Activation of colour changes in ceramic glazes by means of the Nd:YAG picosecond laser

M. Strzelec,*[1] J. Marczak,[1] D. Chmielewska,[2] A. Sarzyński,[1] A. Olszyna,[2] K. Szamałek,[2] and D. Zasada,[3]

[1]*Institute of Optoelectronics, Military University of Technology (MUT), Gen. S. Kaliskiego 2, 00-908 Warszawa,*
[2]*Institute of Ceramics and Building Materials, Postępu 9, 02-676 Warszawa,*
[3]*Faculty of Advanced Technology and Chemistry, MUT, Gen. S. Kaliskiego 2, 00-908 Warszawa*

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Abstract—The authors present the results of experiments associated with colour changes of various ceramic colouring agents utilised in marking and decorating ceramics after its illumination by means of the Nd:YAG picosecond laser. The photographic illustration of the illumination effects was complemented by the results of examinations regarding surface topography and substantial chemical modifications of ceramic materials detected by using methods of materials science.

The progress in laser and computer techniques, along with the fast development of process control software near the end of the 20th century resulted in a rapid increase of industrial usages of laser radiation, including processing [1-2] of ceramic materials followed by their decoration [3-7]. This has inspired numerous applications of a variety of patent claims [8-11]. An interesting type of ceramic product marking technique may be based on a permanent change in the colour of the ceramic glaze itself after laser irradiation without providing the surface with additional materials [12]. The main advantage is the fact that although specific materials change their colour after laser illumination in a consistent manner due to various chemical or physical processes, their surface remains intact, smooth and shiny (Fig. 1). This method of colour change is hereinafter referred to as activation.

The results of experiments regarding laser activation of various ceramic colouring agents utilised in the decoration of ceramics and designed in the Warsaw Institute of Ceramics and Building Materials have been presented in this article. The exact compositions of the glazes are not quoted due to patent pending procedures. The experimental arrangement for ceramic glaze activation consisted of a model PL 2210 diode-pumped Nd:YAG picosecond laser from the EKSPLA company, Lithuania, with a pulse duration of 70ps, a maximum output energy of 2.4mJ and a pulse repetition frequency of 1kHz along with a coupled, computer-controlled "galvo" scanner from the Raylase company, Germany. The scanning speed was programmable within the range between 2 and 10 000mm/s. Illumination of the ceramic glazes was tested using a primary wavelength of 1064nm and two laser harmonics (532nm; 355nm). The best results are presented below, having been obtained in the green range of radiation (532nm).

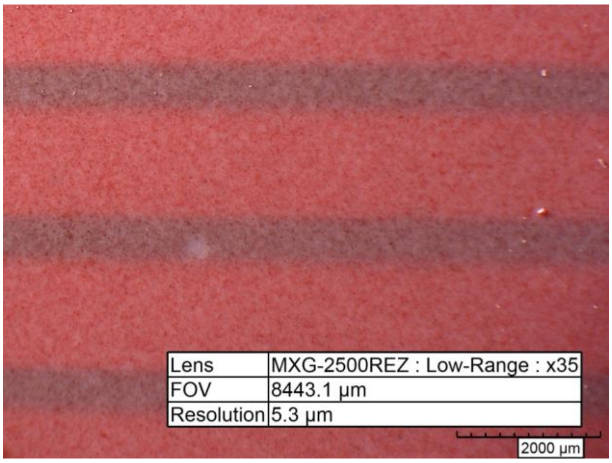

Fig. 1. Change in the violet colour of glaze with a working designation of KT-R15 on a ceramic plate after illumination using radiation with a wavelength of 532nm. The surface photomicrograph taken by means of a Hirox KH 8700 microscope.

The control of glaze colour changes of ceramic and glass products due to laser radiation without affecting the structure and surface smoothness requires the identification of phenomena responsible for these changes. A rather small number of scientific articles related to this subject usually quote the induction of photo-chemical [8, 13] and thermal [14] phenomena, strictly associated with the composition of materials and the parameters of the laser applied, including primarily the wavelength and the density of power absorbed. The effects of the influence of the picosecond laser on the ceramic glaze samples presented in the article were examined by means of a model KH 8700 digital 3D microscope from the Hirox company, Japan (surface topography, cross-sections), a Philips XL-30/LaB6 scanning microscope with an EDS probe enabling to

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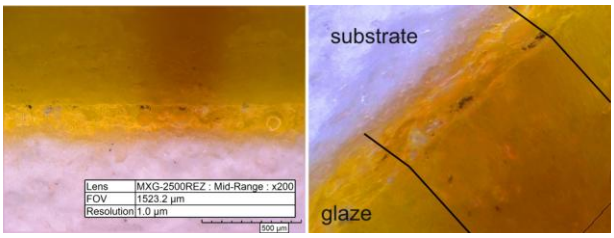
* E-mail: mstrzelec@wat.edu.pl

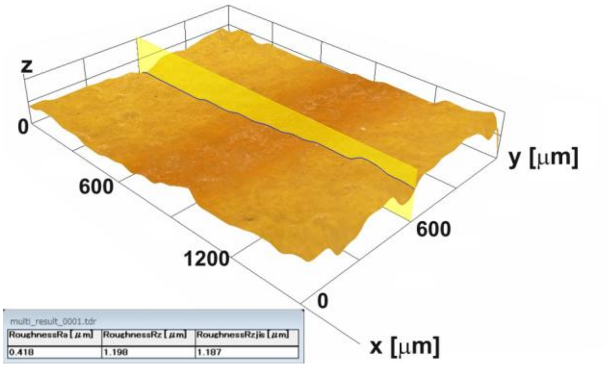
measure the concentration of elements, and a Rigaku Ultima IV X-ray diffractometer.

Figure 2 shows a microscopic cross-section of the laser-activated yellow glaze with a working designation of KT-J15, prepared for X-ray examinations. The photomicrographs, taken while keeping the depth of field with a resolution of 1μm, show that the colour change effect occurs, with its intensity decreasing along with an increase in the depth, virtually within the whole glaze volume in the area affected by the laser beam.



Lens	MXG-2500REZ : Mid-Range : x200
FOV	1523.2 µm
Resolution	1.0 µm

Fig. 2. Microphotographs of the area of yellow colour change of the glaze with a working designation of KT-J15 after irradiating with a picosecond laser beam of 532nm. Laser power/scanning velocity P/v=0.02J/mm.

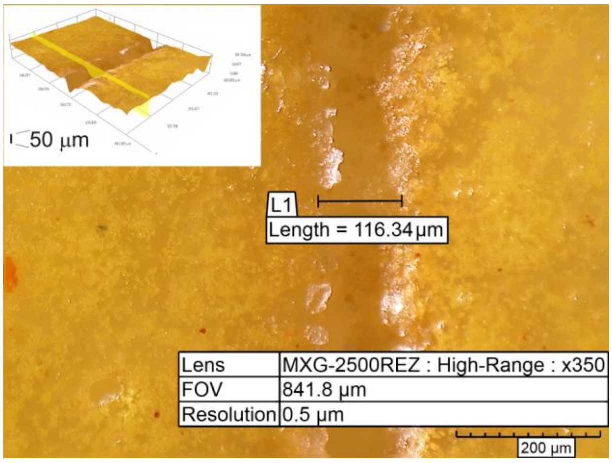


multi_result_0001.tdr

RoughnessRa [µm]	RoughnessRz [µm]	RoughnessRzjis [µm]
0.418	1.198	1.187

Fig. 3. The spatial surface image of the KT-J15 yellow glaze within the area of the colour change path from Fig. 2.

The phenomenon of a ceramic glaze colour change was observed with increasing intensity in the relation between the average laser power and the scanning speed of the beam (energy doses) P/v ranging between 0.01 and 0.03J/mm. At the same time, the surface did not exhibit any significant topography changes, which is confirmed by the 3D image and the results of the measurement of the roughness parameters (Fig. 3). The doses of laser energy higher than 0.03J/mm increased the effect of simultaneous engraving of the sample surfaces. For example, for P/v=0.07J/mm, in the KT-J15 yellow glaze, despite intense penetration by radiation with a 532nm wavelength, the engraving depth reached 50μm (Fig. 4).



Lens	MXG-2500REZ : High-Range : x350
FOV	841.8 µm
Resolution	0.5 µm

Fig. 4. Surface microphotographs of a KT-J15 yellow glaze sample showing distinct material ablation accompanying the colour change when the laser energy dose exceeds its optimum and equals P/v=0.07J/mm.

The observed optical changes of the glaze colour were accompanied by material changes, recorded in a series of X-ray measurements. In the SEM EDS images of the glaze surface within the area affected by the laser beam a rather distinct difference in the composition of elements (Fig. 5a) may be observed, along with a slight decrease in the concentration of oxygen, silicone and zirconium (Fig. 5c-d). These elements are the components of one of the compounds forming the glaze pigment, the zirconium silicate $ZrSiO_4$.

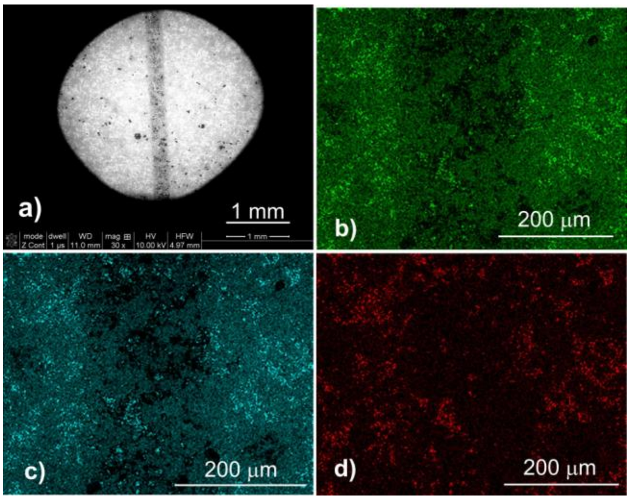


Fig. 5. The SEM EDS maps of the surface area of KT-J15 yellow glaze after laser illumination: a) SEM image (Z cont.); b-d) maps of elements present in the pigment composition: b) oxygen; c) silicone; d) zirconium.

In order to quantitatively determine the changes occurring within the glaze in the direction from the surface towards the ceramic substrate, polished cross-sections of the samples were prepared and SEM EDS measurements were taken regarding the linear distribution of the concentration of elements along the depth of the glaze within the area subject to illumination and next to it. The measurement method is shown in Fig. 6. The recorded changes in the concentration of zirconium silicate components reached, decreasingly, approximately 70μm of the glaze thickness and amounted, on the surface, to approximately 1% for oxygen and silicon and 0.2% for zirconium , respectively.

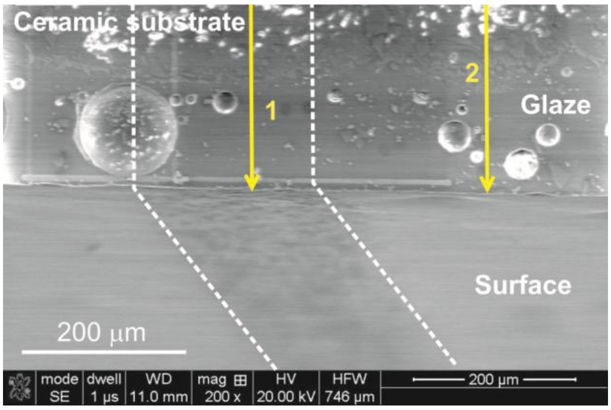


Fig. 6. A SEM image showing the geometry of linear measurement of the distribution of element concentrations in a transverse glaze cross-section. The white dashed lines indicate the approximate activation area. The yellow arrows indicate the direction of measurement within the activated area (1) and next to it (2).

The surface measurement of chemical composition of the glaze within the activated area and before illumination performed using an X-ray diffraction method has confirmed a slight decrease in the concentration of zirconium silicate due to the impact of laser radiation (Fig. 7). Furthermore, no peaks characteristic for other chemical compounds were observed [15]. This indicates the partial decomposition of $ZrSiO_4$ to be the phenomenon responsible for the colour change of the examined glaze due to the influence of the temperature increasing as a result of the volume absorption of laser radiation.

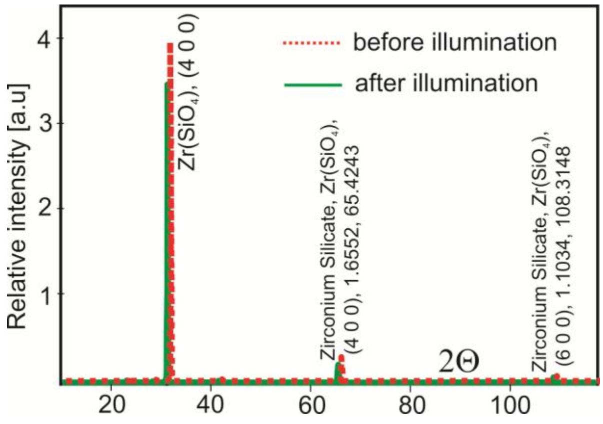


Fig. 7. The XRD spectrum of the KT-J15 yellow glaze surface before and after laser illumination.

The selected examples of activation results for glazes of various original colours have been shown in Fig. 8. The selected spiral pattern ensured a large number of areas for comparative instrumental examinations in the cross-section of the samples.

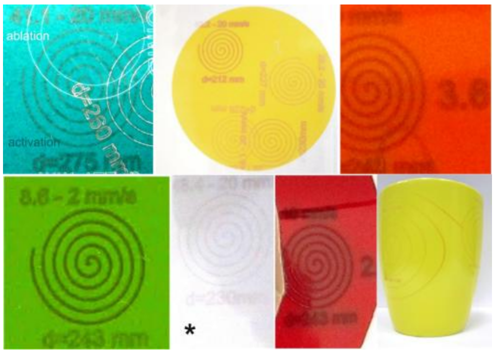


Fig. 8. Examples of activation for selected glaze colours of ceramic products. The asterisk indicates the white glaze used in typical tableware.

The presented technology may be found useful when marking or decorating short series of ceramic products without the use of screen printing and refiring.

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