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Investigations of Thermal Properties of Glass-Crystalline Samples from CMAS System by the Nondestructive Photoacoustic Method

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Abstract

The goal of investigations presented in this paper was to change the microstructure of a glass-crystalline material in order to improve its thermal diffusivity. Thermal diffusivity is an important thermo-physical parameter, which determinates the diffusion of heat through a sample. The paper presents results of nondestructive photoacoustic (PA) studies of this parameter for investigated ceramic material. The thermal diffusivity values are evaluated by the fitting of amplitude and phase theoretical characteristics to experimental data in a proposed PA model. The analysis of the data shows that the change of the microstructure of a glass-crystalline material successfully changes the thermal parameters of investigated ceramic material.

Keywords: Glass-ceramics, Thermal diffusivity, Nondestructive testing, Photoacoustics

BADANIA WŁAŚCIWOŚCI CIEPLNYCH SZKŁO-KRYSTALICZNYCH PRÓBEK Z UKŁADU CMAS ZA POMOCĄ NIENISZCZĄCEJ METODY FOTOAKUSTYCZNEJ

Celem badań przedstawionych w artykule było osiągnięcie zmiany mikrostruktury materiału szkło-krystalicznego poprawiającej jego dyfuzyjność cieplną. Dyfuzyjność cieplna jest ważnym parametrem termo-fizycznym, który charakteryzuje dyfuzję ciepła przez próbkę. Artykuł pokazuje wyniki nieniszczących badań fotoakustycznych (PA) tego parametru dla badanego materiału ceramicznego. Wartości dyfuzyjności cieplnej określane są w proponowanym modelu PA za pomocą dopasowania teoretycznych charakterystyk amplitudowej i fazowej do danych doświadczalnych. Analiza wyników pokazuje, że zmiana mikrostruktury materiału szkło-krystalicznego z powodzeniem zmienia właściwości parametrów cieplnych badanego materiału ceramicznego.

Słowa kluczowe: szkło-ceramika, dyfuzyjność cieplna, badania nieniszczące, fotoakustyka

1. Introduction

Nowadays ceramic materials are very useful for wide potential applications as materials working under conditions of high mechanical and thermal loads [1-2]. Glass-ceramic materials are polycrystalline solids which are prepared by the controlled crystallization [3]. By a proper selection of a chemical composition to obtain specified crystalline phases, it was possible to design materials for specific applications, *e.g.*, body stubs in microelectronics, biomaterials, composite fillers, bonding materials, high-duty and hard materials resistant to wear [4-5]. Mechanical properties of materials could be controlled by many ways, *e.g.*, by generation of a new, additional phase in a glass residue, introduction of an additional component in the form of fibres or particles into the matrix.

The goal of investigations presented in this paper was to change the microstructure of a glass-crystalline material in order to improve its thermal diffusivity. The glass-ceramic material of two-phase composition with precipitation of crystallites from islet silicates Zn_2SiO_4 and a crystalline phase from a spinel group, gahnit $ZnAl_2O_4$ was obtained in the system under investigation. It was revealed that in the test materials from a CMAS group one could obtain the crystalline phase in the form of ghanit as a result of a controlled process of crystallisation and heat treatment [6]. The occurrence of a single spinel phase caused that the obtained glass-ceramic material had higher thermal diffusivity than the material containing both willemite and gahnite crystalline phases typical for this system.

Thermal properties of ceramics are essentially determined by the phase composition and structure. Heat diffusion in materials like ceramics is determined by the thermal diffusivity value. To obtain thermal parameters of investigated materials the nondestructive photoacoustic method was successfully applied. Several methods for nondestructive characterization of thermal and optical parameters have been developed for the last years [7-12]. Photoacoustic method has gained more popularity and found important applications in research and analysis of almost all type of materials [13]. All the photo thermal methods are based on the generation

of thermal waves in the sample as a result of its periodical illumination and next heating the gas in the PA cell. The PA signal is detected as a periodical change of the air pressure in the PA chamber. The thermo diffusion mechanism of the PA effect was described by Rosencwaig and Gersho [14]. For the first time this method was applied by Gosh for the investigations of ZnSeTe mixed crystals [15]. The application of the PA method with the microphone detection was described in the prior papers [16, 17].

2. Experimental details

2.1. Glass-ceramics material heat treatment and chemical composition

Glass-ceramic materials of the following formula $Al_{0.37}B_{0.34}Fe_{0.01}Mg_{0.02}Zn_{0.29}Ca_{0.05}Si_{0.78}O_3$ (Sample A) and $Al_{0.107}B_{0.37}Fe_{0.01}Mg_{0.04}Zn_{0.29}Ca_{0.1}Si_{0.93}O_3$ (Sample B) were obtained by applying a typical glass-making technology. The SEM images of samples A and B are presented in Figs. 1 and 2, respectively.

Raw materials in the form of H_3BO_3, $CaCo_3$, $MgCo_3$, $Al(OH)_3$, SiO_2, FeO and ZnO were molten in a corundum crucible in an electric furnace in the air and at a temperature of 1300ºC for two hours. Molten frit was rapidly cooled down in water prior to drying. Next, the frit was pulverised in a ball grinder until the powder fraction below 63 μm was obtained. Crystallisation of the powdered materials was studied by the DTA method using a thermal analyser manufactured by MOM, Hungary, adapted to work in the air from the ambient temperature to 1000ºC. A powdered test piece 0.8 g in weight was placed in a corundum crucible where corundum was also used as a carrier. Samples Φ15×5 mm in dimension formed from the obtained powder, heat-treated at a temperature of 1100ºC for two hours were the subject of observations focused on the microstructure and determination of fracture toughness. The microstructure of the samples heat-treated and etched with 10 % HF was examined with a scanning electron microscope JEOL JSM-5500 LXJ (Japan).

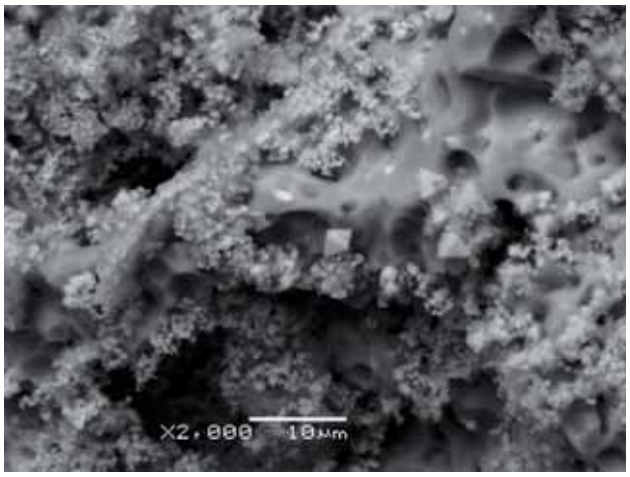

Fig. 1. SEM image of Sample A.

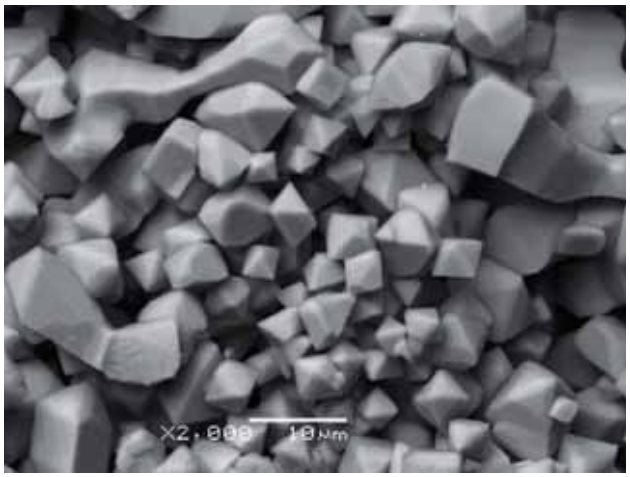

Fig. 2. SEM image of Sample B.

2.2. Measurements

The PA experimental characteristics presented in this paper were measured by the photoacoustic set-up shown in Fig. 3. A very similar set was used for silicon samples characterization described in Ref. [18, 19].

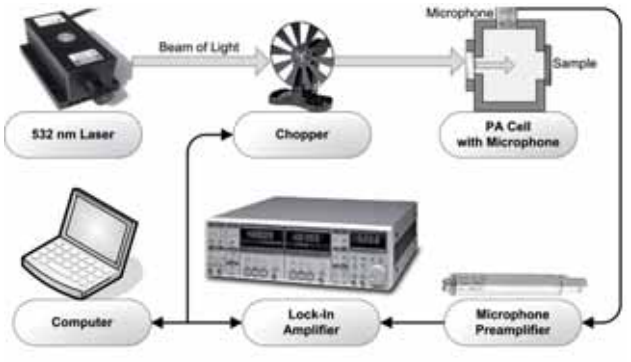

Fig. 3. Schematic diagram of the experimental set-up used in the measurements.

The set-up consisted of a green semiconductor laser (SDL-532-030T), which was the source of an intensity modulated beam of light, and a mechanical modulator (SR540). The PA signal was detected by an electret microphone and was measured by a phase selective lock-in amplifier (Stanford Research SR 830). All measurements were automated and computer controlled.

Thermal diffusivity is a very important parameter which determinates the diffusion of heat through the investigated sample. For determination of the thermal diffusivity of investigated samples the Sf/Sr and PhaseLag PA methods were used [20]. The Sf/Sr and Phase-Lag methods mean that the amplitude ratio and phase difference of PA signals in the front and rear configuration are measured. Each experimental PA characteristics was analyzed numerically in a proposed model given below (1-7):

$$\mu(f,\alpha) = \sqrt{\frac{\alpha}{\pi \cdot f}}, \tag{1}$$

$$\sigma(f,\alpha) = \frac{1+i}{\mu(f,\alpha)}, \tag{2}$$

$$M(f,\alpha,x,\beta,d)=\frac{(e^{\sigma(f,\alpha)\cdot x}+e^{-\sigma(f,\alpha)\cdot x})\cdot(e^{(-\sigma(f,\alpha)-\beta)\cdot x}-e^{(-\sigma(f,\alpha)-\beta)\cdot d})}{\beta+\sigma(f,\alpha)}$$
$$+\frac{R\cdot e^{-2\cdot\sigma(f,\alpha)\cdot d}\cdot e^{\sigma(f,\alpha)\cdot x}+e^{-\sigma(f,\alpha)\cdot x}\cdot(e^{(\sigma(f,\alpha)-\beta)\cdot x}-e^{(\sigma(f,\alpha)-\beta)\cdot d})}{\beta-\sigma(f,\alpha)} \quad (3)$$

$$N(f,\alpha,x,\beta,d)=\frac{(e^{-\sigma(f,\alpha)\cdot x}+R\cdot e^{-2\cdot\sigma(f,\alpha)\cdot d+\sigma(f,\alpha)\cdot x})\cdot(1-e^{(-\sigma(f,\alpha)-\beta)\cdot x})}{\beta+\sigma(f,\alpha)}$$
$$+\frac{e^{-\sigma(f,\alpha)\cdot x}+R\cdot e^{-2\cdot\sigma(f,\alpha)\cdot d+\sigma(f,\alpha)\cdot x}\cdot(1-e^{(\sigma(f,\alpha)-\beta)\cdot x})}{\beta-\sigma(f,\alpha)} \quad (4)$$

$$P(f,\alpha,x,\beta,d)=\frac{\beta\cdot I}{2\cdot\lambda\cdot\sigma(f,\alpha)^2\cdot(1-R\cdot e^{-2\cdot\sigma(f,\alpha)\cdot d})}[M(f,\alpha,x,\beta,d)+N(f,\alpha,x,\beta,d)] \quad (5)$$

$$Amplitude(f,\alpha,x,\beta,d)=|P(f,\alpha,x,\beta,d)| \quad (6)$$

$$Phase(f,\alpha,x,\beta,d)=\frac{180}{\pi}\cdot\arg[P(f,\alpha,x,\beta,d)], \quad (7)$$

where f is a frequency of modulation, α is thermal diffusivity, d is a thickness of the sample, x is a spatial coordinate (x = 0 for illumination configuration and x = d for transmission configuration) and β is a optical absorption coefficient.

Eqs. 8 and 9 describe amplitude ratio and phase difference in reflection (front side) and a transmission (rear side) configuration respectively.

$$\frac{Sf}{Sr}(f,\alpha,\beta,d)=\frac{Amplitude(f,\alpha,0,\beta,d)}{Amplitude(f,\alpha,d,\beta,d)} \quad (8)$$

$$PhaseLag(f,\alpha,\beta,d)=Phase(f,\alpha,0,\beta,d)-Phase(f,\alpha,d,\beta,d) \quad (9)$$

To eliminate any bulk absorption in the sample and obtain only surface absorption ($\beta\to\infty$) samples were pasted on a thermally thin aluminum foil (8 μm) using a thermal paste. The PA amplitude and phase of two samples of the thickness d = 0.105 cm were measured as a function of the modulation frequency. The PA Sf/Sr frequency characteristics for Sample A with SiO_2 addition and Sample B without the composition modification are presented in Fig. 4. The corresponding PA Phase Lag frequency characteristics are presented in Fig. 5.

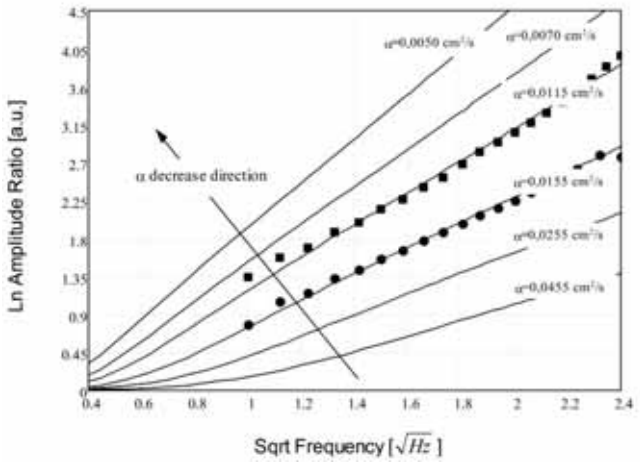

Fig. 4. Experimental and theoretical Sf/Sr characteristics for different thermal diffusivity values. Boxes and circles are experimental data for Sample A and Sample B, respectively.

The solid lines were calculated using Eqs. 8 and 9. From the fitting procedure of theoretical to experimental PA characteristics thermal diffusivity of both samples have been extracted. For Sample A and Sample B (Figs. 1 and 2), thermal diffusivity was estimated as α_A = 0.0115 cm²/s and α_B = 0.0155 cm²/s, respectively.

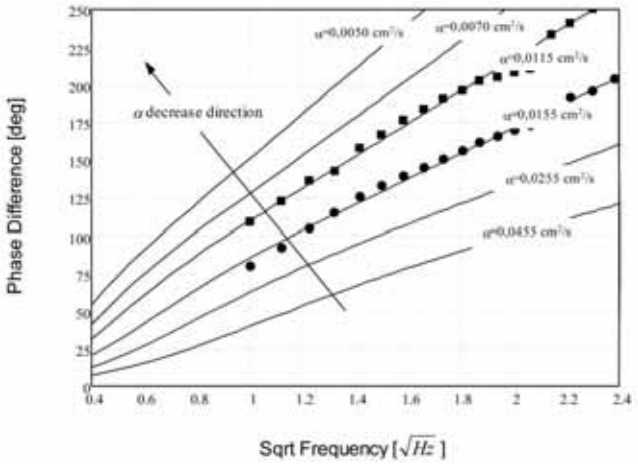

Fig. 5. Experimental and theoretical Phase Lag characteristics for different thermal diffusivity values. Boxes and circles are experimental data for Sample A and Sample B, respectively.

3. Results and discussion

In summary, we have investigated the thermal diffusivity of glass-crystalline samples from CMAS system by the photoacoustic nondestructive technique. By generating single gahnite $ZnAl_2O_4$ phase (Sample B) in the system being tested due to elimination of willemite Zn_2SiO_4 phases, it was possible to increase the thermal diffusivity by 35 %, which is worth mentioning from a view point of their potential application as materials working under conditions of high thermal loads. Due to the heat treatment at the temperature exceeding 920°C, it was possible to obtain materials with

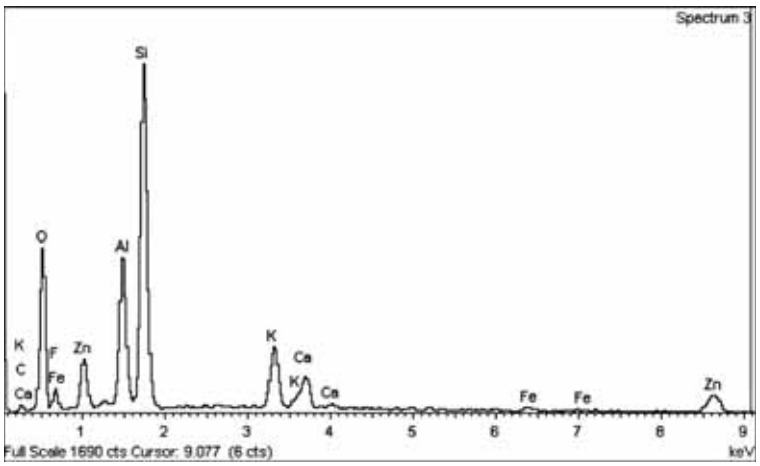

Fig. 6. EDS of heat treated material for 2 h at 1000°C (Sample A).

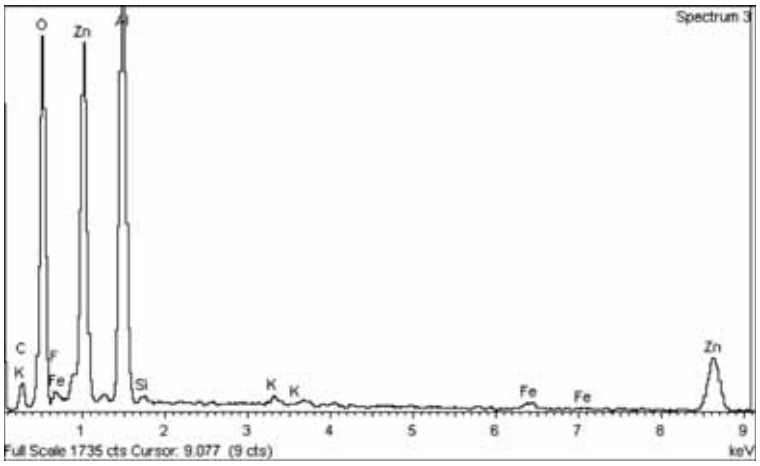

Fig. 7. EDS of heat treated material for 2 h at 1000°C (Sample B).

high level of crystallity with a fine-crystalline phase where the main crystalline phase was in the form of gahnite. As SiO_2 content increased, the willemite (Zn_2SiO_4) was crystallized and the value of thermal diffusivity decreased. The addition of SiO_2 to the glass-ceramic material of the following formula $Al_{0.37}B_{0.34}Fe_{0.01}Mg_{0.02}Zn_{0.29}Ca_{0.05}Si_{0.78}O_3$ inhibits strongly the grain growth of gahnite ($ZnAl_2O_4$). As a temperature of heat treatment was increasing the willemite phase was decaying in favour of gahnite formation. Due to heat treatment at the temperature exceeding 920°C, it was possible to obtain materials with a fine-crystalline phase where the main crystalline phase was in the form of gahnite (Fig. 6 for Sample A and Fig. 7 for Sample B). By generating gahnite in Sample B being tested due to elimination of pyroxene phases, it was possible to increase the thermal diffusivity of material from this group, which was worth mentioning from a viewpoint of their potential application as materials working under conditions of high thermal loads. The presented study shows that the PA technique is an effective tool for thermal characterization of ceramic materials.

4. Conclusions

The presented application of nondestructive photoacoustic spectroscopy clearly shows this technique as an effective tool for the investigation of thermal properties of ceramic materials. The results of investigations performed on different ceramic materials are presented. Experimental photoacoustic amplitude and phase characteristics have been numerically analyzed and values of the thermal diffusivity of the materials extracted. Due to the changes in chemical composition of $Al_{0.37}B_{0.34}Fe_{0.01}Mg_{0.02}Zn_{0.29}Ca_{0.05}Si_{0.78}O_3$, it was possible to obtain glass-crystalline material with a spinel main crystalline phase (gahnite) as a result of heat treatment at the temperature exceeding 920°C. The material with a high crystallinity level containing the fine-crystalline phase of gahnite had better thermal properties than the material represented by the $Al_{0.107}B_{0.37}Fe_{0.01}Mg_{0.04}Zn_{0.29}Ca_{0.1}Si_{0.93}O_3$ formula. An occurrence of the gahnite crystals causes an increase of the thermal diffusivity by 35 % in comparison with the material where willemite was present as a second crystal phase. If the SiO_2 content increases in the material, willemite can crystallize as a second phase and the thermal diffusivity decreases. The goal of investigations presented was to improve thermal diffusivity of the glass-crystalline material investigated by the nondestructive photoacoustic technique.

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