

# Investigation of the Reaction Kinetic of Cordierite Ceramics Production by Using Magnesite Filter Powder

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**ABSTRACT:** Different raw materials are used in the production of cordierite ceramics. In the production of cordierite with optimum properties, the costs of the production should be considered. Firstly, the amount of energy required for the formation of cordierite ceramics should be calculated. For this purpose, in this study, the reaction kinetics of the production of cordierite ceramics was investigated. The raw magnesite and magnesite filter powder were used as MgO source in cordierite formation. Activation energies and Arrhenius constants were calculated from DSC/TG analysis data by Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Coats-Redfern methods. The activation energy was found to be 112 kJ/mol for CW, 118 kJ/mol for CR according to the KAS method, 136 kJ/mol for CW, and 142 kJ/mol for CR according to the FWO method. The phase contents of the cordierite materials sintered at various temperatures and heating rates were determined quantitatively by the Rietveld analysis.

**KEYWORDS:** Cordierite, Kinetics, Rietveld, Kissinger Equation.

## I. INTRODUCTION

The cordierite with optimum properties is present in the  $Mg_2Al_4Si_5O_{18}$  formula at a stoichiometric ratio of 2:2:5 and is magnesium alumina silicate from the oxides of the  $MgO-Al_2O_3-SiO_2$  ternary phase system [1,2]. It contains 13.8% MgO, 34.8%  $Al_2O_3$  and 51.4%  $SiO_2$  according to stoichiometric calculations [3]. Cordierite, a high thermal resistance material, is characterized by its high thermal shock resistance and low thermal conductivity due to its low coefficient of thermal expansion [4, 5]. Besides, the other outstanding properties of cordierite ceramics are low dielectric constant, high refractoriness, excellent mechanical property and good chemical durability [4].

According to the orthorhombic and hexagonal polymorphic structures of  $Mg_2Al_4Si_5O_{18}$  compound, there are 3 accepted forms,  $\alpha$ -cordierite,  $\beta$ -cordierite and  $\mu$ -cordierite. The high temperature form of dimorphous cordierite is indialite ( $\alpha$ -cordierite) [6] and hexagonal structure. It has a stable structure at temperatures below 1450 °C [7]. The indialite lattice parameters are  $a=9.800$ ,  $c=9.345$ [8] and the space group is P6/mcc [9].

Stable  $\beta$ -cordierite forms hydrothermally below 830 °C from glass or from the two other crystalline forms and the lattice parameters of this orthorhombic structure are  $a=17.10$ ,  $b=9.78$  and  $c=9.33$ . According to XRD, the interplanar spacing of  $\beta$ -cordierite is very similar to  $\alpha$ -cordierite [10]. Furthermore, at temperatures below 1400 °C, the low cordierite or  $\beta$ -cordierite, the space group Cccm with orthorhombic structure, slowly turns into high cordierite,  $\alpha$ -cordierite. The  $\mu$ -cordierite is prepared with special compositions such as fine glass powder [7] and is obtained by crystallization of this mixture at low temperatures of 800 to 950 °C [11].

In order to determine the formation temperatures of cordierite, the kinetic parameters must be determined in order to determine the amount of energy required for formation. For this, non-isothermal methods for determining the kinetic parameters of thermal decomposition have many advantages [7]. In this study, the activation energy and pre-

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exponential factor were determined in cordierite formation by Kissinger-Akahira-Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Coats-Redfern methods.

## II. MATERIALS AND METHODS

While the cordierite ceramic material is sintering at high temperatures, the amount of energy that must be exceeded for activation of the chemical reaction is calculated. For this, the thermogravimetric analysis results and the KAS, FWO and Coats-Redfern Methods were used. The activation energy was calculated by KAS and FWO methods and pre-exponential factor (Arrhenius constant) was calculated by Coats-Redfern method.

The conversion rate of the mass losses occurring during phase transformation in CR and CW cordierite samples was calculated according to Equation 1 [7]. Here,  $x$  is the degree of conversion,  $m_i$  is initial sample mass,  $m_f$  is final sample mass, and  $m_t$  is current sample mass at the moment  $t$  during thermogravimetric analysis.

$$x = \frac{m_i - m_t}{m_i - m_f} \quad (1)$$

The respective sample starting masses measured for DSC/TG analysis at 10, 20 and 30 °C/min at each heating rate are 28.5, 28.1 and 28.9 mg in CW cordierite samples, and 24.67, 32.43, 36.77 mg in CR cordierite samples.

### Method of Kissinger-Akahira-Sunose (KAS)

The KAS Method (Extended Kissinger Method) is one of the most important approaches used in determining kinetic parameters by thermal analysis. This method is based on an experiment in which milligram quantities of the reacting material are heat treated at different heating rates while the exothermic peak is recorded [12]. The KAS method is a model-free approach. This non-isoconversional method does not calculate  $E_a$  for each  $x$  conversion value and assumes a constant  $E_a$  [7]. The activation energy and the pre-exponential factor of the thermal decomposition reaction are calculated according to Equation 2 (Kissinger equation) [13].

$$\ln \left( \frac{\beta}{T^2} \right) = \ln \frac{A E_a}{R g(x)} - \frac{E_a}{R T} \quad (2)$$

Here,  $E_a$  is the activation energy (kJ/mol),  $R$  is the universal gas constant (8.314 J/molK),  $\beta$  is the heating rate (K/min),  $T$  is the maximum exothermic peak temperature observed in the DSC curve (K) and  $A$  is the pre-exponential factor (Arrhenius constant) [7]. In the plot of  $\ln(\beta/T^2)$  versus  $1/T$ , the slope gives  $-E_a/R$  and the average activation energy can be determined by calculation in a conversion range from 0 to 1 [13]. A first order reaction order ( $n = 1$ ) is usually assumed [12].

### Method of Flynn–Wall–Ozawa (FWO)

Another method of thermal analysis is the model-free FWO method. In this iso-conversional method,  $E_a$  is determined by the following Equation 3 using the Doyle approach [7].

$$\log (\beta) = \log \frac{A E_a}{R g(x)} - 2,315 - 0,457 \frac{E_a}{R T} \quad (3)$$

In the plot of  $\log (\beta)$  versus  $1/T$ , the slope gives  $-0.457 E_a/R$  and the average activation energy can be determined by calculation in a conversion range from 0 to 1 [13].

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## Method of Coats-Redfern

The Coats-Redfern method is a model free method derived from the Arrhenius equation. The KAS and FWO methods are suitable for calculation of activation energy, but Coats-Redfern method is used to calculate the Arrhenius constant (A) and this equation is given below [13].

$$\ln\left(-\frac{\ln(1-x)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (4)$$

According to Equation 4, in the plot of  $\ln(-\ln(1-x)/T^2)$  versus  $1/T$ , the slope gives  $-E_a/R$ , and breakpoint gives  $\ln(AR/\beta E_a)$  [13]. In the Coats-Redfern method, n is the parameter of Avrami, the degree of reaction and it is chosen according to Table 1. The Arrhenius constant (A) of the KAS and FWO equations can be calculated by Coats-Redfern method.

Table 1. The values of the n parameters for various crystallization mechanisms [14]

Crystallization Mechanism	Growth Dimension	n
Volume crystallization in the condition of number of fixed cores (in which case the number of cores is independent of the heating rate)	3D	3
	2D	2
	1D	1
Volume crystallization with increasing number of nuclei	3D	3
	2D	2
	1D	1
Surface Crystallization		1

## III. EXPERIMENTAL RESULTS

In this study, raw magnesite, magnesite filter powder, 74 micron quartz and kaolin were used as initial raw materials in order to obtain cordierite phase. In our previous paper [15] we have reported the experimental procedure (the preparing method of the CW and CR cordierite compositions and sintering process (1250, 1300, 1325 °C)).

Figure 1 shows the particle size distribution of the samples. The grain size of  $d_{80}$  of CW and CR cordierite powders are 16.95 and 12.07  $\mu\text{m}$ , respectively.

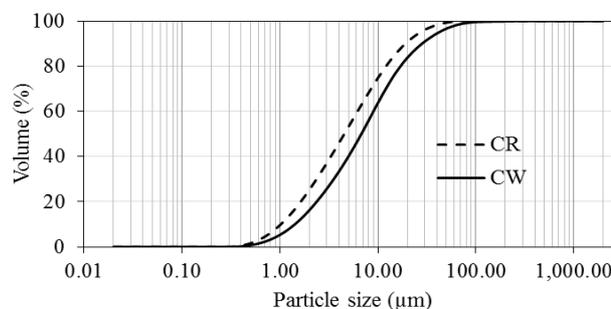


Fig. 1. Particle size distribution of CW and CR cordierite samples

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## Thermal Characterization with DSC/TG Analysis

The loss in masses and peak temperatures observed during the sintering of CR and CW cordierite samples were recorded. Setaram Labsysevo thermal analyzer was used for this purpose. The temperature range was determined as 0-1200 °C and DSC (Differential Scanning Calorimetry) and TG (Thermogravimetric) analyses were carried out under argon inert gas at a flow rate of 50 ml/min. With these analyses, the endothermic and exothermic decompositions and formations, peak values and mass losses, occurred during the reaction, were recorded in the cordierite samples.

In the DSC/TG thermal analysis method two or more basic analysis techniques are applied on a single sample at the same time. In this thesis study, the effect of temperature on cordierite powder material was investigated with reference to alumina. Crystallization activation energy and mass losses due to heat effect were determined from DSC/TG analysis data obtained at different heating rates of 10, 20, 30 °C/min.

## Quantitative Analysis

The crystalline phases were identified by using an X-ray diffractometer (Shimadzu XRD-6000 model) with CuK $\alpha$  radiation (1.54 Å) and the range of the scanning angle was from 5° to 90° with a scanning speed of 2°/min.

Rietveld based quantitative analysis was performed on each of the diffraction patterns using the MAUD (Material Analysis Using Diffraction) programme [16,17], which is designed to simultaneously refine the material structure and the microstructure through the Marquardt least-squares method[18].

## IV. RESULTS AND DISCUSSION

The  $E_a$  activation energies are determined by using KAS and FWO methods, and A Arrhenius constant is determined by using Coats-Redfern method. For this purpose, the degree of conversion values are calculated from Equation 1, the temperatures corresponding to the conversion values in each 0-1 range are determined.

The average activation energies calculated for the conversion values according to the KAS and FWO methods and the A Arrhenius constants calculated by the Coats-Redfern method are given in Table 2 according with the R<sup>2</sup> standard deviation rates.

Table 2.  $E_a$  and A values calculated for CW and CR cordierite samples

Sample	KAS			FWO		
	$E_a$ kJ/mol	R <sup>2</sup>	Coats-Redfern A	$E_a$ kJ/mol	R <sup>2</sup>	Coats-Redfern A
CW	112.41	0.99	8E-11	118.63	0.99	2E-11
CR	136.24	0.95	6E-15	142.85	0.95	2E-15

In the CW cordierite sample, according to the DSC/TG analysis (Fig 2 (a)), the first endothermic peaks was observed at 95, 103 and 127 °C, respectively, at heating rates of 10, 20 and 30 °C/min, which can be attributed to the evaporation of absorption water [19]. The strongest endothermic peak begins at kaolin dehydration at 538 °C leading to the transformation of  $\alpha$ -quartz into hexagonal  $\beta$ -quartz [20, 21, 22]. This conversion is completed at 672, 692 and 714 °C. The cordierite formation on the CW samples started at 979, 991 and 1002 °C and was completed with  $\alpha$ -cordierite formation at 1145, 1115 and 1150 °C.

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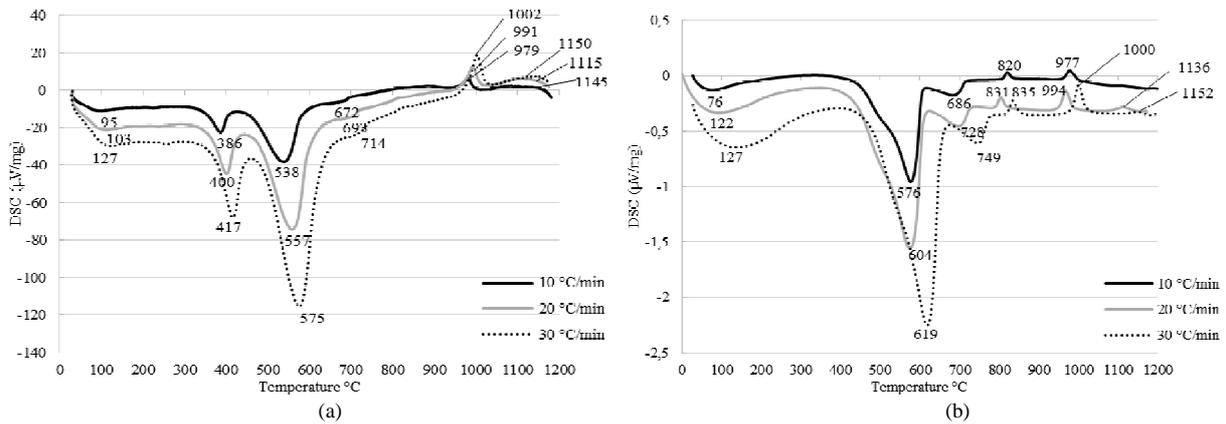


Fig. 2. DSC curve of CW (a) and DSC curve of CR (b) cordierite at different heating rate

The strongest endothermic peak at 576, 619 and 604 °C begins kaoline dehydroxylation [20] and leading to the transformation of  $\alpha$ -quartz into hexagonal  $\beta$ -quartz according to Fig 2 (b) [21,22]. This conversion is completed at 686, 728 ve 749 °C. The exothermic peak temperatures of 820, 831 and 835 °C were first observed in CR cordierite samples. At the cordierite exothermic peaks, two exothermic peaks of 994-1136 °C and 1000-1152 °C were observed with 20 and 30 °C/min, respectively, and these peaks were attributed to crystal phase change [19]. At the 977, 1136 and 1152 °C exothermic peaks,  $\alpha$ -cordierite formation was completed.

Phases formed in CW and CR cordierite samples sintered at each temperature were identified from the XRD raw data. Subsequently obtained crystallographic information files (CIFs) was entered into MAUD. The lists of the PDF card numbers of the phases and crystal structures are given in Table 3. The quantitative ratios of the phases obtained from Rietveld phase analysis results are given in Table 4.

Table 3. The characteristic properties of phases for Rietveld analysis

Phase	Space Group	Crystal Structure	PDF Card No (cif no)
$\alpha$ -cordierite	P6/mcc	Hexagonal	01-082-1884 <sup>a</sup>
			00-013-0293 <sup>b</sup>
$\beta$ -cordierite	Cccm	Orthorhombic	01-076-6035 <sup>a</sup>
			01-072-0172 <sup>b</sup>
Cristobalite	P41212	Tetragonal	00-039-1425
Forsiterite	Pmnb	Orthorhombic	00-034-0189
Quartz	P3221	Hexagonal	00-033-1161
Enstatite	Pbca	Orthorhombic	00-019-0768
Spinel	Fd-3m	Cubic	00-021-1152
Proto-enstatite	Pbcn	Orthorhombic	04-007-8621

Table 4. Rietveld Analysis Results of CW and CR Cordierite Samples

Cordierite Code	CR	CW	CR	CW	CW	CW	CW
<b>Sintering Temperature, (°C)</b>	1250	1250	1300	1300	1300	1300	1325
<b>Heating Rate, (°C/min)</b>	3	3	3	3	2	1.5	3
<b><math>\alpha</math>-cordierite (%)</b>	53.72±1.7 <sup>a</sup>	61.13 <sup>a</sup>	44.45±15.1 <sup>b</sup>	47.37 <sup>a</sup>	54.23 <sup>b</sup>	5.72±0.6 <sup>a</sup>	61.21 <sup>b</sup>
<b><math>\beta</math>-cordierite (%)</b>	-	-	7.33 <sup>a</sup>	1.41±0.1 <sup>b</sup>	11.06±1.3 <sup>b</sup>	70.62±1.6 <sup>b</sup>	12.07±2.0 <sup>b</sup>
<b>Cristobalite (%)</b>	26.08±9.4	16.19±1.1	-	-	7.30±0.3	-	-
<b>Forsiterite (%)</b>	16.1±0.8	7.39±0.5	-	19.81±1.5	17.47±1.1	10.99±0.5	-

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Quartz (%)	4.07±0.2	15.27±0.9	-	1.41±0.1	-	-	-
Enstatite (%)	-	-	48.21±13.7	-	-	-	-
Spinel (%)	-	-	-	-	-	0.98	-
Proto-enstatite (%)	-	-	-	29.97±1.8	9.96±0.45	11.67±0.7	26.71±1.5
Sigma	3.13	2.74	2.33	2.73	2.30	2.09	2.07

\*a and b are the types of  $\alpha$ -cordierite and  $\beta$ -cordierite PDF Card on Table 3.

## V. CONCLUSION

In the production of cordierite ceramics, sintering was carried out at different heating rates (1.5, 2 and 3 °C/min) at 1250, 1300 and 1325 °C. The raw magnesite and heat treated waste magnesite filter powder were used as two different MgO sources. The  $\alpha$ -cordierite formation on the CW sample starts at 991 °C and completes at 1115 °C, while the CR sample starts at 855 °C and completes at 1152 °C.

When the CW and CR cordierite samples sintered at 1250 °C are compared, approximately  $\alpha$ -cordierite is present at 53% CR and 61% CW. As the sintering temperature increases,  $\beta$ -cordierite begins to form. CW cordierite contains 47%  $\alpha$ -cordierite and 1%  $\beta$ -cordierite and CR cordierite contains 44%  $\alpha$ -cordierite and 7%  $\beta$ -cordierite at 1300 °C at a heating rate of 3 °C/min. At 1325 °C, the amount of  $\beta$ -cordierite increased to 12%, while the  $\alpha$ -cordierite was 61%. A total of about 75% of the cordierite phase was observed. The main phase and the desired phase in the cordierite ceramics are  $\alpha$ -cordierite phase.

The Ea values were calculated as 112.41 kJ/mol in the CW cordierite sample and 136.42 kJ/mol in the CR according to the KAS method. The values were calculated as 118.63 kJ/mol in the KAS method and 142.85 kJ/mol in the FWO method for the CR sample. Both methods do not show high differences in the calculated activation energies. The Arrhenius equations for the KAS and FWO equations are calculated by the Coats-Redfern method and are given in Table 2.

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## REFERENCES

- [1] P, Rohan., K, Neufuss., J, Matejíček., J, Dubská., L, Prchlik, C, Holzgartner. Thermal and mechanical properties of cordierite, mullite and steatite produced by plasma spraying. *Ceramics International*, vol. 30, ISSN:0272-8842, p. 597-603, 2004.
- [2] H. Gökçe. Development and characterization of synthetic cordierite ceramics from natural raw materials. Metallurgical Engineering Master Thesis, Institute of Science and Technology, İstanbul Technical University, 127p., 2002.
- [3] H, Yılmaz, F. Kara. RefrakterMalzemeÜretimi. MYO-ÖS,UlusalMeslekYüksekokullarıÖğrenciSempozyumu, BilecikÜniversitesi, 21-22 Ekim, Bilecik from <http://docplayer.biz.tr/7197333-Refrakter-malzeme-uretdmd.html>., 2010.
- [4] Y, Li., X, Cheng., R, Zhang., Y, Wang., H, Zhang. Effect of excess MgO on the properties of cordierite ceramic sintered by solid-state method. *International Journal of Applied Ceramic Technology* vol.12:2, ISSN:1744-7402, p.443-450, 2013.
- [5] X, Xu., X, Xu., X, J, Wu., X, Lao., Y, Zhang., K, Li. Effect of Sm<sub>2</sub>O<sub>3</sub> on microstructure, thermal shock resistance and thermal conductivity of Cordierite-Mullite-Corundum composite ceramics for solar heat transmission pipeline. *Ceramics International*, vol.42, ISSN:0272-8842, p. 13525-13534, 2017.
- [6] R, Dimitrijevic., V, Dondur. Thermally induced conversion of Mg<sup>2+</sup> cation exchanged LTA, FAU, GIS and SOD zeolites: synthesis and characterization  $\gamma$ -cordierite, a new Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub> polymorph. *Journal of the Serbian Chemical Society*, vol.72, ISSN:1820-7421, p. 1351-1362, 2007.
- [7] G, Pahari., J, Singh., T.K, Parya. Non-isothermal decomposition kinetics of cordierite. *Journal of the Australian Ceramic Society*, vol.52, ISSN:2510-1579, p.41-51, 2016.
- [8] E. P, Meagher., G. V, Gibbs. The polymorphism of cordierite II: The crystal structure of indialite. *Canadian Mineralogist*, vol.15, ISSN:1499-1276, p.4349, 1977.
- [9] T, Ebadzadeh., W.E, Lee. Processing-microstructure-property relations in mullite-cordierite composites. *Journal of the European Ceramic Society*, vol.18,ISSN: 0955-2219, p.837-848, 1998.
- [10] M. D, Karkhanavala., F. A, Hummel. The polymorphism of cordierite. *American Ceramic Society*, vol.36, ISSN:1551-2916, p.12, 1953.
- [11] K, Sumi, Y, Kobayashi., E.K, Sumi. Synthesis and sintering of cordierite from ultrafine particles of magnesium hydroxide and kaolinite. *Journal of the American Ceramic Society*, Vol.81, ISSN:1551-2916, p.1029-1032, 1998.
- [12] R.L, Blaine., H. E, Kissinger. Homer Kissinger and the Kissinger equation. *ThermochimicaActa*, vol.540, ISSN:0040-6031, p.1-6,2012

## International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

**Vol. 6, Special Issue 10, May 2017**

- [13] S, Ceylan., Y. Topçu. Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. *Bioresource Technology*, vol.156, ISSN:0960-8524, p.182-188, 2014.
- [14] Z.E, Erkmen. *Modern Fizik Takviyeli Malzeme Karakterizasyonu ve Temel İlkeleri*, p.196-198, ISBN: 9759617950, 2012.
- [15] A, Aşkın., İ Tatar., Ş Kılınç. The Utilization of waste magnesite in the production of the cordierite ceramic. *Energy Procedia*, vol.107, ISSN:1876-6102, p.137-143, 2017
- [16] L, Lutterotti. Total pattern fitting for the combined size-strain-stress-texture determination in thin film diffraction", *Nuclear Inst. and Methods in Physics Research, B*, vol.268, ISSN:0168-583X, p.334-340, 2010.
- [17] L, Lutterotti., S, Matthies., H.R, Wenk., A.J, Schultz., J, Richardson. Texture and structure analysis of deformed limestone from neutron diffraction spectra", *J. Appl. Phys.*, vol.81[2], ISSN:1089-7550, p.594-600, 1997.
- [18] L, Palatinus., G, Chapuis. Superflip - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Cryst.* Vol.40, ISSN:1600-5767, p.786-790, 2007.
- [19] B, Tang., Y.W, Fang., S, Zhang., H.Y, Ning., C.Y, Jing. Preparation and characterization of cordierite powders by water-based sol-gel method. *Indian Journal of Engineering & Materials Sciences*, vol.18, ISSN:0975-1017, p.221-226, 2011.
- [20] Y, Kobayashi., K, Sumi., E, Kato. Preparation of dense cordierite ceramics from magnesium compounds and kaolinite without additives. *Ceramics International*, vol.26, ISSN:0272-8842, p.739-743, 2000.
- [21] M. G, Tucker., D. A, Keen., M. T, Dove. A detailed structural characterization of quartz on heating through the  $\alpha$ - $\beta$  phase transition. *Mineralogical Magazine*, vol.65, ISSN:1471-8022, p.489-507, 2001.
- [22] N, Obradović., S, Filipović, N, Đorđević, D, Kosanović., S, Marković., V, Pavlović., D, Olćan., A, Djordjević., M, Kachlik., K, Maca. Effects of mechanical activation and two-step sintering on the structure and electrical properties of cordierite-based ceramics. *Ceramics International*, vol.42, ISSN:0272-8842, p.13909-13918, 2016.