_2$. As precursor for SiO$_2$ it was used TEOS and different forms of colloidal silica [15-17]. Using TEOS the result was negative, due to the reaction mixture leaving by its burning in the gas phase [15]. Using the colloidal silica, the combustion process between the aluminum nitrate and urea is less energetic due to SiO$_2$ presence as a moderator; therefore results an amorphous powder reflecting the insufficient temperature from the reaction mixture for insuring the mullite formation.

After further annealing of this powder at temperatures above 1200°C, mullite is formed [15, 16]. For the combustion process intensification it was worked with a urea excess and addition of NH$_4$NO$_3$ or H$_2$O$_2$. On this way, directly from the combustion, week crystalline mullite phase was obtained with high (230 m^2/g) BET specific surface area.

Starting from this information, in the present paper it was followed the mullite synthesis by sol-gel method, using TEOS and Al(NO$_3$)$_3$·9H$_2$O, and was tested a modified version by combining the sol-gel with combustion method, adding urea.

2.Experimental

As starting materials were used TEOS (Merck), aluminum nitrate Al(NO$_3$)$_3$·9H$_2$O (Merck), urea CH$_4$N$_2$O (Merck), ethanol C$_2$H$_5$OH (Chimreactiv), colloidal silica (MINDO Dorohoi), aluminum hidrate (ALOR Oradea).

Aluminum nitrate and TEOS were dosed in 6:2 molar ratios, corresponding to the (3Al$_2$O$_3$·2SiO$_2$) mullite stoichiometry and also in 4:1 molar ratio, corresponding to the 2Al$_2$O$_3$·SiO$_2$ stoichiometry. For the obtaining of a homogenous system (clear solution) it has been worked with TEOS:ethanol:water=1:46:63.5:0.14 molar ratio, according to the TEOS–H$_2$O–C$_2$H$_5$OH *ternary* system [4]. The water from the samples was provided by the crystallization water from Al(NO$_3$)$_3$·9H$_2$O. Starting from TEOS, four samples were prepared (M1, M2, M3a and M3b). The compositions of the studied samples are presented in Table 1.

M1 and M2 samples are intended for mullite obtaining by sol-gel method, were SiO$_2$ is the result of hydrolysis / condensation process, developed in presence of Al(NO$_3$)$_3$ – which is embedded in the gel pores. The difference between the two samples consists in the projected stoichiometry, composition 3Al$_2$O$_3$·2SiO$_2$ in sample M1, respectively 2Al$_2$O$_3$·SiO$_2$ in sample M2.

The compositions studied by sol-gel method / *Compoziţiile studiate prin metoda sol-gel*

Sample No. Nr. probă	Raw materials [mols] Materii prime [moli]				The phase composition after annealing at different temparatures Compoziţia fazală după calcinare la diferite temperaturi			
	$Al(NO_3)_3 \cdot 9H_2O$	$Si(OC_2H_5)_4$	CH_4N_2O	C_2H_5OH	1100°C	1150°C	1200°C	1300°C
M1	0.06	0.02	-	0.51	$\gamma\text{-}Al_2O_3$	-	mullite (M)	mullite (M)
M2	0.04	0.01	-	0.51	$\gamma\text{-}Al_2O_3$	-	mullite (M) $\alpha\text{-}Al_2O_3$	-
M3a	0.06	0.02	0.15	0.51	$\gamma\text{-}Al_2O_3$	mullite (M) $\alpha\text{-}Al_2O_3$ $\gamma\text{-}Al_2O_3$.	mullite (M)	mullite (M)
M3b	0.06	0.02	0.15	0.51	$\gamma\text{-}Al2O3$	$\alpha\text{-}Al_2O_3$ mullite (M)	$\alpha\text{-}Al_2O_3$ mullite (M)	-
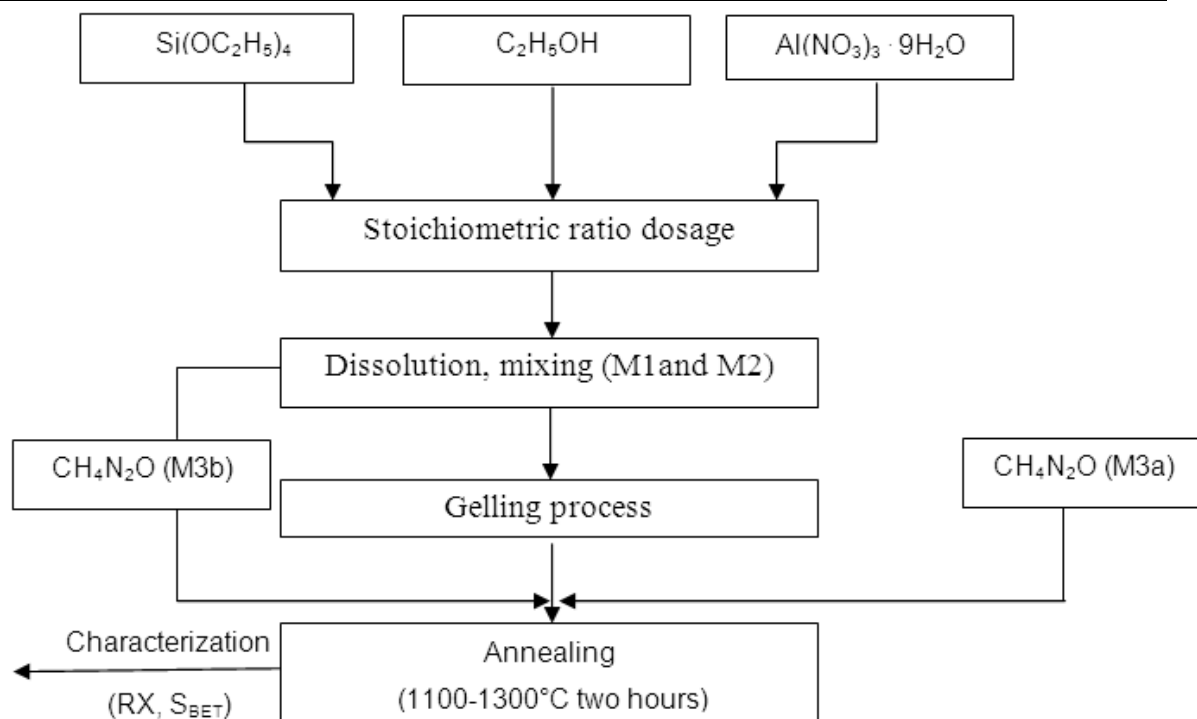
Fig. 1 - The obtaining scheme of the samples / *Schema de obţinere a probelor.*

The sample M3a differs from the sample M1 by the fact that after the hydrolysis / condensation process in the presence of $Al(NO_3)_3$, urea was added; its presence is required for participating in a combustion process with aluminum nitrate. Urea was added based on the reaction presented in equation (1):

$$2Al(NO_3)_3 + 5CH_4N_2O \rightarrow Al_2O_3 + 5CO_2 + \\ + 10\ H_2O + 8N_2 \qquad (1)$$
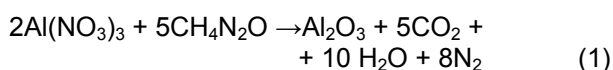
with the mention that urea was taken with 20 % excess in report with the necessary stoichiometric quantity.

The sample M3b starts from a mixture with the same composition as M3a, but differs from M3a by the processing mode: in case of the sample M3b the working mode is the one characteristic for combustion synthesis, the hydrolysis / condensation process of TEOS no longer starts; after the reagents dissolution combustion process is initiated.

General scheme for obtaining samples has been described in Figure 1.

Reagents quantities were calculated for the obtaining of 0.01 moles of oxide powder (mullite).

The necessary quantities of TEOS were measured with pipette and were introduced in a Berzelius glass which was on a magnetic stirrer.

The composition studied by classical method / *Compoziția studiată prin metoda clasică*

Sample No. *Nr. probă*	Raw materials [mols] *Materii prime [moli]*		The phase composition after annealing at different temparatures *Compoziția fazală după calcinare la diferite temperaturi*	
	Quartz(SiO$_2$) *Cuarț (SiO$_2$)*	Al$_2$O$_3$	1100°C	1300°C
R	2	3	quartz(Q) / *cuart (Q)* cristobalite (Crist.) / *cristobalit* (Crist.) α-Al$_2$O$_3$	cuartz (Q) / *quartz(Q)* cristobalite (Crist.) / *cristobalit* (Crist.) α-Al$_2$O$_3$

The necessary ethanol quantity was volumetrically dosed and was added under continuously stirring over TEOS. Aluminum nitrate was added in small proportions under continuously stirring over the TEOS and ethanol results a clear solution. The solutions were left for the gelling process for 7 to 14 day. After that it was dried in the stove (M1) respectively in the other urea was added (M3a) and after that it was introduced in a preheated kiln at 500°C.

The resulted powders were annealed at temperatures between 1100-1300°C, two hours soaking time.

For comparison, a referenced sample was prepared – *noted R* – the synthesis methods used was the classical method, based on the annealing of some oxide mixtures. The sample composition is presented in Table 2.

After the the raw materials dosing, the samples were subjected to wet homogenization in a ball mill for 30 minutes and dried in a stove. The dried samples were introduced in crucibles for annealing at temperatures between 1100-1300°C with two hours soaking time.

Phase composition of the annealed samples was determined by X-ray diffraction using a DRON 3 spectropfotometer, CuK$_\alpha$ radiation. The XRD pattern interpretation was performed using JCPDS date base.

The specific surface area of samples M1 and M3a, annealed at 1200°C and 1300°C was performed by nitrogen adsorption (BET), using a MICROMERITICS, ASAP 2020 apparatus.

3.Results and discussion

At the samples introduction in the preheated kiln at 500°C it can be noticed essential differences between them:
- M1 and M2 samples suffer a week inflammatory process assigned to the ethanol rest from the mixture. Then follows an intense NO$_x$ release, resulted from the Al(NO$_3$)$_3$ mixture decomposition.
- M3a sample suffers an energetic combustion process, with strong and lasting (35 seconds) flames. It is essential that practically NO$_x$ emissions are missing, confirming the redox processes development according to the equation (1).

- sample M3b undergoes a combustion process more energetic and longer than M3a (55 seconds) suggesting that beside the redox processes according to the equation (1) TEOS participates at the combustion process as gas.

In case of sample M1 obtained by sol-gel method and annealed at 1100°C, the sample is predominant amorphous, only week crystalline γ-Al$_2$O$_3$ is formed (Fig. 2). After annealing at 1200°C respectively at 1300°C, the projected phase can be notice, mining that the entire SiO$_2$ quantity is bonded in mullite (Fig. 2).
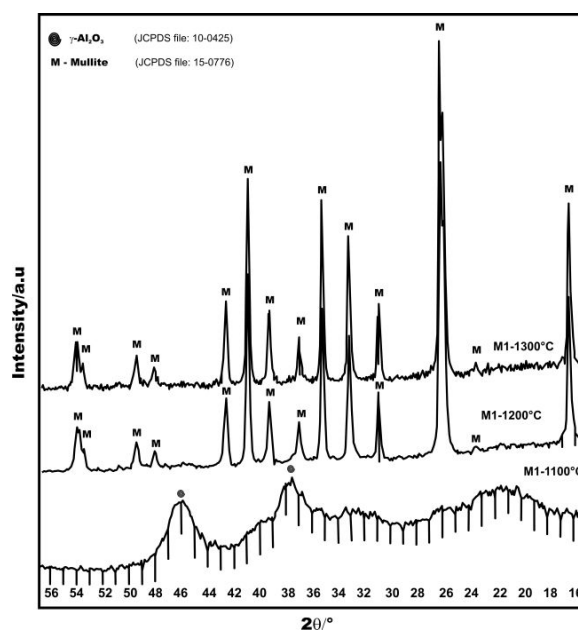

Fig. 2 - XRD patterns of the sample M1 obtained by sol-gel method and annealed at different temperatures/ *Spectrele de difracție RX ale probei M1 obținută prin metoda sol-gel și calcinată la diferite temperaturi* .

In case of sample M2 (2Al$_2$O$_3$·SiO$_2$), annealed at 1200°C, the present crystalline phases are mullite and corundum. This can be explained by the 2:1, Al$_2$O$_3$/ SiO$_2$ molar ratio. Because the sample is richer in Al$_2$O$_3$ it cannot be found totally bounded in mullite (Fig. 3).

In case of sample M3a, XRD patterns presented in Figure 4 show a similar phase composition with M1: at 1100°C the sample is amorphous and at 1200°C the single phase is mullite; rising the temperature at 1300°C the XRD pattern presents no changes.
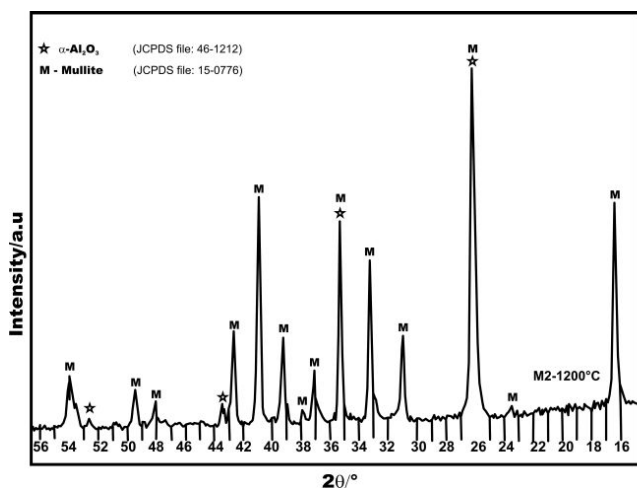
Fig. 3 - XRD pattern of the sample M2 obtained by sol-gel method and annealed at 1200°C / *Spectrul de difracție RX ale probei M2 obținută prin metoda sol-gel și calcinată la 1200°C.*
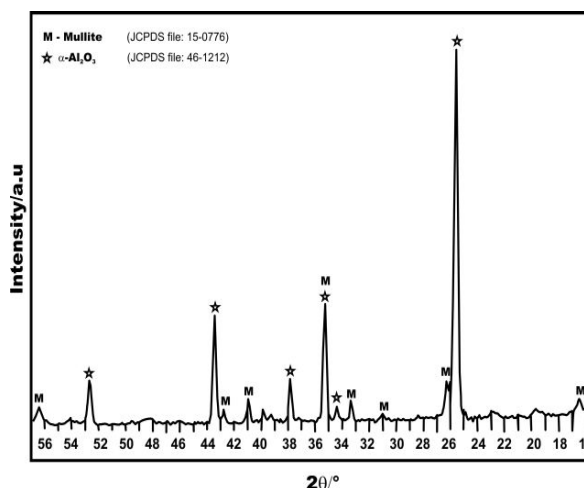

Fig. 5 - XRD pattern of the sample M3b annealed at 1200°C / *Spectrul de difracție RX ale probei M3b calcinată la 1200°C.*
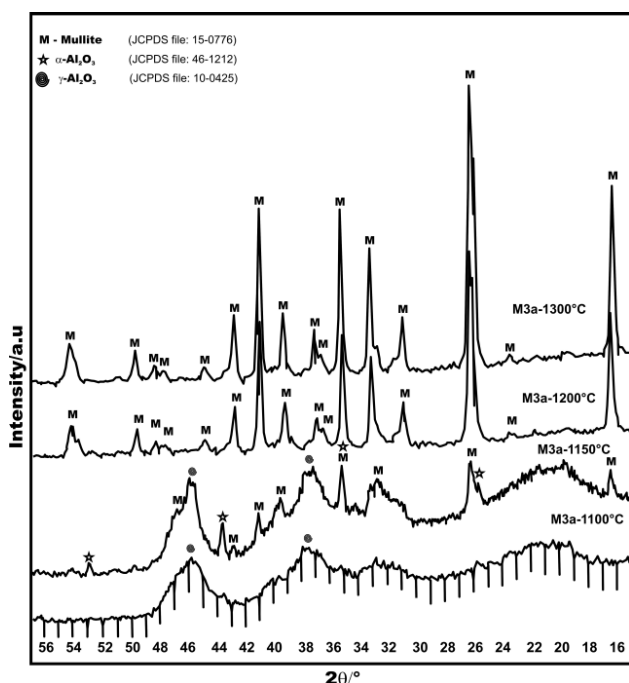

Fig. 4 - XRD patterns of the sample M3a obtained by sol-gel method and annealed at different temperatures / *Spectrele de difracție RX ale probei M3a obținută prin metoda sol-gel și calcinată la diferite temperaturi.*

In case of M3a sample, the phase analysis was performed also a sample annealed at 1150°C; it can be noticed the maximum diffraction peaks for mullite along with the γ-Al_2O_3 and very small amount of α-Al_2O_3. It can be appreciated that the reduced proportions of α-Al_2O_3 and the absence of crystalline SiO_2 (cristobalite) are essential for the mullite formation around 1150°C and practically finished at 1200°C.

In case of sample M3b, after annealing at 1200°C the main phase on the XRD pattern (Fig. 5) is α-Al_2O_3 and only a reduced proportion of mullite. The major difference between the phase composition of sample M3a and M3b annealed at 1200°C can be explained by the lack of hydrolysis

process with the formation of a SiO_2 gel; TEOS present in reaction mixture undergoes a combustion process in the gas phase leaving the reaction mixture in considerable proportion. This result confirms some information from the literature [15] and in the same time underlines the correct development of the TEOS hydrolysis / condensation process, in the presence of aluminum nitrate or other precursor for Al_2O_3.

Regarding the specific surface area values of the samples annealed at 1200°C and 1300°C (Table 3) it can be noticed smaller values for the sample M3a, respectively bigger particles size calculated values compared with sample one. The particles size was calculate using the relation (2):

$$d_{BET} = \frac{6000}{S_{BET} \cdot \rho}$$ (2)

where: d_{BET} – particle size diameter;
        S_{BET} – specific surface area;
        ρ- density.

This reflects the higher reactivity of the M3a mixture, prepared with the urea addition. In both mixtures, by raising the temperature from 1200°C to 1300°C, the mullite specific surface area is reduced. Even if in the mullite formation, between samples M1 and M3a major differences are not noticed (in both cases the required temperature for the mullite formation as single phase is 1200°C), there is a clear difference in favor of sample M3a because at the annealing, the NO_x release was absent. M1 sample behaves completely different; generally as in the case of in case of methods based on the annealing of some $Al(NO_3)_3$ mixtures - which above 100°C decomposes with intense NO_x emissions in the absence of a reducing agent – fuel.

In case of the reference R sample, obtained by classical method, mullite phase is absent even at 1300°C, the maximum diffraction peaks characteristic for mullite are absent on the

Table 3

Specific surface area and particles size values / *Valorile suprafețelor specifice şi dimensiunea particulelor*

Sample No. *Nr. probă*	1200°C		1300°C	
	S_0 (m^2/g)	d(µm)	S_0 (m^2/g)	d(µm)
M1	2.3	0.82	1.7	1.12
M3a	1.2	1.58	1.1	1.67

XRD patterns presented in Figure 6.

These results in full agreement with the literature data, justify the interest for applying the unconventional synthesis methods for the mullite obtaining at lower temperatures.

4.Conclusions

Using the sol-gel method based on the annealing of some mixtures where TEOS was used as precursor for SiO_2 and $Al(NO_3)_3$, allows the obtaining of mullite as unique phase at 1200°C.

Between sample M1 obtained by sol-gel method using TEOS, $Al(NO_3)_3 \cdot 9H_2O$ and ethanol and sample M3 with urea addition, representing a combination between sol-gel and combustion synthesis, do not exist major differences regarding the temperature of mullite formation; instead there is a clear difference in favor of the combined method (sample M3a), because at the annealing the NO_x gases are absent.
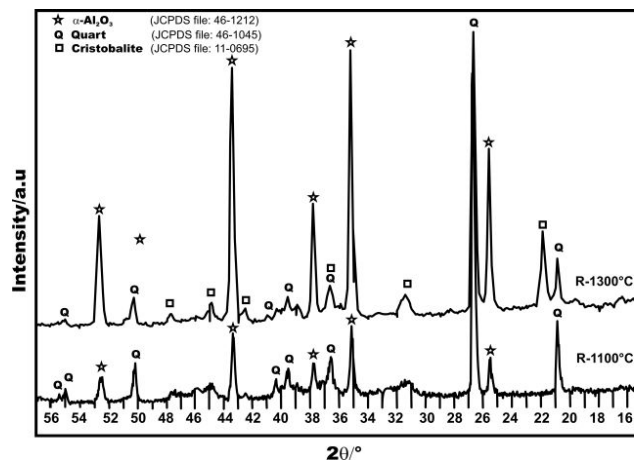

Fig.6 - XRD patterns of the sample R obtained by classical method and annealed at different temperatures / *Spectrele de difracție RX ale probei R obținută prin metoda clasică şi calcinată la diferite temperaturi.*

REFERENCES

1. S. Solacolu, F. Paul, Physical Chemistry of Silicate and Oxide Solids, Dacia Publishing House, Cluj-Napoca, 1984 (in Romanian).
2. I. Teoreanu, N. Ciocea, Tehnology of Ceramic and Refractory Products, vol II, Technical Publishing House, Bucharest, 1985 (in Romanian).
3. H. Scheider, J. Schreuer, and B. Hildmann, Structure and Properties of Mullite, A review, Journal of European Ceramic Society, 2008, **28**, 329.
4. H. Schneider and E. Eberhard, Thermal Expansion of Mullite, Journal of European Ceramic Society,1990, **73**, 2073;
5. H. Balmori-Ramirez, E. Rocha-Rangel, E. Refugio-Garcia, and R.C. Bradt, Dense Mullite from Attrition- Milled Kyanite and Aluminium Metal, Journal of European Ceramic Society, 2004, **87**, (1), 144.
6. L.B. Kong, Y.B. Gan, J. Ma, T.S. Zhang, F. Boey, and R.F. Zhang, Mullite Phase Formation and Reaction Sequences With the Presence of Pentoxides, Journal of Alloys and Compounds, 2003, **351**, 264.
7. J.E. Lee, J.W. Kim, Y.G. Jung, C.Y. Jo, and U. Paik, Effects of Precursor pH and Sintering Temperature on Synthesizing and Morphology of Sol-Gel Processed Mullite, Ceramics International, 2002, **28**, 935.
8. K. Wang, and M. D. Sacks, Mullite Formation by Endothermic Reaction of α-Alumina/Silica Microcomposite Particles, Journal of European Ceramic Society,1996, 79, (1), 12.
9. J. Leivo, M. Lindén, J.M. Rosenholm, M. Ritola, C.V. Teixeira, E. Levänen, and T. Mäntylä, Evolution of Aluminosilicate Structure and Mullite Crystallization from Homogeneous Nanoparticulate Sol-Gel Precursor With Organic additives, Journal of European Ceramic Society, 2008, **28**, 1749.
10. T. Yogo, and I. A. Aksay, Synthesis of Mullite Fibre from an Aaluminosiloxane Precursor, Journal of Materials Chemistry, 1994, **4**, (2), 353.
11. D.R. Treadwell, D.M. Dabbs, and I.A. Aksay, Mullite ($3Al_2O_3$-$2SiO_2$) Synthesis with Aluminosiloxanes, Chemistry of Materials,1996, **8**, 2056.
12. C. Carla, O. Bertran, and A. Bertran, Mullite Formation from Mixtures of Alumina and Silica Sols: Mechanism and pH Effect, Journal of the Brazilian Chemical Society, 2005, **16**, (2), 251.
13. L.S. Cividanes, T.M.B. Campos, C.A. Bertran, D.D. Brunelli, and G.P. Thim, Effect of Urea on the Mullite Crystallization, Journal of Non-Crystalline Solids, 2010, doi:10.1016/j.jnoncrysol.2010.05.076;
14. L.S. Cividanes, D.D. Brunelli, C.A. Bertran, T.M.B. Campos, and G.P. Thim, Ureea Effect on the Mechanism of Mullite Crystallization, Journal of Materials Science., 2011 **46**, 7384.
15. O. Burgos-Montes, R Moreno, M.T. Colomer, and J.C. Farinãs, Influence of Combustion Aids on Suspension Combustion Synthesis of Mullite Powders, Journal of European Ceramic Society, 2006, **26**, 3365.
16. O. Burgos-Montes, R. Moreno, M. T. Colomer, and J.C. Farinas, Syntesis of Mullite Powders Through a Suspension Combustion Process, Journal of European Ceramic Society, 2006, **89**, (2), 484.
17. O. Burgos-Montes, and R. Moreno, Colloidal Behaviour of Mullite Powders Produced By Combustion Synthesis, Journal of European Ceramic Society, 2007, **27**, 4751.
18. K.C. Patil, S.T. Aruna, S. and Ekambaram, Combustion Synthesis, Current Opinion in Solid State and Materials Science,1997, **2**, 158.
19. K.C. Patil, S.T. Aruna, and T. Mimani, Combustion Synthesis: an Update, Current Opinion in Solid State and Materials Science, 2002, **6**, 507.
20. R. Ianoş, I. Lazău, and C. Păcurariu, Fuel Mixture Approach for Solution Combustion Synthesis $Ca_3Al_2O_6$ Powders, Cement and Concrete Research 2009, **39**, 566.