

# The influence of the raw materials mixture on the properties of forsterite ceramics

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**Abstract.** Forsterite ceramics is a part of the refractory magnesium ceramics. The aim of this paper is to characterize the properties of forsterite ceramics in dependence on different compositions of the raw material mixture. Forsterite ceramics is not currently produced in the Czech Republic. Forsterite ceramics is used in industry for its high refractoriness and also for its coefficient of linear thermal expansion which is close to metals. The primary objective of this article is to synthesize forsterite ceramics via solid state reaction. Different raw materials were used for materials mixtures and properties of fired samples were investigated, considering the influence of the raw materials mixtures. Specifically the apparent porosity, water absorption, mineralogical composition, coefficient of linear thermal expansion and refractoriness were investigated.

## 1. Introduction

Forsterite is an end-member mineral of the olivine solid solution series which contains magnesium in its structure. Chemical formula of forsterite is  $2\text{MgO} \cdot \text{SiO}_2$ . In nature, forsterite can be found as a solid solution of olivine which has the chemical formula  $(\text{Mg}^{2+}, \text{Fe}^{2+})_2[\text{SiO}_4]$  [1].

In the industry, forsterite is used as a refractory material due to its high refractoriness up to  $1850^\circ\text{C}$  and its refractoriness under load of  $1600^\circ\text{C}$  [2]. Another significant property of forsterite is its coefficient of linear thermal expansion, which is very similar to the metals coefficient with increasing temperature. This is the reason why is forsterite ceramics widely used in electrical engineering. In the civil engineering industry, forsterite can be used as a lining of the sintering zone of a rotary kiln for cement production or as a lining of metallurgical furnaces [3]. Table 1 contains physical and chemical properties of forsterite.



**Table 1.** Physical and chemical properties of forsterite.

chemical formula:	2MgO·SiO <sub>2</sub>	
chemical composition:	57.29 % MgO + 42.71 % SiO <sub>2</sub>	
crystal system:	orthorhombic	
Mohs scale of mineral hardness:	7	
molar mass:	140.69 g/mol	
density:	3 270 kg·m <sup>-3</sup>	
melting point:	1 890°C	
refractoriness:	1 850°C	[2]
refractoriness under load:	1 600°C	[2]
coefficient of linear thermal expansion $\alpha_{30-100^\circ\text{C}}$ :	$8 \cdot 10^{-6} - 11 \cdot 10^{-6} \text{ K}^{-1}$	[3]

## 2. Experimental

Powders of magnesite (purity 98 %, MgO: 44.2 wt%,  $d_{50} = 2 \mu\text{m}$ , Fichema, s. r. o.) and talc (purity 97 %,  $d_{50} = 4.7 \mu\text{m}$ , Fichema, s. r. o.) were mixed with a weight proportion corresponding to forsterite (table 2 – mixture A). Powders of talc and magnesium oxide (pharmaceutical purity 99.7 %, Fichema, s.r.o.) were mixed with a weight proportion corresponding to forsterite (table 2 – mixture B) and powders of magnesium oxide and micro-milled silica sand (high purity 99.6 %,  $d_{50} = 6 \mu\text{m}$ , surface area 8592 m<sup>2</sup>·kg<sup>-1</sup>, Sklopísek Střeleč, a. s.) were mixed with a weight proportion corresponding to forsterite (table 2 – mixture C). Chemical composition of used materials is presented in table 3.

Individual mixtures (MIX A, B, C) were mixed in a rotary homogenizer for 24 hours to ensure homogenous mixture. The prepared mixtures were uniaxially compacted at about 20 MPa into samples with dimensions 100×50×10 mm. The green bodies were dried in a laboratory drier at 110°C and then sintered at temperatures 1200°C and 1300°C with a heating rate of 4°C/min and soaking time of 2 hours at the maximum temperature in an electrical furnace in the air atmosphere. Pyrometric cones were also prepared from all mixtures to determine refractoriness.

**Table 2.** Raw material mixtures composition.

raw material	mixture A	mixture B	mixture C
magnesite	53.8 wt%	-	-
talc	36.2 wt%	56.4 wt%	-
magnesium oxide	-	33.6 wt%	54.3 wt%
silica sand	-	-	35.7 wt%
clay B1	10.0 wt%	10.0 wt%	10.0 wt%

**Table 3.** Chemical composition of used materials.

raw material	MgO [%]	SiO <sub>2</sub> [%]	CaO [%]	Fe <sub>2</sub> O <sub>3</sub> [%]	Al <sub>2</sub> O <sub>3</sub> [%]	K <sub>2</sub> O+Na <sub>2</sub> O [%]	TiO <sub>2</sub> [%]	LOI [%]	Total [%]
magnesite	44.2	0.0	0.4	0.04	0.0	0.0	0.0	52	96.64
talc	31.5	59.1	1.0	0.7	1.0	0.2	0.0	6.5	100.00
magnesium oxide	99.7	0.0	0.05	0.003	0.0	0.0	0.0	0.25	100.00
silica sand	0.05	99.6	0.02	0.03	0.2	0.1	0.0	0.0	100.00
clay B1	0.36	48.7	0.28	2.66	33.84	1.99	0.83	11.25	99.91

After firing the apparent porosity and water absorption were determined by the official standard EN 993-1:1995 [4] (vacuum water absorption). Pyrometric cones were also prepared according to standard EN 993-12 [5] to determine refractoriness. Coefficient of linear thermal expansion was determined according to standard EN 993-19: Determination of thermal expansion by a differential method [6].

The phases presented in the synthesized forsterite powders were identified by X-ray diffraction (PANALYTICAL Empyrean XRD) with Cu K $\alpha$  as the radiation source, accelerating voltage 45 kV, beam current 40 mA in the range from 5° to 80° with a step scan of 0.01°. The obtained X-ray diffraction patterns were compared with the Crystallography Open Database (COD) [7].

### 3. Results and discussion

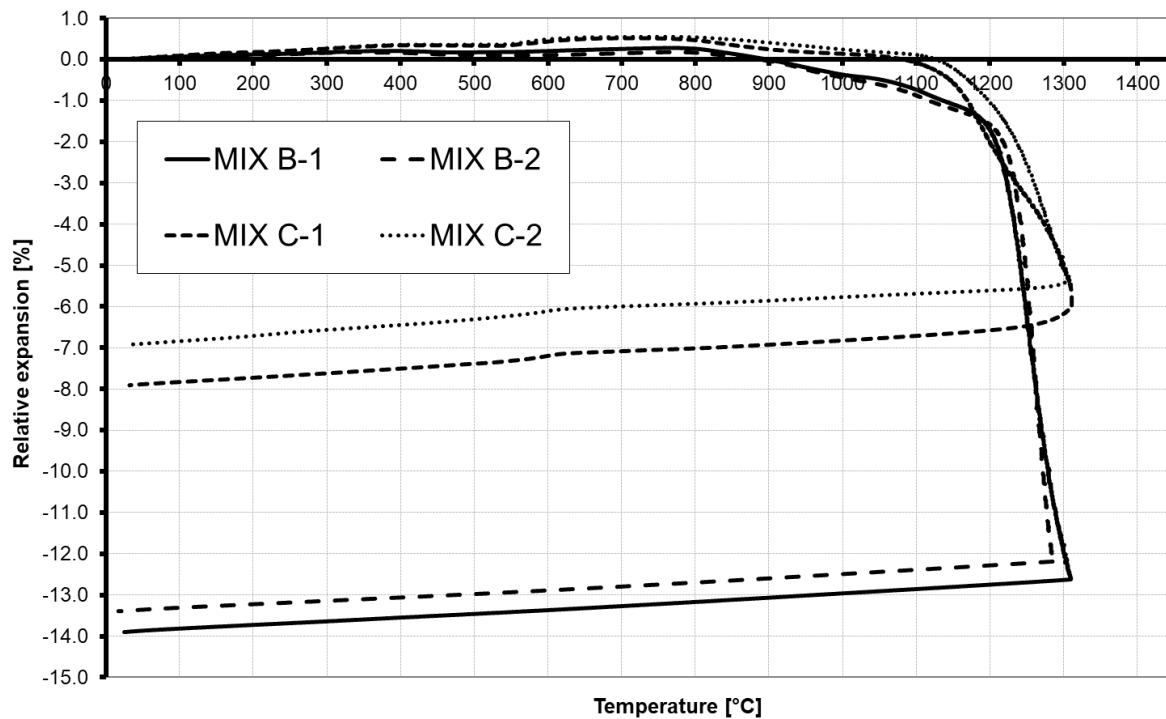
The most important properties of forsterite are high refractoriness and coefficient of linear thermal expansion which is close to metals. Coefficient of linear thermal expansion was determined from dilatometric curves (figure 1) by differential method. Higher firing shrinkage of mixture B (MIX B) is caused by talc, which is eutectic flux and accelerates sintering of the samples for temperatures above 1200°C.

Mean coefficient of linear thermal expansion of mixture B (MIX B) for temperature interval 20-1300°C is  $9.81 \cdot 10^{-6} \text{ K}^{-1}$  and for mixture C (MIX C) is  $15.25 \cdot 10^{-6} \text{ K}^{-1}$ . M. Bouhifd et al. [8] determined the coefficient of linear thermal expansion for forsterite in temperature interval 20-1300°C has linear growth and was found to be in the interval  $(10-36) \cdot 10^{-6} \text{ K}^{-1}$ . Coefficient of tested samples is within the range given by the reference values.

Apparent porosity and water absorption values of tested samples are presented in table 4. Mean apparent porosity of mixture A (MIX A) was high due to loss on ignition of magnesite (magnesium carbonate), which decomposes to magnesium oxide and carbon dioxide. This decomposition is the cause of higher apparent porosity and water absorption in mixture A. Samples of mixture B (MIX B) fired at 1300°C were sintered with low values of apparent porosity and water absorption.

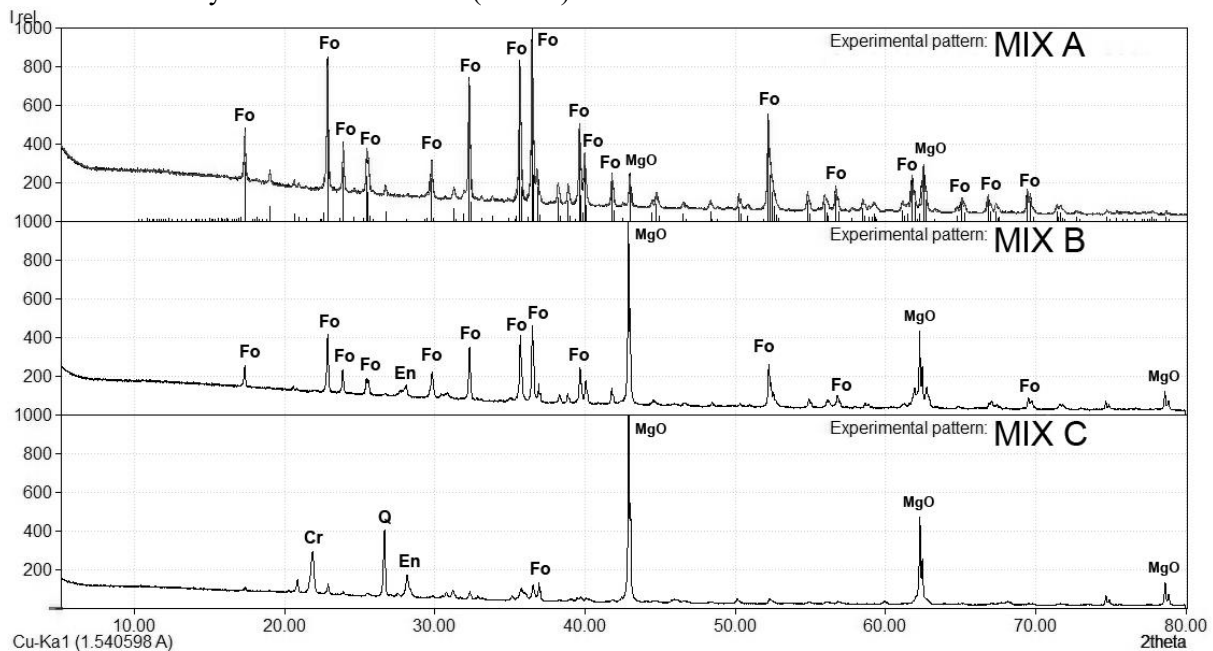
**Table 4.** Apparent porosity and water absorption of mixtures A, B and C at different firing temperatures.

mixture	firing temperature [°C]	apparent porosity [%]	water absorption [%]
MIX A	1200	53.7	36.4
	1300	48.9	29.6
MIX B	1200	36.1	18.1
	1300	11.6	5.4
MIX C	1200	42.7	23.8
	1300	39.1	20.7



**Figure 1.** Thermal dilatometric analysis during firing (1300°C, heating rate 5°C/min).

Mineralogical composition of all mixtures is presented in table 5. The result of phase analysis by X-ray diffraction (XRD) of fired samples is shown in figure 2. Quantitative representation of minerals was carried out by Rietveld refinement (table 5).



**Figure 2.** X-ray diffraction (XRD) of all mixtures (Fo = forsterite, En = enstatite, MgO = periclase, Q = quartz, Cr = cristobalite).

Samples from mixture A were almost pure crystalline forsterite. This occurred due to magnesite, which decomposes at temperatures above 500°C and released carbon dioxide resulted in higher reactivity to form forsterite. Intensive synthesis of forsterite begins at 1100°C if magnesite and talc are used as raw materials [3].

Samples from mixture B contained high amount of forsterite, but secondary phases (periclase MgO and enstatite  $\text{MgSiO}_3$ ) were also present. This was probably due to merging of fine magnesium oxide particles, which resulted in micro-inhomogeneity of mixture B. With increasing temperature, the amount of forsterite in samples from mixture B was also increasing. This effect occurred due to flux ability of talc, which is present in the mixture B.

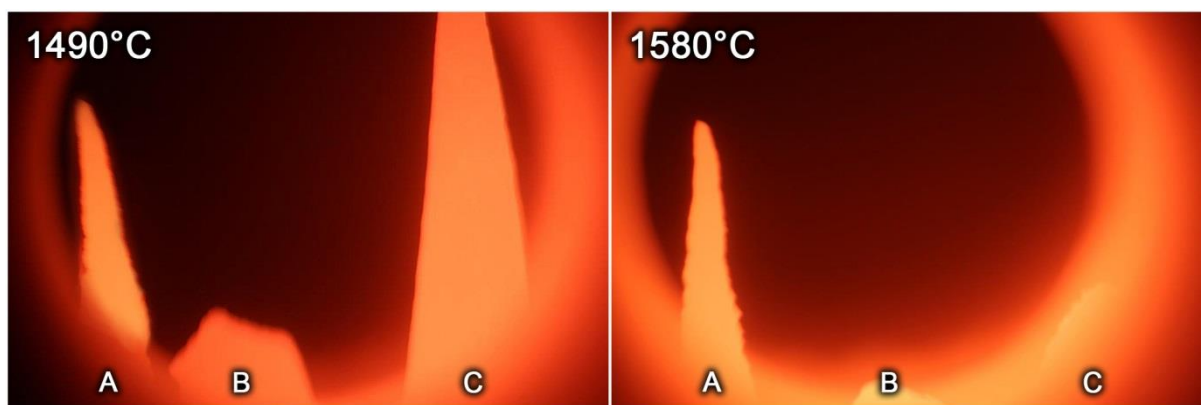
Samples of mixture C contained relatively low amount of forsterite with secondary phases of periclase (MgO), enstatite ( $\text{MgSiO}_3$ ), quartz ( $\text{SiO}_2$ ) and at temperature of 1300°C also cristobalite. With increasing temperature, the amount of forsterite and enstatite in samples from mixture C was also increasing. However, the temperature of 1300°C was not high enough for intense sintering of raw materials to occur.

**Table 5.** Results of X-ray diffraction and Rietveld refinement of samples fired at different temperature.

mixture	firing temperature [°C]	identified minerals	quantitative representation of minerals using the Rietveld refinement
MIX A	1200	forsterite (Fo), periclase (P)	95 % Fo + 5 % P
	1300	forsterite (Fo), periclase (P)	95 % Fo + 5 % P
MIX B	1200	forsterite (Fo), periclase (P), enstatite (En)	59 % Fo + 29 % P + 12 % En
	1300	forsterite (Fo), periclase (P), enstatite (En)	73 % Fo + 22 % P + 4 % En
MIX C	1200	forsterite (Fo), periclase (P), enstatite (En), quartz (Q)	14 % Fo + 42 % P + 18 % En + 26 % Q
	1300	forsterite (Fo), periclase (P), enstatite (En), quartz (Q), cristobalite (Cr)	22 % Fo + 44 % P + 20 % En + 7 % Q + 7 % Cr

The pyrometric cone equivalent test was carried out to determine the refractoriness of all mixtures. The effect of mineralogical composition on the refractoriness of all mixtures is shown in figure 2. Pyrometric cone from mixture B bent at 1490°C (figure 2 on the left) and pyrometric cone from mixture C bent at 1580°C. The test was terminated at 1620°C, because the pyrometric cone from mixture A fell down. This occurred probably due to creation of eutectic melt in the pad, which was formed from clay B1 and corundum.

Pyrometric cone from mixture A was not bent after the test, refractoriness of this mixture is therefore above 1620°C. Refractoriness of pure forsterite is approximately 1850°C [2]. Lower refractoriness of mixtures B and C was due to secondary phase of enstatite, whose melting point is 1557°C.



**Figure 3.** Pyrometric cone equivalent test: left – bending of cone from mixture B, right – bending of cone from mixture C.

#### 4. Conclusion

In this article, forsterite was successfully synthesized via solid-state reaction from all mixtures. The influence of the raw material mixture was analyzed in terms of mineralogical composition, apparent porosity, water absorption, refractoriness and coefficient of linear thermal expansion.

Mixture A was composed of magnesite and talc, mixture B was composed of talc and magnesium oxide and mixture C was composed of magnesium oxide and silica sand. All mixtures contained 10 % of clay B1 which improves binding properties of the green body and sinterability during firing. Dry pressed samples were sintered at 1200°C and 1300°C. Mineralogical composition of individual mixtures varied. Samples from mixture A (magnesite and talc) were nearly pure forsterite with secondary phase of periclase, samples from mixture B (talc and magnesium oxide) contained high amounts of forsterite with secondary phases of periclase and enstatite and samples from mixture C (magnesium oxide and silica sand) contained minor amounts of forsterite with secondary phases of periclase, enstatite, quartz and cristobalite.

In terms of apparent porosity and water absorption, the raw materials and the sintering temperature plays an important role. Samples from mixture A had high apparent porosity and water absorption due to decomposition of magnesite (magnesium carbonate). Samples from mixture B sintered at 1300°C were densified with low apparent porosity and water absorption due to talc in the mixture B which is eutectic flux and accelerates sintering.

Refractoriness of samples from mixture B is 1490°C, from mixture C is 1580°C and from mixture A is above 1620°C. Refractoriness of pure forsterite is above 1800°C. Lower refractoriness of samples from mixtures B and C was due to the presence of secondary phase enstatite. Melting point of enstatite is 1557°C. Mean coefficient of linear thermal expansion of mixtures for temperature interval 20-1300°C is between  $(9.8-15.3) \cdot 10^{-6} \text{ K}^{-1}$ , which is in the range of reference values for forsterite.

In conclusion, the results revealed that firing the samples from mixture A (magnesite, talc) are almost pure forsterite ceramics with high porosity and refractoriness. Samples from mixture B (talc, magnesium oxide) contain high amount of forsterite and are densified with low porosity and water absorption and samples from mixture C (magnesium oxide, silica sand) are porous and to achieve higher amounts of forsterite, sintering temperature needs to be above 1500°C.

It could be possible to utilize fly ash as a source of silicon dioxide ( $\text{SiO}_2$ ). Fly ash is a secondary energy product from coal combustion in power plants. Therefore it is inexpensive and its recycling is important for the environment and sustainable development. Raw materials mixture from fly ash to form forsterite would consist of 53.7 wt% of fly ash and 46.3 wt% of magnesium oxide. Utilization of fly ash as a raw material could have potential economic benefit in the final price of forsterite refractory ceramics.

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