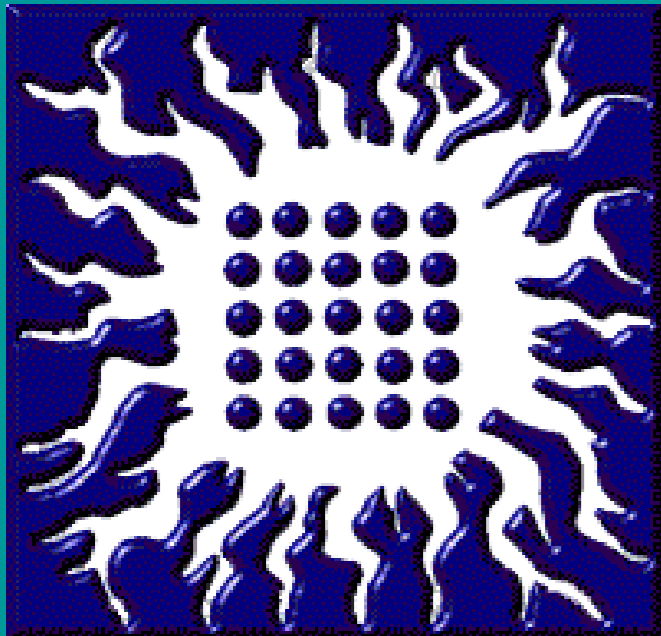


Combustion synthesis of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ oxyapatite

S. Zec¹, J. Dukić¹, S. Bošković¹, B. Matović¹, R. Petrović²

¹Institute of Nuclear Sciences Vinča, Materials Science Laboratory, 11001Belgrade, POB 522, Serbia

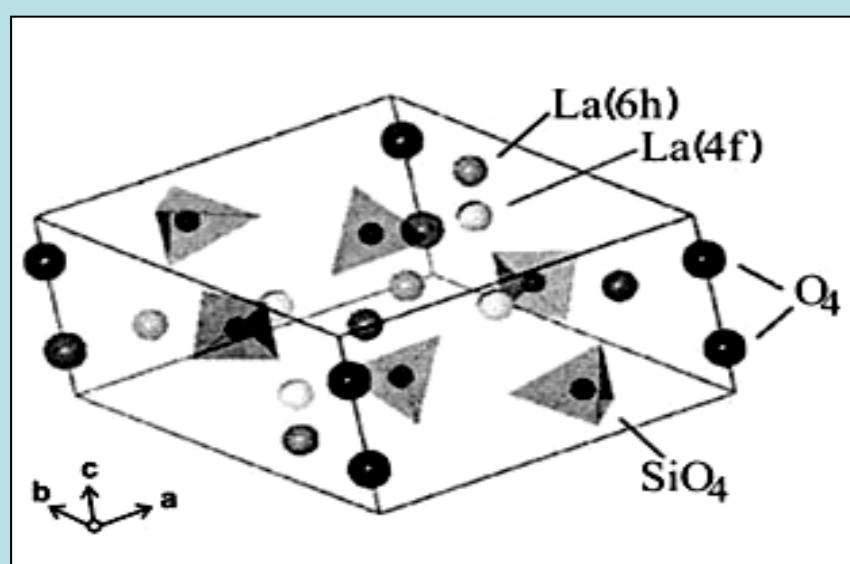
²Faculty of Technology and Metallurgy, 11000Belgrade, Karnegijeva 4, Serbia



$\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ has been synthesized by a new method that represents the combination of sol-gel and combustion procedures using glycine as the fuel. Synthesis were performed using ethanol-water solutions of oxides precursors, lanthanum nitrate and tetraethyl orthosilicate. The optimum synthesis parameters have been established by varying molar ratio of tetraethyl orthosilicate to water and glycine to NO_3^- ions. The phase identification and the structural characterization were performed by X-ray powder diffraction. The pure nanocrystalline $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ with the crystallite size of 80 nm was directly synthesized by combustion process of homogeneous gel that was generated in solution with the following molar ratios: glycine: $\text{NO}_3^- = 0.56$ and TEOS: water = 1:20. Well-crystallized $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ structure was obtained at 1200°C. The lattice parameters $a = 9.7156(9)$ and $c = 7.1810(8)$ Å confirmed the composition of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$.

Introduction

Lanthanum silicates with apatite-type crystal structure, $\text{La}_{10-x}(\text{SiO}_4)_6\text{O}_{2+2x}$ became very attractive as new solid ionic conductors because they showed quite high oxide ionic conductivity at medium temperatures. The high ionic conductivity of lanthanum silicates is closely related to the apatite structure in which some oxide ions are placed at the hexagonal channel sites along c-axis enabling oxide ion migration through the conduction channel. The conductivity of apatite-type compounds is highly anisotropic and dominant in the c-axis direction.



Crystal structure of La-oxyapatite

A new method we developed to synthesize La-oxyapatite represents the combination of sol-gel and combustion process. Combustion reaction involves a highly exothermic redox reaction between metal nitrates as an oxidant and an organic fuel to produce fine metal oxide powders in a short time. The autoignition starts only above minimum values of fuel to oxidant ratio depending on the nature of the fuel. In this work glycine is used as the fuel due to its low cost, high reduction capacity related to chemical composition and its capability to act as complexant and gelation agent preventing metal ions precipitation. The fuel to oxidant ratio is an important parameter of the combustion synthesis because it determines the enthalpy and the adiabatic flame temperature of the combustion reaction as well as the amount of evolved gaseous products, influencing the physical properties of the as-synthesized powders. The enthalpy (ΔH°) and the adiabatic flame temperature (T_{ad}) of the combustion reaction can be calculated according to the relations:

$$\Delta H^\circ = \sum (n\Delta H_f^\circ)_{\text{products}} - \sum (n\Delta H_f^\circ)_{\text{reactants}}$$

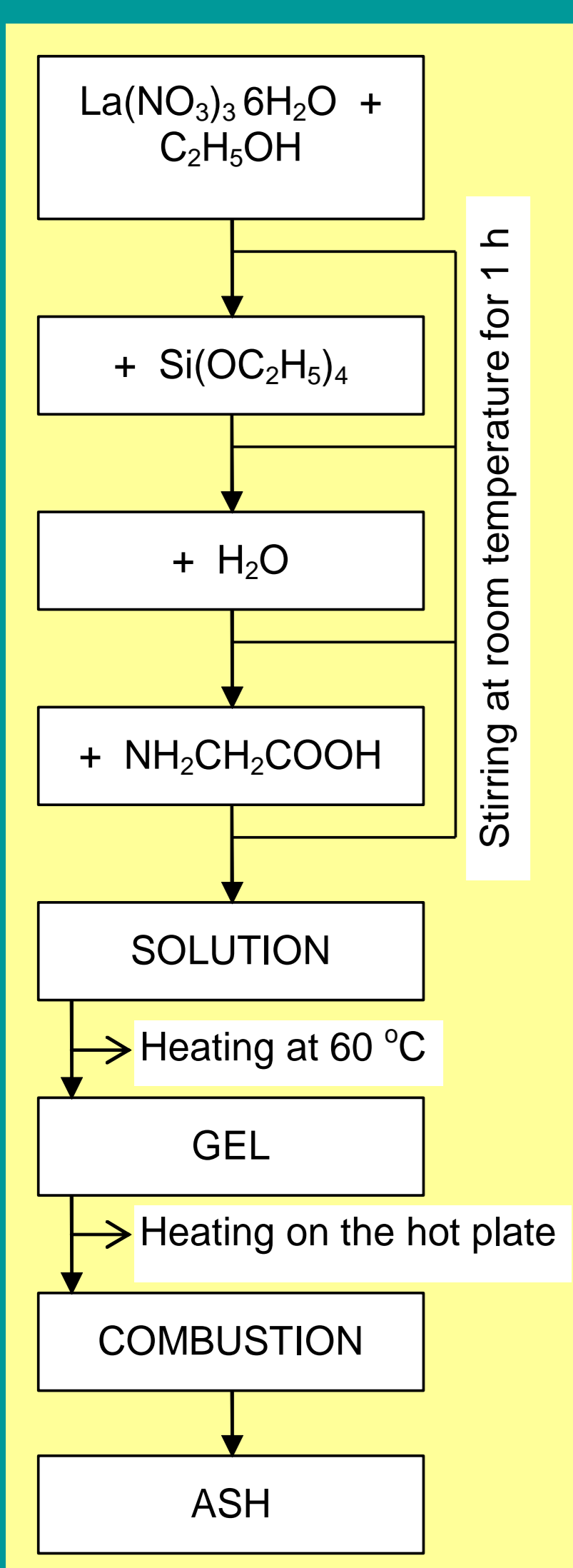
and

$$Q = -\Delta H^\circ = \int_{298}^{T_{ad}} \sum (nC_p)_{\text{products}} dT$$

In which n represents the number of moles, ΔH_f° standard molar enthalpy, Q is the absorbed heat and C_p is the heat capacity of the products at constant pressure.

Sol-gel process provides silica through hydrolysis of metal alkoxide among which TEOS is usually used. The hydrolysis of TEOS is followed by condensation reactions in which silanol groups (-Si-OH) are participating which results in siloxane bonds (Si-O-Si) formation and separation of water or ethanol as the side products. It should be outlined that molar ratio of TEOS, water and ethanol influences both the rate of hydrolysis and homogeneity of the gel.

Experimental



Flowchart of sol-gel combustion process

Reagents:

- Lanthanum nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (10.74 g)
- Tetraethyl orthosilicate (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$ (molar ratio La:Si = 4.67:3)
- Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$
- ethanol, $\text{C}_2\text{H}_5\text{OH}$
- distilled water, H_2O

Ash calcined at 600 °C for 2 h was pressed uniaxially into pellets and heated at 1200 °C for 5 h in a tubular furnace.

X-ray diffraction (XRD) analyses

- CuK_α radiation ($\lambda = 1.5406$ Å)
- Phases identification (JCPDS)
- Lattice parameters (program WINCELL)
- Crystallite size: $D = \frac{0.89 \cdot \lambda}{\beta \cdot \cos \theta}$
- $\beta = (B^2 - b^2)^{1/2}$
- B - full width at half maximum of peak
- b - correction of instrument broadening
- θ - angle of the diffraction peak
- λ - wavelength of radiation

Results

Three synthesis experiments designated as S1, S2 and S3 were performed by varying the molar ratio of TEOS to added water (TH) and glycine to NO_3^- (GN). The relevant parameters related S1, S2 and S3 syntheses are summarized in Table 1.

Table 1. Relevant syntheses parameters

Synthesis	GN ^a	TH ^b	Ethanol (ml)	ΔH° (kcal)	T_{ad} (°C)	Evolved gases (mol)
S1	0.56	1:20	20	-172.7	1017	15.8
S2	0.33	1:20	20	-35.2	284	14.0
S3	0.33	1:5	20	-35.2	284	14.0

^aGN - molar ratio glycine to NO_3^- ; ^bTH - molar ratio TEOS to H_2O ; ΔH° : enthalpy of combustion reaction; T_{ad} : adiabatic flame temperature

Table 2. Relevant thermodynamic data

Compound ^a	ΔH_f° (kcalmol ⁻¹)	C_p (calmol ⁻¹ K ⁻¹)
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (c)	-732.23	-
$\text{NH}_2\text{CH}_2\text{COOH}$ (c)	-126.31	-
La_2O_3 (c)	-428.70	26.0
CO_2 (g)	-94.05	10.34+0.00274 ^b
H_2O (g)	-57.79	7.20+0.00360 ^b
N_2 (g)	0	6.50+0.00100 ^b
O_2 (g)	0	5.92+0.00367 ^b

^a(c) - crystalline, (g) - gas, ^bT - absolute temperature

$\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ was formed from La_2O_3 and SiO_2 according to the chemical equation:



Combustion reaction with GN = 0.56 corresponds the stoichiometric glycine-nitrate redox reaction and can be expressed as:



The fuel-deficient combustion reaction in which GN = 0.33 can be represented with equation:



Enthalpy (ΔH°) and adiabatic flame temperature (T_{ad}) of combustion reactions were calculated using relevant thermodynamic data listed in Table 2.

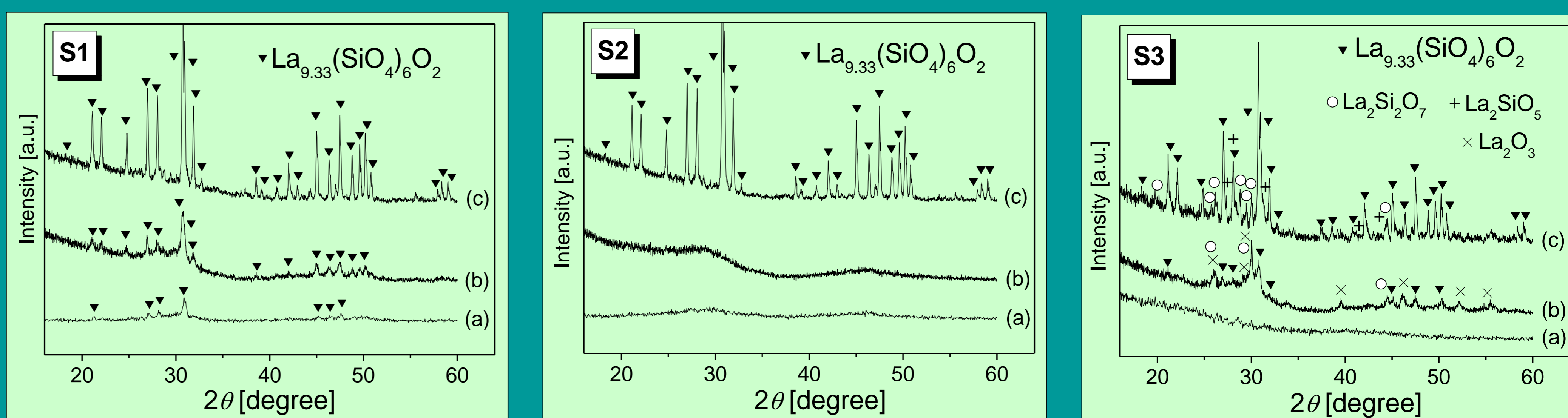


Fig. 1. XRD patterns of products from S1, S2 and S3 syntheses: (a) as-combusted ash, (b) ash calcined at 600°C for 2h and (c) ash heated at 1200°C for 5h

➤ The self-propagating combustion reactions were observed in all three synthesis procedures after autoignition of dried gels initiated by heating on the hot plate.

➤ The high values (Table 1) of reaction heat, adiabatic flame temperature and evolved gases of exothermic reaction (R2) in S1 synthesis enable direct synthesis of crystalline $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ oxyapatite from homogeneous gel (TH = 1:20) during combustion (Fig. 1- S1a). The produced crystalline $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ has the nano-size crystallites of 80 nm. The crystallite size of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ was not significantly changed when the ash was calcined at 600 °C (Fig. 1- S1b), while the well-crystallized pure $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ oxyapatite with the crystallite size of 300 nm was obtained at 1200 °C (Fig. 1- S1c). The lattice parameters of its hexagonal unit cell, $a = 9.7156(9)$ and $c = 7.1810(8)$ Å, confirmed the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ chemical composition, which has been expected according to the molar ratio of lanthanum to silicon in starting reagents.

➤ Crystallized phases were not observed in as-combusted and calcined ash at 600 °C from S2 synthesis (Fig. 1- S2a and -S2b) due to small fuel content in reaction R3. However, the rise of temperature to 1200 °C allowed oxides obtained from corresponding homogeneous gel by combustion to react forming a single phase of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ (Fig. 2 - S2c). The values of its crystallite size of 280 nm and the lattice parameters, $a = 9.718(1)$ and $c = 7.177(1)$ Å are very close to those obtained for this phase in the case of S1 synthesis.

➤ S3 synthesis, performed with fuel-deficient content and TH = 1:5, gave from inhomogeneous gel non-crystalline ash after combustion (Fig. 1- S3a), while calcined and heated products (Fig. 1- S3b and -S3c) contain beside oxyapatite phase also La_2O_3 , $\text{La}_2\text{Si}_2\text{O}_7$ and La_2SiO_5 . The low values of the lattice parameters of oxyapatite phase, $a = 9.688(9)$ and $c = 7.166(2)$ Å, suggest the chemical composition different from $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$, probably related to the defect apatite structure with the lanthanum content less than 9.33.

Conclusion

Synthesis of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ with the apatite-type structure has been studied since it shows high oxide-ion conductivity at medium temperatures and can be used as an electrolyte for solid oxide fuel cells. $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ had been synthesized in our work by a new method which represents combination of combustion and sol-gel procedures. Syntheses were performed from ethanol-water solutions using lanthanum nitrate and tetraethyl orthosilicate as precursors to oxides. Glycine as a fuel was for the first time applied in the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ synthesis by combustion procedure. The molar ratio of TEOS to water as well as the molar ratio of glycine to NO_3^- was varied with the aim to establish optimum synthesis parameters. The homogenous gel obtained from solution with the molar ratio TEOS: H_2O : $\text{C}_2\text{H}_5\text{OH}$ = 1:20:22 enabled the single phase synthesis of pure $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$. The combustion process under GN = 0.56 produced directly crystalline $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ powder with the nano-size crystallites of 80 nm, while the non-crystalline phase was formed during combustion with lower glycine content. The well-crystallized $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ structure with the crystallite size of 300 nm was obtained at 1200°C, significantly lower temperature than known for the solid-state reaction (1400°C). The lattice parameters $a = 9.7156(9)$ and $c = 7.1810(8)$ Å confirmed precisely the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ composition.

Acknowledgment: The authors gratefully acknowledge support of the Project No. 142003 by the Ministry of Science of the Republic of Serbia.