International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:9, No:7, 2015

# Transformation of Aluminum Unstable Oxyhydroxides in Ultrafine α-$Al_2O_3$ in Presence of Various Seeds

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***Abstract*—**Ceramic obtained on the base of aluminum oxide has wide application range, because it has unique properties, for example, wear-resistance, dielectric characteristics, and exploitation ability at high temperatures and in corrosive atmosphere. Low temperature synthesis of α-$Al_2O_3$ is energo-economical process and it is topical for developing technologies of corundum ceramics fabrication.

In the present work possibilities of low temperature transformation of oxyhydroxides in α-$Al_2O_3$, during the presence of small amount of rare–earth elements compounds (also Th, Re), have been discussed. Aluminum unstable oxyhydroxides have been obtained by hydrolysis of aluminium isopropoxide, nitrates, sulphate, and chloride in alkaline environment at 80-90ºC temperatures. β-$Al(OH)_3$ has been received from aluminum powder by ultrasonic development. Drying of oxyhydroxide sol has been conducted with presence of various types seeds, which amount reaches 0,1-0,2% (mas). Neodymium, holmium, thorium, lanthanum, cerium, gadolinium, disprosium nitrates and rhenium carbonyls have been used as seeds and they have been added to the sol specimens in amount of 0.1-0.2% (mas) calculated on metals. Annealing of obtained gels is carried out at 70–1100ºC for 2 hrs. The same specimen transforms in α-$Al_2O_3$ at 1100ºC. At this temperature in case of presence of lanthanum and gadolinium transformation takes place by 70-85%. In case of presence of thorium stabilization of γ-and θ-phases takes place. It is established, that thorium causes inhibition of α-phase generation at 1100ºC, and at the time when in all other doped specimens α-phase is generated at lower temperatures (1000-1050ºC). Synthesis of various type compounds and simultaneous consolidation has developed in the furnace of OXY-GON. Composite materials containing oxide and non-oxide components close to theoretical data have been obtained in this furnace respectively. During the work the following devices have been used: X-ray diffractometer DRON-3M (Cu-Kα, Ni filter, 2º/min), High temperature vacuum furnace OXY-GON, electronic scanning microscopes Nikon ECLIPSE LV 150, NMM-800TRF, planetary mill Pulverisette 7 premium line, SHIMADZU Dynamic Ultra Micro Hardness Tester, DUH-211S, Analysette 12 Dyna sizer.

***Keywords*—**α-Alumina, combustion, consolidation, phase transformation, seeding.

## I. Introduction

At present the greatest attention is given to using of nanotechnologies, obtaining of α-$Al_2O_3$ nanopowders and nanostructural ceramic materials based on them. Many methods are used for obtaining ultrafine α-$Al_2O_3$, including sol-gel process, precipitation, chemical dissolution, plasma-chemical, electrochemical, microemulsion, hydrothermal, aerosol, corrosive polymer-precursor, high temperature oxidation and others. After transformation of aluminum hydrates phases different kinds of $Al_2O_3$ (α, χ, η, δ, κ, θ, γ, ρ) are obtained. At high temperatures α-$Al_2O_3$ is formed, that is obtained by gradually heating of intermediate phases of aluminum hydroxides or alumina ~1200°C [1]-[5]. Low temperature synthesis of α-$Al_2O_3$ is energy saving process and is topical for improving fabrication technology of corundum ceramics. At high temperature enlargement of nanosized particle (10-70 nm) takes place up to 200-1000 nm that is undesirable process and is the main disadvantage of existing fabrication technology of α-$Al_2O_3$. Therefore transformation at low temperature is one of the significant point, that implies preliminary inclusion of dopants in low temperature synthesis process (in condition of drying-heating and annealing, dissolution of precursors and hydrolyze), for obtaining ultrafine α-$Al_2O_3$ nanopowders [6]-[10]. At present several method of the direct obtaining of α-$Al_2O_3$ is known. At the lowest temperature (-550°C) diaspore transfers into thermodynamic stable form. It includes in bauxite composition and in Bayer process together with other aluminum compounds dissolves in $NH_4OH$ and finally it is excreted in form of bayerite. Its obtaining from aluminum compounds is very difficult and expensive process [10].

The goal of the work is, obtaining of aluminum isopropoxide, nitrate and aluminum powder from the local resources; establishing of low temperature transformation possibilities of aluminum unstable oxohydroxides into α-$Al_2O_3$ in the presence of rare-earth metals compounds (also other dopants) with small amount and developing technology of fabricating materials with various functional purposes from oxide and non-oxide compounds by using OXY-GON high temperature vacuum furnace.

## II. Experiment

Obtaining of α-$Al_2O_3$ by oxidation-reduction reaction: 3g (0,05 mol) urea and dopant are added to (0,02mol) $Al(NO_3)_3 \cdot 9H2O$. The mixture is stirred during 10 min, in a result thick viscous mass is received, which is poured in porcelain bowl. The bowl is placed in muffle furnace heated up to ~500oC-temperature, where it is combusted ~2 min. Temperature of mixture reaches 1500°C. Temperature is measured by IR-thermometer. In a result white bulk powder is obtained (Fig. 1).

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Aluminum isopropoxide is obtained by the following chemical reaction:

$$Al + 3(CH_3)_2CHOH \rightarrow Al(OCH(CH_3)_2)_3 + 1.5H_2$$

Metal aluminum granules, powder and plates are washed out with ethanol, then with 5% NaOH solution, then again with $C_2H_5OH$ and are dried at 120°C. Purified aluminum is placed in ball-mills for grinding during 2 hrs. 50g alumina is taken from the obtained mass and placed in flask. Then 500ml anhydrous isopropanol, with 2 g hydrargyrum (II) chloride is poured in the flask. Reaction mixture is boiled and 0,2 g iodine crystals are added. From the reaction mixture excess alcohol is removed and 260g $Al(OCH(CH_3)_2)_3$ is obtained. Secondary distillation of the obtained isopropoxide is conducted from 0.5l flask. 245 g aluminum isopropoxide is obtained, which is crystallized after cooling. It is established from X-ray –fluorescence analysis, that quantity of other metals impurity is lower than $10^{-2}$%.

Obtaining of α-$Al_2O_3$ powder: Sol of unstable aluminum oxohydroxide was obtained by hydrolysis of $Al(OC_3H_7)_3$. 30g aluminum isopropoxide is dissolved in 540ml water and is heated at 80-85°C in condition of constant stirring approximately 6-8 hrs. Then for peptization 1-2ml $HNO_3$ and dopants are added and continue stirring for 3hrs at 110°C. Water is removed from the obtained sol and xerogel is dried at ~120°C. Obtaining of ultrafine α-$Al_2O_3$ from xerogel was conducted by its annealing from the room temperature up to 1250°C in high temperature furnace by the following temperature regime: from 25°C up to 500°C with velocity of 3°C/min, from 500°C up to 1000°C with velocity of 5°C/min, and up to 1250°C temperature with velocity of 10°C/min. Annealing of aluminum and obtaining of α-$Al_2O_3$ was conducted with the analogous regimes.

Obtaining of corundum product by hot pressing method in OXY-GON furnace: powdery composites are preliminary heated on the air up to 1200˚C (2 hrs). Powders are placed in preliminarily annealed (1400˚C) graphite molds, which are covered inside with graflex plate. The plate is covered with thin layer of boron nitride. Graphite mold is placed in high temperatures vacuum furnace (OXY-GON) and powder is pressed under 500 kgf loading. The chamber is cooled by water, which temperature does not exceed 20˚C. After vacuuming the chamber it is heated according to the preliminarily established regimes up to 1500˚C and after this powders are pressed under maximal loadings 10 000 kgf. This pressure is maintained for 60–70 min. Maximum temperature of sintering is 1600˚C (1 hrs). Cooling of graphite molds is conducted in vacuum by 5˚C/min velocity. After cooling below 100˚C temperature pure argon is included in the chamber. Obtained corundum product is black, because thermal dissociation of $Al_2O_3$ and formation of defect crystalline lattice take place in vacuum. In purpose of whitening of the sample it is annealed on the air at 1500–1600˚C during 2 hrs.

## III. Results and Discussions

Easy method of obtaining α-$Al_2O_3$ is often used in laboratory practice that is based on the interaction between aluminum nitrates and organic compounds (Solution Combustion Synthesis) [11], [12]. In this case $NO^{3-}$ ions are oxidizers, and organic compounds, including amines and their products, oxyacids, alcohols, carbohydrates, urea and its products, oligomers and polymers are reducers. The cheapest compound is urea. Initiation temperature of reaction is 450-500°C. The reaction is exothermic and temperature of reaction mixture reaches 800-1500°C. Temperature of reaction mixture changes according to oxidizers/reducers ratio. Reaction speed is rather high 2-4cm/sec. Bulk density of obtained α-alumina powder reaches 30-70 mg/ml (Fig. 1). They are easily fragmented and nanosized particles are generated [13].

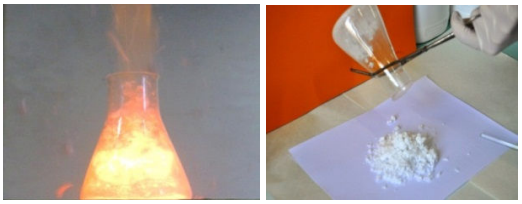

Fig. 1 Obtaining α-$Al_2O_3$ powder from $(NO_3)_3$-$NH_2CONH_2$ compound by oxidation-reduction reaction

Disadvantage of this method is small content of alumina in large amount of reaction mixture (-10%mas). We have studied possibilities of obtaining α-$Al_2O_3$ from $Al(NO_3)_3$-$NH_2CONH_2$–Al system. Inclusion of aluminum aimed at increasing alumina, because after $2Al(NO_3)_3 \cdot 9H_2O + 5NH_2CONH_2$ reaction oxidizers are allocated: nitrogen (IV) oxide and oxygen. Despite, the reaction temperature reaches a ~1500°C, aluminum powder (5-75 mkm) does not oxidizes. α-$Al_2O_3$ is obtained by annealing reaction product (Al+$Al_2O_3$ amorphous) at 800°C (2hrs). It is established, by X-ray –phase and chemical analysis, that metal aluminum does not oxidizes in such conditions, because particles surface is covered by alumina layer, formed in a result of reaction.

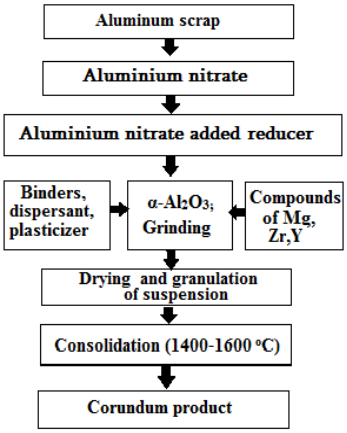


Fig. 2 Simplified scheme of obtaining corundum products from aluminum scrap

Based on α-$Al_2O_3$ powders obtained by oxidation-reduction reaction, pressing powdery composites α-$Al_2O_3$-MgO, α-$Al_2O_3$-$Y_2O_3$-MgO, α-$Al_2O_3$-$Y_2O_3$-$ZrO_2$ and others were synthesized. Dopants MgO, $Y_2O_3$, $ZrO_2$ were included in reaction mixture in different forms of nitrates. Optimal temperature regimes of pressing have been chosen for each composite.

It is established by structural-morphological studies that sizes of primary crystals of powders are within 50-300nm and they generate large sized easily breakable agglomerates (1-3 mkm).

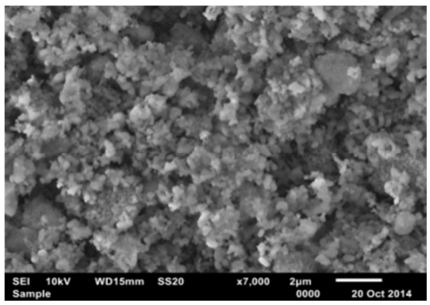


Fig. 3 Micro images of α-$Al_2O_3$-$Y_2O_3$-$ZrO_2$ powdery composites

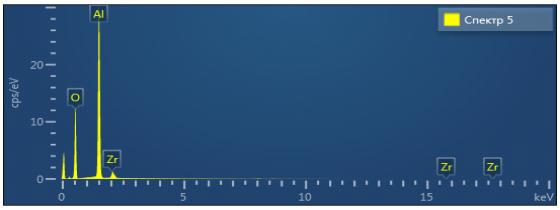


Fig. 4 Energy-dispersive micro-X-ray spectrum of α-$Al_2O_3$-$Y_2O_3$-$ZrO_2$ powdery composite

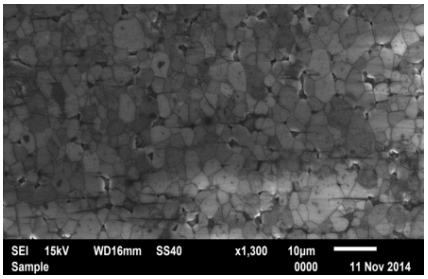


Fig. 5 Micrographs of ceramic composites obtained at 1600°C ($Al_2O_3$-$ZrO_2$-MgO)

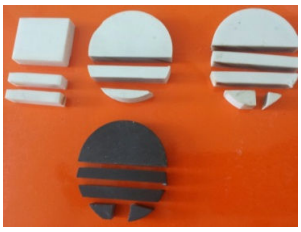

Fig. 6 Corundum ceramics materials with different compositions and experimental specimens fabricated from them

Aluminum isopropoxide was synthesized from metal aluminum scrap, and after its hydrolysis unstable aluminum oxohydroxides and oxides are obtained. Ultrafine α-$Al_2O_3$ is obtained by sol-gel method according to the following scheme (Fig. 7).

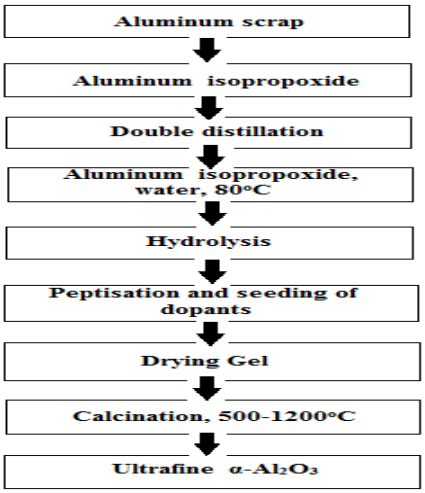


Fig. 7 General scheme of obtaining α-$Al_2O_3$ by sol-gel method

In a result of hydrolyze aluminum isopropoxide, mixture of aluminum oxohydroxides ($Al_2O_3 \cdot xH_2O$) are generated and its peptization is conducted by adding nitric acid. Nitrates of cerium, holmium, thorium, gadolinium, dysprosium, lanthanum and neodymium are added to sol (0.1-0.2% mas.) calculated on metal. Drying of dopant-added gel is conducted at 120°C. It is established; that gel does not contain non-hydrolyzed Al-O-C bonds. Thermal treatment of obtained xerogel was conducted at 120°C (a), 500°C (b) and at 800 °C (c) for 2 hrs (Fig. 8).

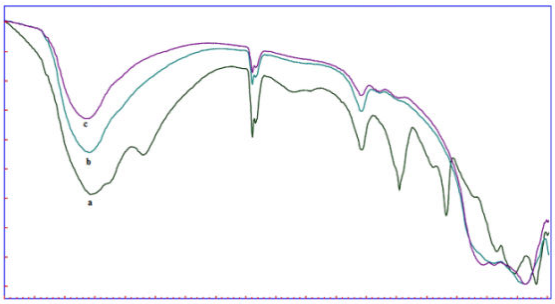


Fig. 8 IR spectra of gels obtained aluminum isopropoxide annealed at different temperatures (a-120°C, b-500°C, c-800°C)

It is shown from IF spectra, that in all three samples in area of 3429-1635 $cm^{-1}$ absorption sols of O-H are revealed, and in area of 476-758 $cm^{-1}$ -Al-O coordination bonds are observed.

It is established from DSC, that xerogel dried at 120°C, absorbs water vapor on the air, and then desorbs it by heating at 60-150°C. At 300-500°C temperatures intensive condensation of hydroxide group and desorption of water take place (Fig. 9). All samples are characterized with dehydration

of aluminum oxohydroxides and generation of unstable alumina. They mainly consist of γ and θ phases.

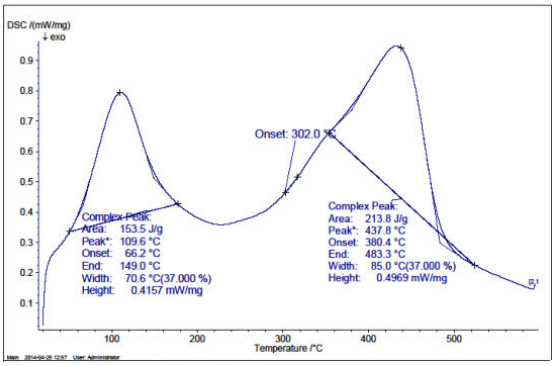


Fig. 9 Differential scanning calorimetry curve (DSC, 20-600°C) of aluminum oxohydroxide obtained by sol-gel method

Influence of lanthanum, cerium, neodymium, gadolinium, dysprosium, holmium and thorium ions on the transformation of unstable aluminum compounds into in alpha-alumina were studied. It is established from X-ray-phase analysis, that in a presence of holmium, formation of $\alpha$-$Al_2O_3$ begins at temperature lower than 1000°C and at 1100°C temperature it transfers in $\alpha$-$Al_2O_3$ (Fig. 10).

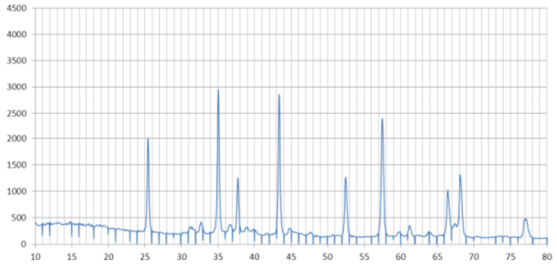

Fig. 10 Transformation of metastable aluminum oxo-hydroxide in alpha-phase by adding holmium nitrate (1100°C)

In a presence of lanthanum, dysprosium, cerium and gadolinium transformation at 1100°C takes place by 70-85%. And in a presence of thorium, stabilization of gamma and theta-alumina phases takes place (Fig. 11), while in samples doped with all other metals the same phase generates at lower temperatures (1000-1050°C).

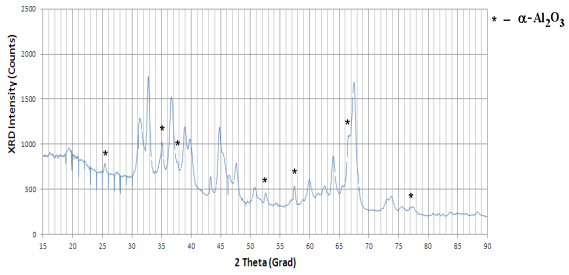


Fig. 11 Transformation of metastable aluminum oxohydroxide in alpha-phase by adding thormium nitrate (1100°C)

Selective obtaining of metastable aluminum compounds is difficult task. One method of obtaining aluminum hydrate-bayerite is ultrasonic development of aluminum powder at 70-90°C in ammonium hydroxide solution. We studied influence of adding neodymium nitrate on generation and transformation processes of unstable oxo-hydroxides. It is established, that by adding neodymium compound in alkaline environment bayerite is obtained from metal aluminum and by adding rhenium carbonyl-boehmite is received (Fig. 12). After their thermal treatment (70-1100°C) transformation of unstable phases into alpha-alumina takes place: neodymium and rhenium containing powders completely transfer into $\alpha$-$Al_2O_3$, while from powder without dopant, mixture of α and γ phases is obtained (Fig. 13). Thus, adding of promotes formation of alpha-alumina.

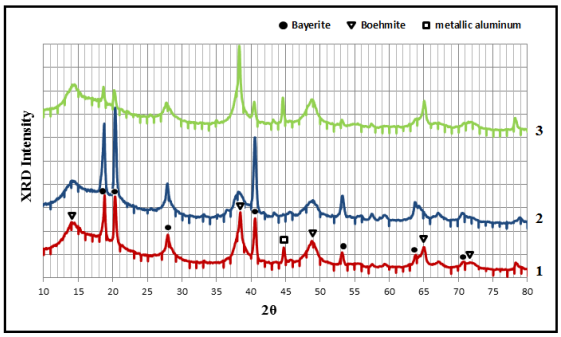


Fig. 12 X-ray of unstable oxohydroxides obtained from metal aluminum in ammonium hydroxide solution at 85°C: 1. Without dopant, 2. dopant–neodymium nitrate, 3. dopant–rhenium carbonyl

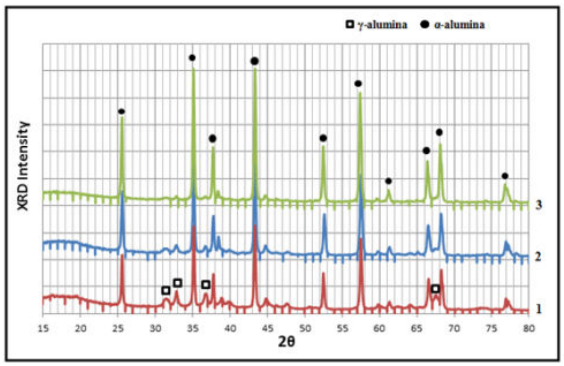


Fig. 13 X-ray of unstable oxohydroxides obtained from metal aluminum in ammonium hydroxide solution at 85°C: (powders are annealed at 1100°C): 1. Without dopant, 2. dopant – neodymium nitrate, 3. dopant – rhenium carbonyl

## IV. Conclusions

In the present work obtaining of aluminum isopropoxide, nitrate and aluminum powder from scrap aluminum and their further transformation in $\alpha$-$Al_2O_3$ have been studied. It is shown possibilities of low temperature transformation of aluminum oxyhydroxides in $\alpha$-$Al_2O_3$ during the presence of small amount of rare–earth elements compounds (also other dopants). Low temperature synthesis of $\alpha$-$Al_2O_3$ is energy

saving process and it is quit actual for perfection of technology of corundum ceramics production.

Technology for obtaining corundum ceramics was developed which is based on simultaneous pressing and consolidation methods of powdery composites in high temperature vacuum furnace OXY-GON. Besides, implementation of solid-phase reactions is possible in the furnace. Corundum ceramic products were obtained by sintering at 1600$^{o}$C (1 hr), which is characterized by high strength, microhardness and fracture resistance, absence of open porosity, corrosion resistance. Their density achieves 99,5-99,6% of the theoretical.

## REFERENCES

[1] H. Hou, Y. Xie, Q. Yang, Q. Guo, C. Tan. Perapration and characterization of γ-AlOOH nanotubes and nanorods. Nanotechnol., 2005, 16(6), 714-721.

[2] Y. Xia, Y.Yang, P. Sun, Y. Wu, B. Mayers, A. Gates, Y.Yin, F. Kim, H. Yan, Onedimensional nanostructures: Synthesis, characterization and applications. Adv. Mater., 2003, 15(5), 353-357.

[3] G. L. Teoh, K. Y. Liew, W. A. K. Mahmood. Synthesis and characterization of sol–gel alumina nanofibers. J. Sol-Gel Sci. Technol., 2007, 44(3), 177-180.

[4] M. G. Ma, J. F. Zhu. A Facile solvothermal route to synthesis of γ-alumina with bundle-like and flower-like morphologies. Mater. Let, 2009, 63, 881-885.

[5] Q. Yang, Y. Deng, W. Hu. Synthesis of alumina nanofibers by a mercury-mediated method. Ceram. Intern, 2009, 35(1), 531-537.

[6] S. Cava, S.M. Tebcherani, I.A. Souza, S.A. Pianaro, C.A. Paskocimas, E. Longo, J.A. Varela. Structural characterization of phase transition of Al2O3 nanopowders obtained by polymeric precursor method. Materials Chemistry and Physics, 2007, 103, 394–399.

[7] A. Odaka, T. Yamaguchi, A. T. Fujita, B. S. Taruta, K. Kitajima. Densification of rare-earth (Lu, Gd, Nd)-doped alumina nanopowders obtained by a sol−gel route under seeding. Powder Technology, 2009, 193(1), 26-31.

[8] Yiguang Wang, C. Suryanarayana, Linan An. Phase Transformation in nanometer-sized χ-alumina by mechanical milling. J. Am. Cer. Soc., 2005, 88(3), 780-783.

[9] Y. Yoshizawa, K. Hirao, S. Kanzaki. Fabrication of low cost fine-grained alumina powders by seeding for high performance sintered bodies. Journal of the European Ceramic Society, 2013, 33(13–14), 2365-2830.

[10] R. L. Smith, G. S. Rohrer, A. J. Perrotta. The Influence of diaspore seeding and chloride concentration on the transformation of "Diasporic" precursors to corundum. J. Am. Cer. Soc., 2001, 84(8), 1896-1902.

[11] A. Sharma, O.P. Modi, G.K. Gupta. Combustion synthesis of nanocrystalline $Al_2O_3$ powder using aluminium nitrate and urea as reactants-influence of reactant composition. Advances in Applied Science Research, 2012, 3 (6), 3819-3824.

[12] T.V. Kuchukhidxe, V.G. Gabunia, Z.V. Phachulia, N.T. Jalagonia, R.V. Chedia. Some Issues of Ultrafine Alfa-alumina Powders Fabricated by Low Temperature Synthesis. 2014, 8, 303-312, ISSN 1314-7269, http://www.scientific-publications.net.

[13] T.V. Kuchukhidze, N. T. Jalagonia, V. G. Gabunia, T. N. Archuadze, Q. G. Sarajishvili, R.V.Chedia. Influence of Some Metal Ions on Low Temperature Transformation of Alumina Metastable Oxides in α−Al2O3. 3th International Conference « Nanotechnologies» NANO-2014, 20-24 0ctomber, 2014, Tbilisi, Georgia.