Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 6607–6612

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Mechanical properties of ceramic bodies based on calcite waste

Radomír Sokolář[a,*], Lucie Vodová[a], Simona Grygarová[a], Igor Štubňa[b], Peter Šín[b]

[a] Institute of Technology of Building Materials and Components, Brno University of Technology, 602 00 Brno, Czech Republic
[b] Department of Physics, Constantine the Philosopher University, 949 74 Nitra, Slovakia

Received 12 April 2012; received in revised form 15 May 2012; accepted 16 May 2012
Available online 23 May 2012

Abstract

Physico-mechanical properties (flexural strength, Young modulus, bulk density, change of dimensions, porosity) as well as the mineralogical composition were studied on samples with difference content of calcite after firing at 900, 1000, 1100 and 1200 °C. It was found that anorthite and mullite are the main crystalline phases of the fired samples containing the calcite. The anorthite/mullite ratio depends on the firing temperature and the initial amount of calcite waste. The higher the temperature of the firing and the higher the amount of calcite waste, the more anorthite is created in the samples. Presence of calcite decreases sample contraction during sintering. Porosity decreases with the increase of the firing temperature, but the sample with the content of calcite 20 wt% shows approximately constant porosity. Flexural strength and Young modulus of the reference sample and the sample with 10 wt% of calcite waste increase in their value. These mechanical parameters increases very slightly for the sample with 20 wt% of calcite waste.

Keywords: Calcite; Ceramic body; Mineralogical composition; Young modulus

---

1. Introduction

Ceramic masses, which contain calcite, are often used in the brick industry. Instead of the relatively large calcite stones, it is profitable to exploit fine-grain quarry waste. According to estimation, there is about 10^5 t of such waste in limestone quarries in the Czech Republic. An advantage of the calcite addition is a small irreversible contraction of the fired body during and after firing [1]. That is caused by the presence of anorthite which arises in the fired body at temperatures above 950 °C through metastable gehlenite. Gehlenite can be created by three ways: (a) from CaO and metakaolinite, (b) from CaO and metastable spinel phase, which precedes formation of mullite, and (c) from CaO and mullite. The next step is to transform gehlenite into anorthite [2]. Creation of gehlenite and anorthite is accompanied with an increase in the fired body's volume [3]. This volume change occurs at a temperature interval where intensive contraction takes place due to sintering and collapse of the metakaolinite lattice. Emergence of gehlenite and anorthite reduces the contraction of the fired body, which is clearly visible on thermodilatometric curve [1].

Creation of anorthite in ceramic samples with different waste addition of $CaCO_3$, $Ca(OH)_2$, marble dust and plaster cast was studied in [4]. In every case, two steps in the creation of anorthite were confirmed – first, gehlenit appeared in the exothermic reaction at 950 °C and second, anorthite appeared in the exothermic reaction at 980 °C. Similar results were obtained in [5].

Since the ceramic sample contains kaolinite and/or illite as plastic constituents, dehydroxylation in the temperature region 450 °C–650 °C takes place. This endothermic process is linked to a significant mass loss. A contraction of the kaolinite volume is also registered. The volume of the illite continues to expand in this temperature region [6,7]. Both crystalline lattices, metakaolinite and dehydroxylated illite, exothermically collapse at the temperatures above 950 °C which is accompanied with significant volume contraction [6,8].

The next important process is a decomposition of calcite between 750 °C and 850 °C, which presents itself with a high mass loss of the calcite phase (up to 44 wt%) and a volume contraction. The new CaO phase is porous [9,10].

---

[*] Corresponding author. Tel.: +420 54114 7501; fax: +420 54114 7502.
E-mail address: sokolar.r@fce.vutbr.cz (R. Sokolář).

http://dx.doi.org/10.1016/j.ceramint.2012.05.046

If the sample is not dried, physically bounded water is released at temperatures lower than 200 °C [7].

The objective of the paper is an experimental study of phase development and mechanical properties of samples with a different content of calcite waste depending on firing temperature.

2. Experimental

We used three types of samples, see Table 1. Clay B1, supplied by LB-Minerals s.r.o. is a constituent of every sample. As grog we used clay B1 fired at 1000 °C with a soaking time 90 min at the highest temperature. Clay B1 consists of kaolinite (65 wt%), illite (25 wt%), muscovite (3 wt%), 5 wt% of free quartz and 2 wt% of undefined filler [11]. Calcite waste came from crushing of the limestone in quarry Omya, a.s., Vápenná, Czech Republic. Chemical compositions of clay B1 and calcite waste are in Table 2. The calcite waste was dried and then milled for 24 h in the laboratory dry ball mill. The equivalent mean spherical diameter $d(0.5)$ of the milled calcite waste was 17.4 μm (measured with the particle size analyzer Mastersizer 2000).

Grog was ground and sieved and then mixed with clay, milled calcite waste, and water to obtain a plastic mass with water content ~20 wt%. From this plastic mass two types of samples were prepared. One of them was for measurement of Young modulus. These samples were cylindrical and were made with a laboratory extruder. After open air free drying, their dimension was $\emptyset 11 \times 140$ mm. The second type of the samples were of prismatic shape $20 \times 20 \times 100$ mm. These samples were used for measurement of irreversible thermal contraction, flexural strength, absorptivity, volume mass and XRD analysis.

After drying, the samples, both cylindrical and prismatic, were fired at 900 °C, 1000 °C, 1100 °C and 1200 °C. Heating rate was 4 °C min^{-1}.

The bulk density was determined using the Archimedes method (EN ISO 10545-3).

Measurement of Young modulus used method which utilizes a fundamental flexural mode of the resonant vibration of the sample. The resonant frequency, sample dimensions and mass are used for calculating of Young modulus E. For a cylindrical sample with a uniform square cross-section, we have [12]

$$E = 1.65623 \frac{ml^3}{d^4} f^2, \qquad (1)$$

where f is a resonant frequency of the fundamental mode, m is the mass, l is the length and d is the diameter of the sample.

Since the ratio $l/d = 12.7 < 20$, Young modulus must be multiplied by the correction coefficient T_{1c}. Assuming Poisson's ratio $\mu = 0.2$, the correction coefficient was calculated from a formula given in ASTM C 848–88, $T_{1c} = 1.03186$.

The flexural strength was measured using the three-point-bending method on the prismatic samples with square cross-section. The flexural strength σ_f was calculated from formula

$$\sigma_f = \frac{3F_f l}{2a^3}, \qquad (2)$$

where F_f is the maximum loading force at the moment of rupture, l is the span between supports and a is the dimension of the square cross-section.

Water absorption at room temperature E_1 was measured according to DIN 51 056. A sample dried in an oven and cooled (to room temperature) sample was weighed. Then the sample was submerged in water in four steps: 0.25 of the volume immediately after weighing, then 0.5 of the volume after 1 h, then 0.75 of the volume after 1 h, and the full volume after 22 h. The sample stayed submerged in the water for 72 h. The amount of the absorbed water was determined from the masses of the dry and wet sample

$$E_1 = \frac{m_{wet} - m_{dry}}{m_{dry}} \qquad (3)$$

Vacuum-saturated absorption E_2 was measured according to DIN 51 056. The dried sample of the known mass was put into a vacuum chamber. After pumping, pressure of 2500 Pa was held for 15 min. Then water was poured over the sample for 30 min. Afterwards, the vacuum chamber was opened, and the sample remained under water for the next 30 min. Then the sample was weighed. The value E_2 was calculated from the right side of Eq. (3).

The XRD analysis was performed with the diffractometer Phillips PW 1170 with Cu anticathode ($\lambda_{\alpha 1} = 0.15406$ nm), accelerating voltage 40 kV, beam current 25 mA and scanning rate 1° 20′ min^{-1}.

Table 1
Composition of test samples (wt%).

Sample	Clay	Grog	Calcite waste
A	60	40	–
B	60	30	10
C	60	20	20

Table 2
Chemical composition of clay and calcite waste in wt%.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Sulfates	LOI
Clay	48.6	33.8	2.6	0.8	0.28	0.36	1.98	0.10	–	11.3
Calcite waste	0.01	0.08	0.09	0.01	54.55	0.6	0.02	–	0.87	43.77

3. Results and discussion

Creation of new phases during firing at temperatures 900, 1000, 1100 and 1200 °C was studied from the results of XRD analyses, Figs. 1–3. Sample A contained mullite after firing at 1100 °C and cristobalite after firing at 1200 °C. Dmisteibergite $CaO.Al_2O_3.2SiO_2$, which is a hexagonal form of anorthite, was observed in samples B and C after their firing at 900 °C, see Figs. 2 and 3. Dmisteibergite vanished as the firing temperature was increased. It was present in a smaller amount in samples B and C fired at 1000 °C and absented in these samples after firing at 1100 and 1200 °C. Anorthite and mullite become the main crystalline phases. The ratio of anorthite/mullite depends on the firing temperature and the initial amount of calcite. The higher the temperature of the firing and the higher the amount of calcite, the higher the amount of anorthite created in the samples.

Results of thermodilatometry are visible in Fig. 4. It is obvious that the presence of calcite in samples B and C decreases their contraction during firing at temperatures above ~850 °C. The same can be said about the final contraction measured at a room temperature, see Table 3. Since the mass of the sample does not change at the highest temperatures, the volume mass follows the sample dimensions, Table 3. Sample C seems to be an exception from

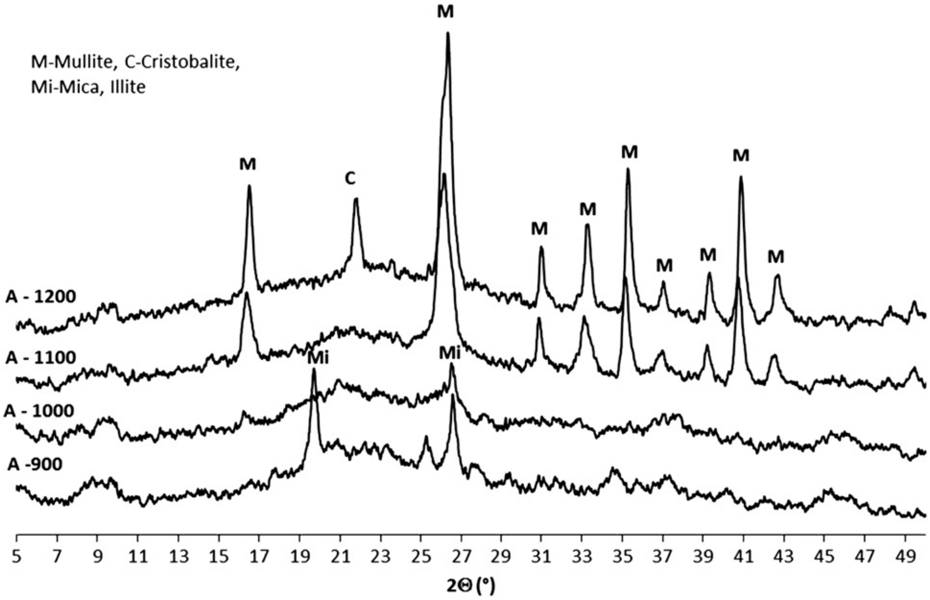

Fig. 1. XRD patterns of the sample A fired at 900, 1000, 1100 and 1200 °C.

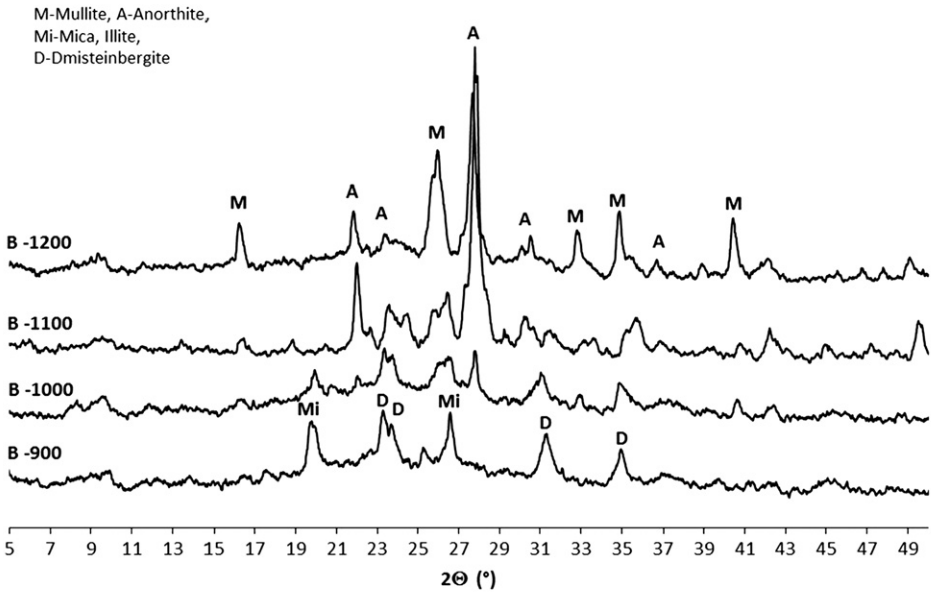

Fig. 2. XRD patterns of the sample B fired at 900, 1000, 1100 and 1200 °C.

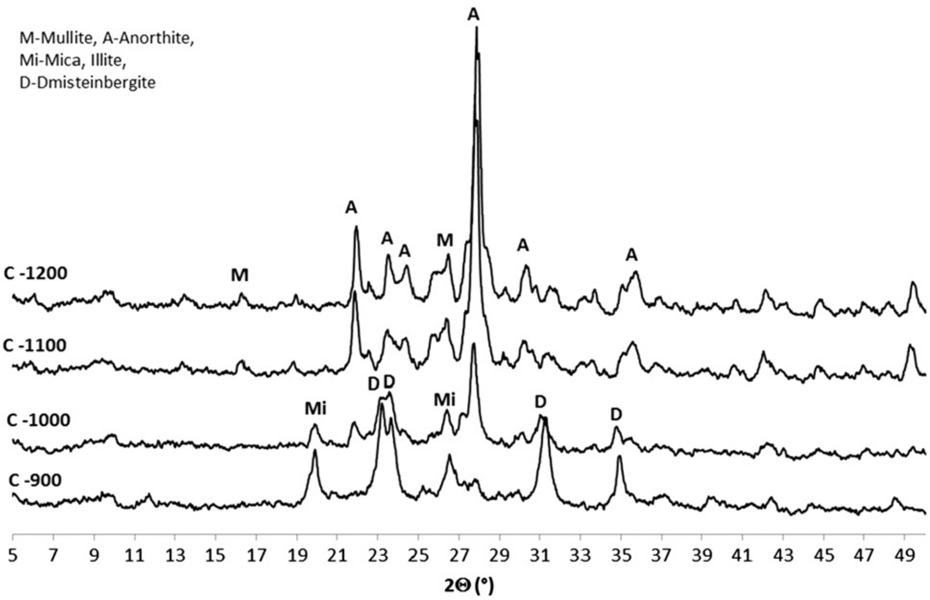

Fig. 3. XRD patterns of the sample C fired at 900, 1000, 1100 and 1200 °C.

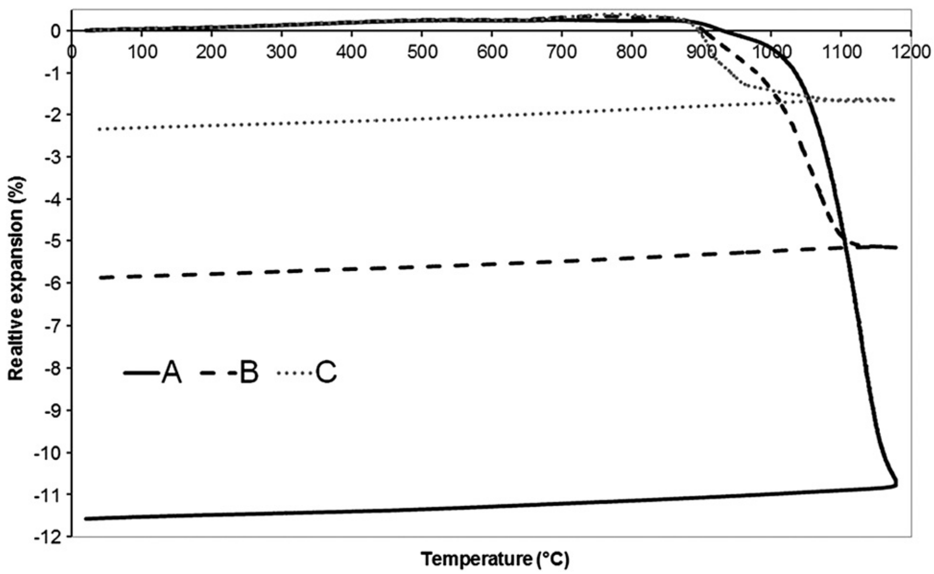

Fig. 4. Thermodilatometric curves of the samples A, B and C.

this rule. A relatively high amount of calcite (20 wt%) causes only a slight increase in the volume density and the final relative contraction. Both absorptivities, water absorption E_1 and vacuum-saturated water absorption E_2, almost do not depend on the firing temperature, Table 3.

Temperatures between 900 °C and 1200 °C can be considered the region of intensive sintering. An admixture of calcite works as a flux and significantly decreases porosity at firing temperature 900 °C and 1000 °C, as is indirectly evident through the water absorptions E_1 and E_2, see Table 3. Sintering also leads to the final contraction, as given in Table 3, as well as to an improvement in Young modulus and flexural mechanical strength, see Table 3. Except for sintering, there is a presence of mullite in the samples fired at 1100 °C and 1200 °C, which also positively contributes to Young modulus and flexural strength.

The development of Young modulus and flexural strength of samples A and B during the increase of the firing temperature is in accordance with decreasing of the absorptivities E_1 and E_2, i.e. with decreasing of the porosity, see Table 3. It is a consequence of sintering and creation of the new phases (mullite and anorthite). The behavior of sample C is different. An increase in the firing temperature has no influence on the porosity and only a small influence on Young modulus and flexural strength, which slightly increase. The development of Young modulus from room temperature up to 1250 °C is illustrated in Fig. 5. Graphs of Young modulus are practically identical

Table 3
Bulk density ρ, relative contraction after firing $\Delta l/l_0$, water absorption E_1 and E_2, Young modulus E and flexural strength σ_f.

Sample	Temperature (°C)	ρ (kg m^{-3})	$\Delta l/l_0$ (%)	E_1 (%)	E_2 (%)	E (GPa)	σ_f (MPa)
A	900	1429	0.74	30.2	32.5	12.48	9.7
	1000	1497	2.91	24.7	26.8	28.83	16.1
	1100	2168	11.52	6.2	7.5	67.21	46.4
	1200	2402	13.11	0.1	0.1	96.67	65.2
B	900	1492	1.34	23.0	28.8	21.07	14.9
	1000	1604	3.89	16.4	22.0	34.38	28.1
	1100	1724	5.88	12.2	17.8	40.71	34.2
	1200	1829	6.01	8.5	14.0	45.23	39.0
C	900	1515	2.07	17.4	23.1	28.85	18.4
	1000	1525	2.69	16.9	23.3	30.68	25.2
	1100	1527	2.77	16.7	26.2	31.60	29.8
	1200	1568	2.91	14.0	25.0	33.23	31.5

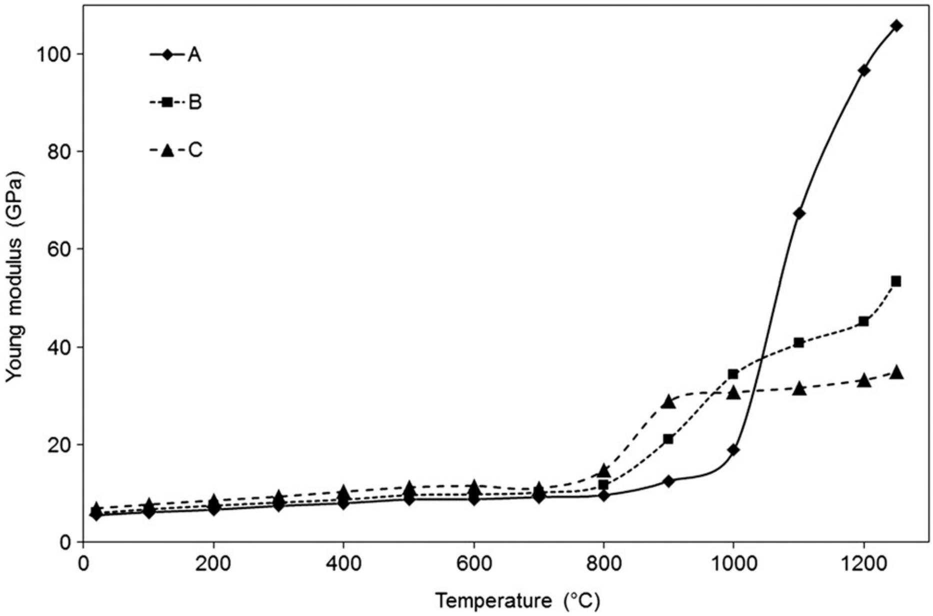

Fig. 5. Dependence of Young modulus on the firing temperature for samples A, B and C.

for temperatures below 700–800 °C which is the temperature region of an intensive decomposition of calcite. This endothermic reaction begins with the formation of mesoporous structure of nanocrystals CaO (~5 nm in thickness) and pores (2–50 nm in diameter) in place of the initial crystals $CaCO_3$ [9]. The presence of these pores can explain why Young modulus stops increasing, which would be expected due to sintering.

Young modulus of sample A, which does not contain calcite, steeply increases in value as the result of sintering. Results for sample B are between the samples A and C. The effect of decomposition of calcite is also evident above ~900 °C, but not as intensively as in sample C.

4. Conclusion

Mechanical properties of three types of samples (reference sample without calcite waste, sample with 10 wt% and sample with 20 wt% of the calcite waste) were investigated after their firing at 900, 1000, 1100 and 1200 °C. It was found that anorthite and mullite are the main crystalline phases of the fired samples containing the calcite waste. The ratio of anorthite/mullite depends on the firing temperature and the initial amount of calcite. The higher the temperature of the firing and the higher the amount of calcite, the more anorthite is created in the samples.

Presence of calcite waste decreases sample contraction during sintering.

Water absorption decreases with an increase in the firing temperature, but the sample with the content of calcite 20 wt% shows approximately constant water absorption.

Mechanical strength and Young modulus of the reference sample and the sample with 10 wt% of calcite increase in their value. These mechanical parameters increase very slightly for the sample with 20 wt% of calcite.

Acknowledgment

This work was supported by the bilateral grant APVV SK-CZ-0005-09 financed by the Ministry of Education of the Czech Republic and Ministry of Education of the Slovak Republic and by the Czech Science Foundation no. P104/10/0885 “Analyzis of waste stone dusts and sludges influence on properties of ceramic body and microstructure” and grant VEGA 1/0216/09.

References

[1] R. Sokolář, Effect of calcite on the brick body closing, Interceram 59 (1) (2010) 57–62.

[2] A. Ruotsala, Solid state formation of anorthite from some clay mineral–calcium mineral mixtures, The American Mineralogist 48 (1963) 792–803.

[3] P. Pytlík, R. Sokolář, Building ceramics. First edition Brno: CERM, 2002 (in Czech).

[4] S. Kurama, E. Ozel, The influence of different CaO source in the production of anorthite ceramics, Ceramics International 35 (2) (2009) 827–830.

[5] K. Traoré, T.S. Kabré, P. Blanchard, Gehlenite and anorthite crystallisation from kaolinite and calcite mix, Ceramics International 29 (4) (2003) 377–383.

[6] A.F. Gualtieri, S. Ferrari, Kinetics of illite dehydroxylation, Physics and Chemistry of Minerals 33 (2006) 490–501.

[7] V. Hanykýř, J. Kutzendorfer, Technology of ceramics. Second editon, Prague: SiliS, 2008 (in Czech).

[8] J. Hlaváč A base of silicate technology. First edition Prague: SNTL 1981 (in Czech).

[9] C. Rodriguez-Navarro, E. Ruiz-Agudo, A. Luque, A.B. Rodriguez-Navarro, M. Ortega-Huertas, Thermal decomposition of calcite: mechanism of formation and textured evolution of CaO nanocrystals, The American Mineralogist 94 (2009) 578–593.

[10] A. Tóth, Investigation of limestone during and after thermal treatment. Ph.D. thesis, UKF Nitra, Nitra 2010 (in Slovak).

[11] R. Sokolář, L. Vodová, The effect of fluidized fly ash on the properties of dry pressed ceramic tiles based on fly ash – clay body, Ceramics International 37 (7) (2011) 2879–2885.

[12] I. Štubňa, A. Trník, L. Vozár, Determination of Young’s modulus of ceramics from flexural vibration at elevated temperatures, Acta Acustica united with Acustica 97 (1) (2011) 97–101.