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Characterization of $Mg_{1-x}Ni_xAl_2O_4$ solid solutions prepared by combustion synthesis

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Abstract

$Mg_{1-x}Ni_xAl_2O_4$ ($x = 0$, 0.25, 0.5, 0.75 and 1) solid solutions have been prepared by combustion synthesis. After annealing the combustion synthesized powders at 1000 °C for 3 h single-phase $Mg_{1-x}Ni_xAl_2O_4$ was obtained over the entire range of compositions. The lattice parameter of $Mg_{1-x}Ni_xAl_2O_4$ gradually increased from 8.049 Å ($NiAl_2O_4$) to 8.085 Å ($MgAl_2O_4$), which certified the formation of the spinel solid solutions. All samples prepared by combustion synthesis had blue color shades, denoting the inclusion of Ni^{2+} in the spinel structure in octahedral and tetrahedral configuration. The crystallite size of $Mg_{1-x}Ni_xAl_2O_4$ was in the range of 35–39 nm and the specific surface area varied between 5.8 and 7.0 m^2/g.

Keywords: Powders-chemical preparation; Spectroscopy; Color; Spinels; Combustion synthesis

1. Introduction

The close similarity between the ionic radii of Mg^{2+} and Ni^{2+} in fourfold (Mg^{2+} – 0.57 Å, Ni^{2+} – 0.55 Å) and sixfold coordination (Mg^{2+} – 0.72 Å, Ni^{2+} – 0.69 Å) as well as the similar crystalline structure of the corresponding metal aluminates facilitates the formation of spinel solid solutions, $Mg_{1-x}Ni_xA1_2O_4$.[1]

In terms of crystalline structure, magnesium aluminate is a normal spinel, $Mg^{[4]}Al_2{}^{[6]}O_4$, in which Mg^{2+} ions fill the tetrahedral sites and Al^{3+} ions occupy the octahedral positions in the cubic closed packing of O^{2-} anions. On the other hand, the cation arrangement in nickel aluminate is typical for a partially inverse spinel, $(Ni_{1-z}Al_z)^{[4]}[Ni_zAl_{2-z}]^{[6]}O_4$, in which Ni^{2+} and Al^{3+} ions are randomly located in both tetrahedral and octahedral positions, respectively. At ambient temperature and pressure the inversion parameter z of $NiAl_2O_4$ is around 0.8 (z stands for the site occupancy factor of Al^{3+} on tetrahedral sites) and it decreases as the temperature increases.[2,3]

Despite the well known structure and applications of $MgAl_2O_4$ and $NiAl_2O_4$, little attention has been paid to the investigation of $MgAl_2O_4$–$NiAl_2O_4$ solid solutions in terms of synthesis and characterization. Several authors[4,5] have investigated the distribution of Ni^{2+} ions among octahedral and tetrahedral sites in $NiAl_2O_4$–$MgAl_2O_4$ spinel solid solutions. Recently, Huang et al.[6] studied the effect of Ni^{2+} substitution for Mg^{2+} on the $Mg_{1-x}Ni_xAl_2O_4$ structure and microwave dielectric properties of $Mg_{1-x}Ni_xAl_2O_4$ solid solutions. $Mg_{1-x}Ni_xAl_2O_4/Al_2O_3$-supported rhodium catalysts, in which Mg^{2+} was partly replaced by Ni^{2+} ions, showed excellent performances in the ethanol steam reforming at atmospheric pressure.[7] Most of the $NiAl_2O_4$–$MgAl_2O_4$ solid solutions were prepared by solid state method,[6,7] which requires elevated temperature and long soaking time. For instance, the formation of $Mg_{1-x}Ni_xAl_2O_4$ solid solutions starting from the corresponding metal oxides demands a heat treatment of at least 2 h at 1200 °C.[6]

The present paper reports an innovative study concerning the preparation of $Mg_{1-x}Ni_xAl_2O_4$ using a chemical synthesis method, known as solution combustion synthesis.[8–10] Properties of the obtained $MgAl_2O_4$–$NiAl_2O_4$ solid solutions were characterized.

2. Experimental

2.1. Synthesis of $Mg_{1-x}Ni_xAl_2O_4$ solid solutions

$Mg_{1-x}Ni_xAl_2O_4$ ($x = 0$, 0.25, 0.5, 0.75 and 1) powders were prepared by using the solution combustion technique (samples

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Table 1
Molar composition of the samples prepared by solution combustion synthesis (samples 6–10).

Sample	$Mg(NO_3)_2 \cdot 6H_2O$, Merck	$Ni(NO_3)_2 \cdot 6H_2O$, Merck	$Al(NO_3)_3 \cdot 9H_2O$, Merck	$C_3H_7NO_2$, Merck	$C_2H_5NO_2$, Fluka	CH_4N_2O, Merck
6 ($x = 0$)	1	–	2	2/3	–	5
7 ($x = 0.25$)	3/4	1/4	2	1/2	5/18	5
8 ($x = 0.5$)	1/2	1/2	2	1/3	5/9	5
9 ($x = 0.75$)	1/4	3/4	2	1/6	5/6	5
10 ($x = 1$)	–	1	2	–	10/9	5

6–10). The starting raw materials and the molar ratio of the investigated compositions are presented in Table 1. Recipes were designed in order to obtain 0.07 mol of $Mg_{1-x}Ni_xAl_2O_4$. The general procedure followed in the case of combustion synthesis (samples 6–10) consists in the preparation of aqueous solutions (Fig. 1) containing the starting materials mixed under the right proportion (Table 1). Stoichiometric metal nitrate/fuel molar ratios were used in all samples and it was assumed that combustion reactions by-products are $CO_{2(g)}$, $H_2O_{(g)}$ and $N_{2(g)}$. The starting raw materials were dissolved in 30.0 mL of warm distilled water (Fig. 1). The resulting clear solutions were rapidly heated to 300 °C in a heating mantle. After most of the water had evaporated, an exothermic self-sustaining combustion reaction occurred, which lasted for about 60 s. During the combustion reaction, the raw material mixture reached incandescence, and a fluffy powder was obtained. The reaction product was easily crumbled using a pestle and a mortar and then annealed at 1000 °C for 3 h (Fig. 1). The resulted powders were characterized in terms of phase composition, specific surface area and color behavior.

2.2. Characterization methods

Thermal behavior of the samples was studied over the temperature range of 25–900 °C using a Netzsch STA 449 C instrument equipped with platinum crucibles. TG and DTA curves were recorded at a heating rate of 10 °C/min under an air flow rate of 20 mL/min. The phase composition of the powders was investigated by X-ray diffraction (XRD), using a Bruker D8 Advance System (monochromatic Cu Kα radiation) operating at 40 kV and 40 mA. The average crystallite size, D, was calculated from the X-ray peak broadening using Scherrer's equation. The lattice parameter, a, was determined based on the available peak position of the $h\,k\,l$ planes. The specific surface area of the powders, S, was measured by BET (Brunauer, Emmett, Teller) nitrogen gas adsorption technique using a Micromeritics ASAP 2020 instrument. Diffuse reflectance spectroscopy (DRS) was performed at room temperature, in the range of 360–750 nm, using a Cary 300 Bio Varian UV–VIS spectrophotometer under D_{65} illuminant and 10° standard observer angle. CIEL*a*b* chromatic coordinates were also determined. In order to evaluate the behavior of the pigments in coloring ceramic glazes, 6 wt.% $Mg_{1-x}Ni_xAl_2O_4$ was added to a transparent glaze and then fired at 1160 °C for 30 min.

3. Results and discussion

Although in the case of samples 6–10, combustion reactions were very vigorous and flames appeared during the process, the color of samples with different proportions of Ni^{2+} is not

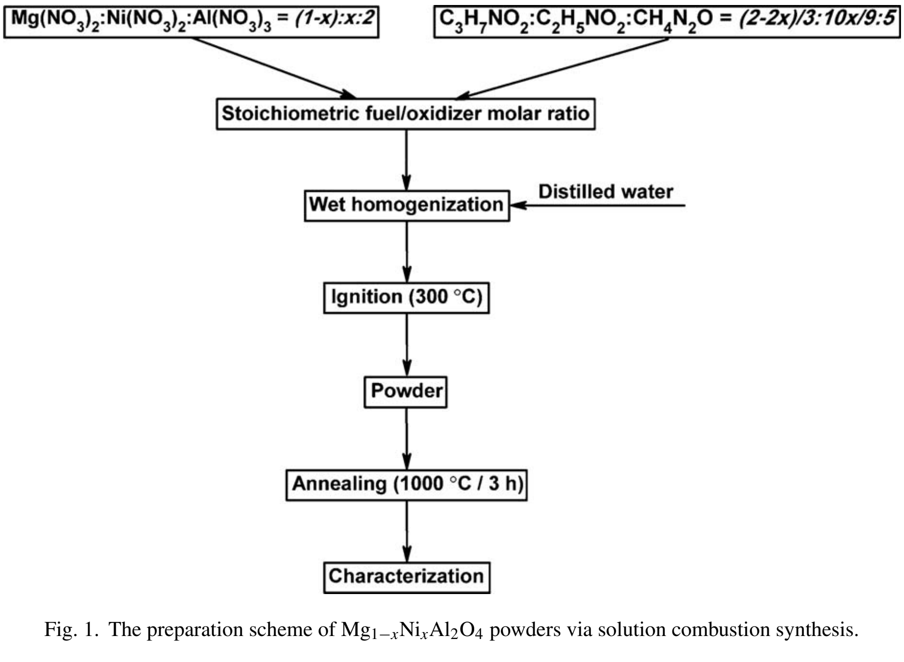

Fig. 1. The preparation scheme of $Mg_{1-x}Ni_xAl_2O_4$ powders via solution combustion synthesis.

Fig. 2. Images of the samples prepared by solution combustion synthesis.

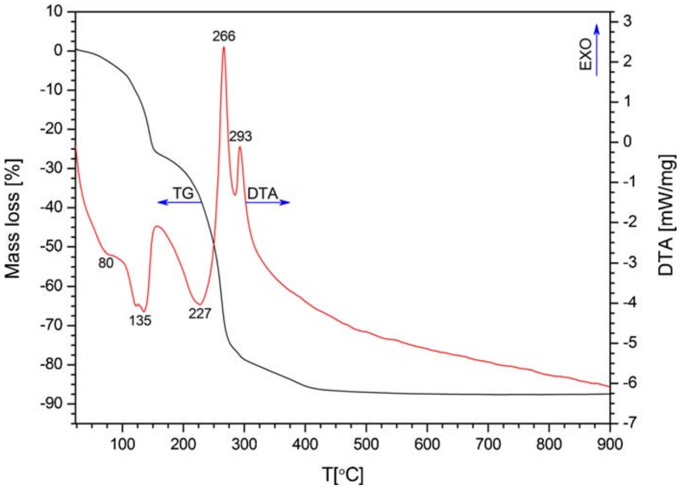

Fig. 3. TG–DTA curves of the precursor mixture 8.

homogeneous (Fig. 2). The lack of color uniformity suggests a large temperature gradient in various parts of the sample during the combustion process, which alters the quality of the final product. On the other hand, the presence of blue color in the area where combustion temperature was high enough indicates that solid solution formation has been achieved (Fig. 2).

Thermal analysis of precursor mixture 8 (Fig. 3) shows that up to 150 °C sample losses about 26% of its original mass mainly due to water removal (80 °C) and partial decomposition of urea and aluminum nitrate (135 °C). As the temperature increases, glycine and alanine start to decompose (227 °C) triggering the ignition of the combustion reaction.[1] The occurrence of combustion reaction (1) is marked on the TG curve as a rapid and major mass loss, which is accompanied by a sharp split exothermic process (266–293 °C). Above 400 °C the mass of sample 8 ($Mg_{0.5}Ni_{0.5}Al_2O_4$) remains constant, whist the DTA curve shows no other effect (Fig. 3).

$$\begin{aligned}&(1-x)Mg(NO_3)_2 + xNi(NO_3)_2 + 2Al(NO_3)_3\\&\quad + 2(1-x)/3C_3H_7NO_2 + 10x/9C_2H_5NO_2\\&\quad + 5CH_4N_2O \rightarrow Mg_{1-x}Ni_xAl_2O_4 + (63+2x)/9CO_2\\&\quad + (111+4x)/9H_2O + 2(42+x)/9N_2 \qquad (1)\end{aligned}$$

After annealing for 3 h at 1000 °C, $Mg_{1-x}Ni_xAl_2O_4$ samples prepared by solution combustion synthesis, exhibit different blue color shades (Fig. 4). The blue color intensifies from sample 7 to sample 10, as the substitution degree of Mg^{2+} by Ni^{2+} increases. XRD analysis revealed that $Mg_{1-x}Ni_xAl_2O_4$ solid solution is the only crystalline phase contained in samples 6–10 (Fig. 5). No traces of free metal oxides could be identified on the diffraction patterns of samples 6–10.

The phase composition of samples 6–10 corroborated with their blue color indicates that the formation of spinel solid solutions has reached completion. A closer analysis of the XRD patterns of samples 6–10 shows a slight shift of the peaks position to higher 2θ values (Fig. 5 – detail). This shift is directly proportional to the substitution degree of Mg^{2+} by Ni^{2+} and it increases linearly between the two end terms of the solid solution: $MgAl_2O_4$ ($x=0$) and $NiAl_2O_4$ ($x=1$). The lattice parameter, a, of the 5 compositions (samples 6–10) represents additional evidence, which demonstrates the formation of spinel solid solutions (Table 2).

An excellent agreement can be found between the calculated values of the lattice parameter (Table 2) of samples 6 ($MgAl_2O_4$) and 10 ($NiAl_2O_4$) on one hand, and the standard values of the lattice parameter given in PDF files 21-1152 ($MgAl_2O_4$) and 10-0339 ($NiAl_2O_4$) on the other hand. The deviation of the lattice parameter from the standard PDF file value is 0.025% in the case of sample 6 ($MgAl_2O_4$) and 0.012% in the case of sample 10 ($NiAl_2O_4$). Samples containing in addition to Al^{3+}, both Mg^{2+} and Ni^{2+} lead to the formation of solid solutions characterized by intermediate values of the lattice cell parameter. The plot of lattice parameter, a, versus the substitution degree of Mg^{2+} by Ni^{2+}, x, is practically a straight line (Fig. 6), which indicates once again the formation of designed solid solutions over the entire range of compositions ($x=0$–1).

On the other hand, the decrease of the lattice parameter from 8.085 Å in the case of sample 6 ($MgAl_2O_4$) down to 8.048 Å in the case of sample 10 ($NiAl_2O_4$) is related to the difference between the ionic radii of Mg^{2+} and Ni^{2+}. To be exact, the ionic radius of Mg^{2+} in tetrahedral coordination (0.57 Å) is a little bit larger than the ionic radius of Ni^{2+} in tetrahedral coordination (0.55 Å).[1]

Fig. 4. Images of samples 6–10 after annealing at 1000 °C for 3 h.

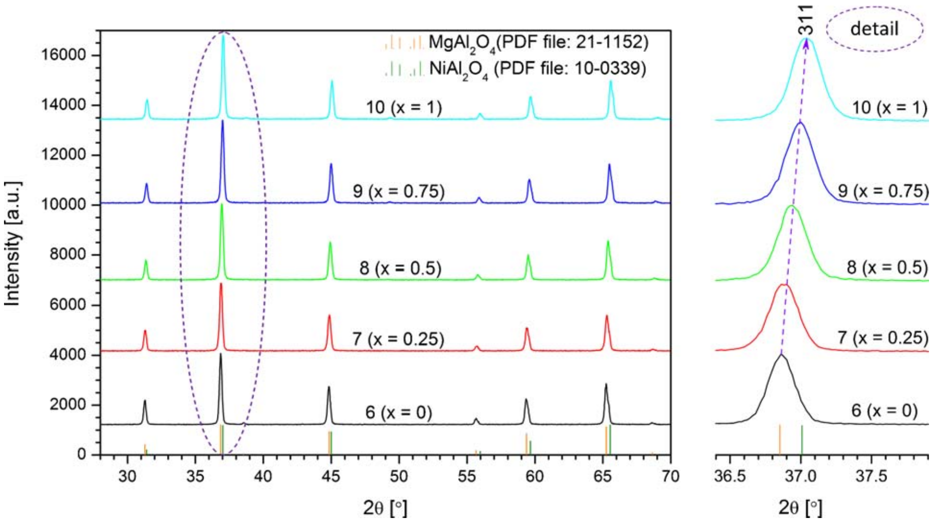

Fig. 5. XRD patterns of powders 6–10 after annealing at 1000 °C for 3 h.

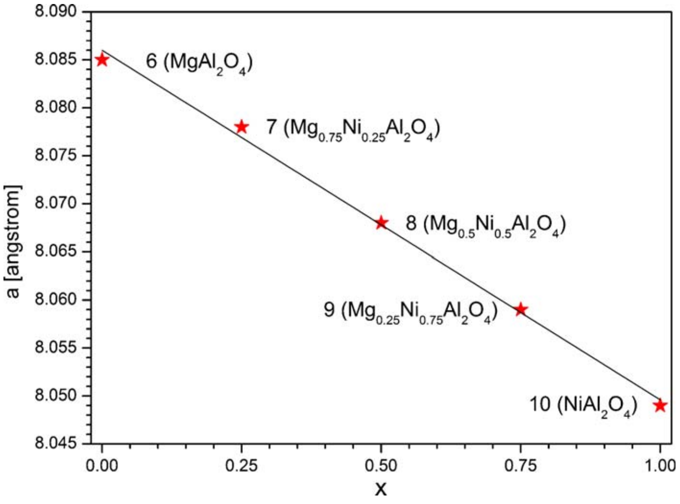

Fig. 6. The evolution of lattice parameter (a) as a function of substitution degree (x) of Mg^{2+} by Ni^{2+} in samples 6–10 after annealing at 1000 °C for 3 h.

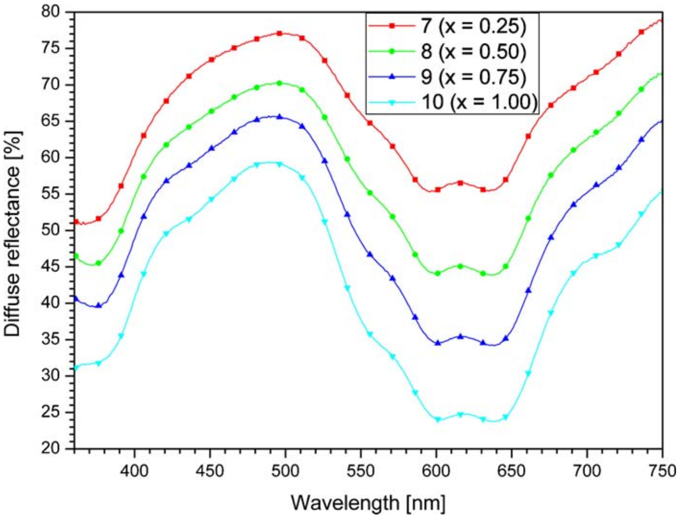

Fig. 7. Diffuse reflectance spectra of samples 7–10, prepared by combustion synthesis and calcined at 1000 °C for 3 h.

The average crystallite size does not show significant variations from one sample to another (Table 2). Still, one can notice the trend of slight decrease of crystallite size from sample 6 (39 nm) to sample 10 (35 nm). The specific surface area of the powders (Table 2) shows a similar tendency, as it decreases from sample 6 (7.0 m^2/g) to sample 10 (5.8 m^2/g). Since the combustion synthesized powders have been annealed under the same conditions (1000 °C/3 h), there are only minor differences in terms of crystallite size and specific surface area.

The diffuse reflectance spectra of samples 7–10 prepared by combustion synthesis (Fig. 7) are characterized by 3 intense absorption bands situated at 370 nm, 600 nm (with a shoulder at 560 nm) and 640 nm. Two weak absorption bands (430 nm and 720 nm) can be also identified on the DRS spectra of samples

Table 2
Lattice parameter (a), crystallite size (D), specific surface area (S) and CIEL*a*b* color coordinates of samples 6–10 after annealing at 1000 °C for 3 h.

Sample	a (Å)	D (nm)	S (m^2/g)	L*	a*	b*
6 ($MgAl_2O_4$)	8.085^c (8.083^s)	39	7.0	–	–	–
7 ($Mg_{0.75}Ni_{0.25}Al_2O_4$)	8.078^c	37	6.8	85.10	−9.05	−5.67
8 ($Mg_{0.5}Ni_{0.5}Al_2O_4$)	8.068^c	36	6.5	80.26	−11.78	−8.23
9 ($Mg_{0.25}Ni_{0.75}Al_2O_4$)	8.058^c	36	6.3	75.85	−14.98	−11.30
10 ($NiAl_2O_4$)	8.049^c (8.048^s)	35	5.8	69.69	−18.78	−15.32

c – calculated values, s – values given in the PDF files 21-1152 ($MgAl_2O_4$) and 10-0339 ($NiAl_2O_4$).

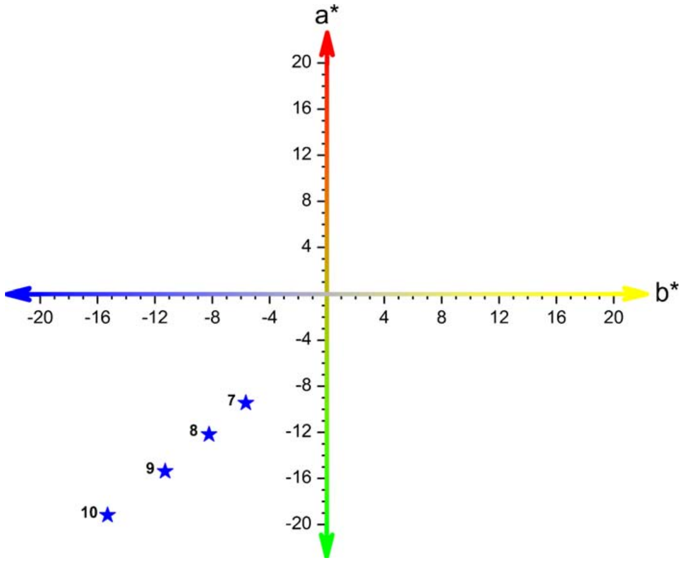

Fig. 8. a^* versus b^* for samples 7–10 prepared by combustion synthesis, after annealing at 1000 °C for 3 h.

7–10 (Fig. 7). According to the literature,[10–14] these absorption bands may be assigned to the presence of Ni^{2+} in the spinel structure occupying both octahedral and tetrahedral sites. The absorption bands situated at 600 nm (with a shoulder at 560 nm) and 640 nm correspond to $^3T_1(F) \rightarrow {}^3T_1(P)$ electronic transition which occurs in tetrahedral Ni^{2+} (Fig. 7). The bands observed at 370 nm and 430 nm are ascribed to charge transfer processes. The band from 720 nm is related to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition in octahedral Ni^{2+}.

CIEL*a^*b^* chromatic coordinates of the powders annealed at 1000 °C for 3 h (Table 2) confirmed the visual observations regarding the color of Ni^{2+} containing samples (Fig. 4). Samples 7–10 are located in the blue–green region (Fig. 8). A linear increase of the blue proportion (negative b^*) can be observed in samples 7–10 prepared by combustion synthesis. In other words, as the amount of Ni^{2+}, which occupies both tetrahedral and octahedral sites in $Mg_{1-x}Ni_xAl_2O_4$, increases, the blue hue of the sample intensifies.

The evolution of L^* parameter as a function of $Mg^{2+} \leftrightarrow Ni^{2+}$ substitution (Table 2) shows a progressive decrease as the amount of Ni^{2+} increases. The color ability of samples 7–10 was tested by adding 6 wt.% of pigment to a transparent glossy glaze. After firing at 1160 °C for 30 min all samples show signs of color degradation, which indicate that these pigments do not resist the aggression of melted glaze. The color degradation may be related to the large specific surface area and small crystallite size of $Mg_{1-x}Ni_xAl_2O_4$ pigments prepared by solution combustion synthesis.

4. Conclusions

$Mg_{1-x}Ni_xAl_2O_4$ ($x = 0$, 0.25, 0.5, 0.75 and 1) solid solutions have been prepared by solution combustion technique. Combustion synthesis proved to facilitate the $Mg^{2+} \leftrightarrow Ni^{2+}$ substitution and the formation of spinel structure. After annealing the combustion synthesized powders at 1000 °C for 3 h nanocrystalline $Mg_{1-x}Ni_xAl_2O_4$ were obtained over the entire range of compositions ($x = 0$, 0.25, 0.5, 0.75 and 1). The formation of the designed solid solutions was certified by the evolution of lattice parameter, which gradually increases from 8.049 Å ($NiAl_2O_4$) to 8.085 Å ($MgAl_2O_4$). All samples prepared by combustion synthesis had blue color shades, denoting the inclusion of Ni^{2+} in the spinel structure in octahedral and tetrahedral configuration. $Mg_{1-x}Ni_xAl_2O_4$ crystallite size was in the range of 35–39 nm and the specific surface area of the powders varied between 5.8 and 7.0 m^2/g.

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