Original Article

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SHATTUCKITE SYNTHESIS AND THE PATTERN FORMATION BY THE SCANNING LASER BEAM

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Abstract

Using X-ray diffraction it has been demonstrated that polycrystalline shattuckite can be synthesized by pulsed IR laser excitation of the thin layer of $CuCl_2$ aqueous solution with an organosilicon compound placed upon a paper or polymeric film substrate. This process can be realized directly in standard atmospheric conditions at room temperature. Samples exhibit change of colour at different angles of illumination due to birefringence and interference. Any desired pattern can be obtained by scanning of a laser beam on the substrate surface.
Keywords: Synthesis; Shattuckite; Diffraction.

1 INTRODUCTION

Shattuckite $Cu_5(SiO_3)_4(OH)_2$ is a copper silicate hydroxide mineral which crystallizes in the orthorhombic dipyramidal crystal structure (Space Group: Pcab). Shattuckite crystal has rather high refractive index $n_\alpha = 1.753$, $n_\beta = 1.782$, $n_\gamma = 1.815$ and exhibit pleochroizm from pale to deep blue [1-3]. Shattuckite has strongly elongated unit cell with cell axial ratios a: b: c = 0.498: 1: 0.272 (a = 0.988 nm, b = 1.981 nm, c = 0.538 nm) [2,3]. For investigation are used natural small crystalline or polycrystalline samples from different mines, which contain different admixtures and obtained results cannot be considered as general. At present there is scanty information about properties of this material [4-6] and methods of its synthesis. As a result in practice it used now as not expensive gem stone in jewelry. In the only reported work of the laboratory shattuckite synthesis [7] the hydrothermal method for crystal growth was used. However, this process takes up to 7 days and requires high pressure and temperature up to 10^3 kg/cm^2 ($\sim 10^8$ Pa) and 500-600°C respectively.

In this work it has been first demonstrated that shattuckite can be synthesized by laser excitation of the thin layer of copper(II) chloride aqueous solution in standard atmospheric conditions at room temperature and any desired shattuckite pattern can be obtained by scanning of the laser beam on the substrate surface.

2 PREPARATION AND PROCESS

As substrates were used banknote paper covered by organosilicon varnish typically applied for paper banknote manufacturing and commercially available polymeric film PET (polyethylene terephthalate) covered with an organosilicon compound protective layer. On the horizontally placed substrate was deposited a layer of saturated $CuCl_2$ aqueous solution.

Samples were irradiated by a single-mode Nd:YAG IR laser with a wavelength 1.06 μm. The pulse duration and laser beam diameter were 10 ns and 20 μm respectively. A single pulse energy was about 10 μJ. It corresponds to the power density in a pulse of the order $\sim 10^8$ W/cm^2 and energy fluence through the irradiated area in a single pulse 3 J/cm^2. The pulse repetition frequency was 3 kHz. The beam was linearly swept irradiating a predetermined area on the substrate matrix forming the pattern shown below. Laser irradiation was carried out in standard air conditions at room temperature. The scanning process was controlled by a computer.

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3 RESULTS OF MEASUREMENTS

The shattuckite crystal structure formation has been determined by means of X-ray diffraction analysis. The measurements were performed on the "ComplefleX" X-ray reflectometer (CDP Systems). For the identification of a crystalline form was used PDF-4 database supplied with the "Phaser-2" diffractometer (Bruker GmbH). As Phaser-2 is a simple powder diffractometer without a sample rocking ability only diffraction measurements of the substrate could be repeated.

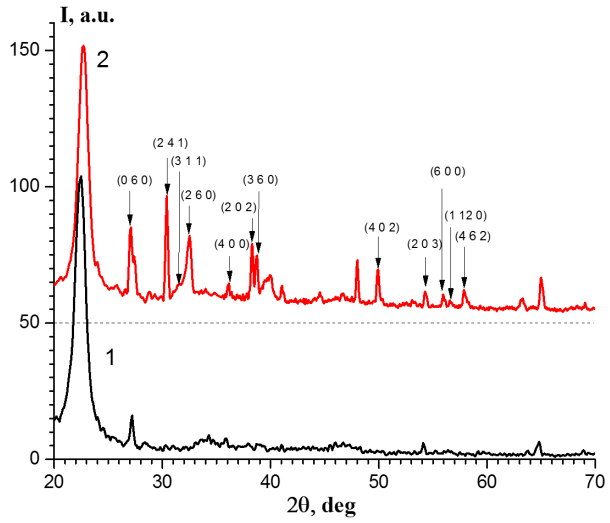

Figure 1. θ−2θ X-ray diffraction scans: 1 – original paper sample; 2 - laser processed paper sample covered by $CuCl_2$ aqueous solution.

The CuK_α spectral line (0.154 nm) was selected by HOPG thin film monochromator placed in a position of a spectrum analyzer in front of an X-ray detector [8]. Diffraction data were measured in the θ−2θ scanning mode with an angle step in a range $\Delta\theta = 0.025 \div 0.05°$. By sample rotating around the normal to the sample surface and its rocking in the angle range (θ-5°, θ+5°) was found the sample orientation providing the maximum number and intensity of diffraction reflexes. X-ray diffraction scans of original (curve 1) and laser processed (curve 2) samples are shown in Figure 1.

The most intense diffraction peak is observed from the paper matrix at $2\theta = 22.67°$. It was used for diffraction data normalization. The experimental curve 2 was moved up for convenience of comparison. As can be seen from Figure 1 there are at any rate 12 diffraction peaks that can be attributed to shattuckite crystalline form. However, diffraction intensities differ from those tabulated in the PDF-4 database for a homogeneous powder sample. In addition, 9 small peaks approximately coincide with this phase. Other diffraction peaks from matrix can't be with rather high probability attributed to definite crystalline structures.

Optical images of the obtained structures are shown in Figures 2a, b. The pattern is a head profile (15 x 20 mm) formed by the laser beam scanning. The first image (2a) received at a fixed angle of reflection. The second image (2b) received at a variable angle of reflection from a broad spectrum light source. Observed colour changing may be explained by birefringence phenomena, which is characteristic for shattuckite [1].

Atomic force microscopy images of the laser irradiated sample surface are shown in Figure 3.

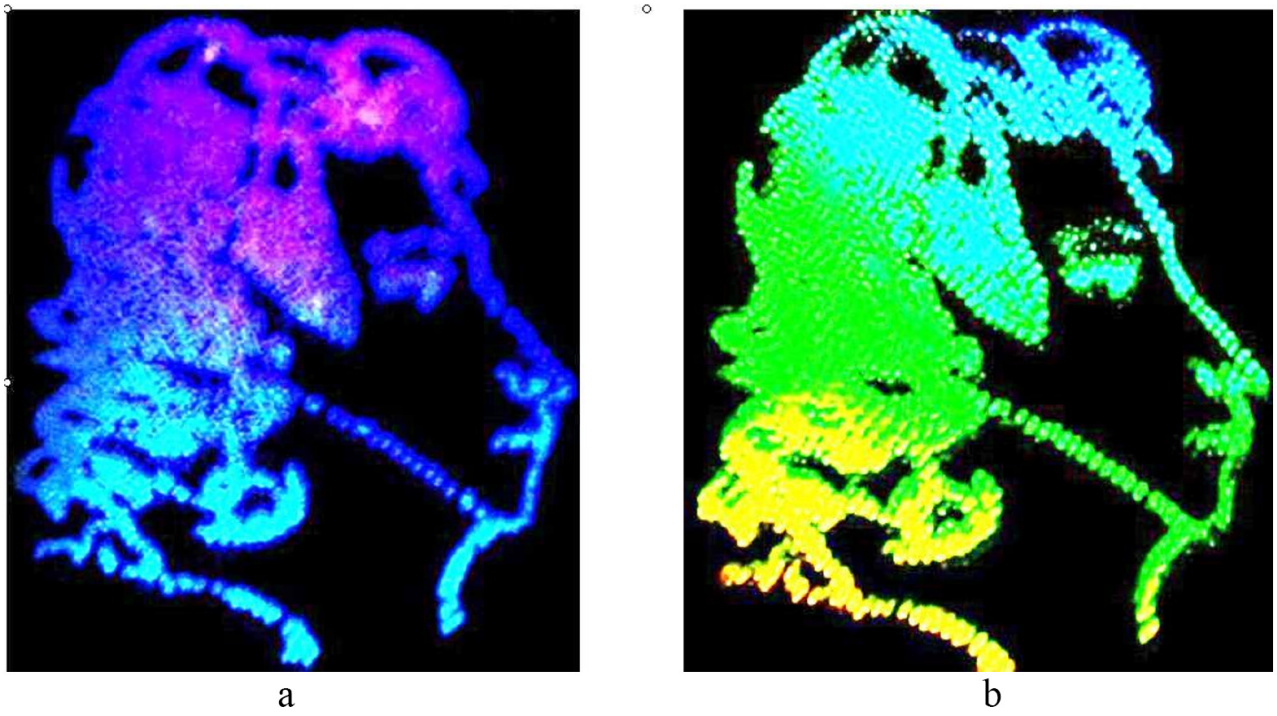

Figure 2. Optical microscopy image of the shattuckite pattern (profile of poet A. Pushkin): (a) fixed light reflection angle; (b) varying reflection angle.

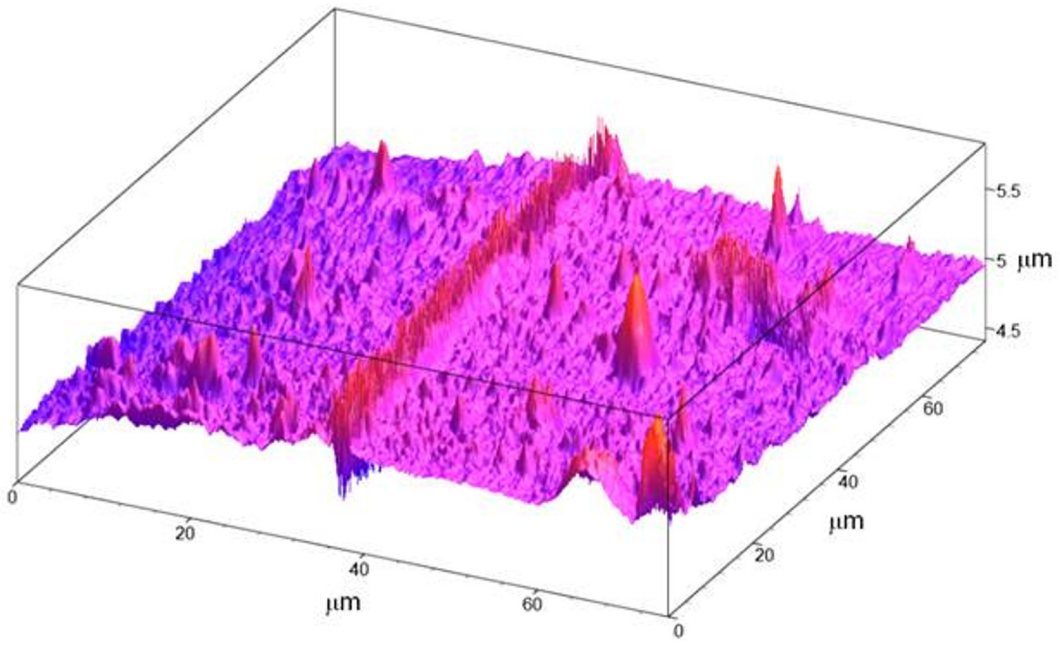

Figure 3. Atomic force microscopy images of the sample surface.

The first specific feature is the formation of sharp pyramid and cone-like structures randomly distributed on the surface with maximum height up to 0.5 μm. Another peculiarity is a wall formed by the densely located pyramids and cones with an average height of 0.3 μm.

4 DISCUSSION

The above mentioned power density of a laser pulse and energy fluence result in the explosive boiling state in the irradiated sample area [9] which is quickly cooled. According to experimental measurements and calculations [10] the maximum temperature during laser irradiation may be in range 3000-3500°C. One may conjecture that high pressure required for shattuckite growth are created due to an acoustic pressure accompanying pulsed laser heating of the paper matrix with deposited $CuCl_2$ aqueous solution. The crystal growth should be very fast during a time range of a few milliseconds. In case of sequential linear scan mode the heat flux front created by laser irradiation primarily moves in the direction perpendicular to a line scan. It reasonable to expect that in this direction large mechanical stress should be created that leads to rotational displacement of shattuckite grains. It explains strong orientation dependence of the X-ray diffraction intensity. Formation of pyramid walls may be also explained by the movement of a heat flux front and probably by interaction of adjacent heat flux fronts generated by sequential laser line scans. Like a natural shattuckite, obtained crystalline structures are unsolvable in water and weak acids that may be considered as additional proof in favor X-ray data identification. It is reasonable to assume that by changing irradiation conditions and deposited layer composition other materials may be synthesized by this method.

5 CONCLUSION

We hope that the discovered technique of shattuckite synthesis by laser irradiation and formation of any desired pattern by a laser scanning beam should stimulate more detailed shattuckite properties investigation and search of its useful applications. From practical point of view, it is very important that this process can be realized directly in standard atmospheric condition at room temperature and total scan time of an area ~1 cm^2 may require less than 1 s.

REFERENCES

1 Bowell R, Cook R. Connoisseur's Choice: Shattuckite, Kunene District, Kaokoveld, Namibia. Rocks and Minerals. 2009;84(6):544-550. http://dx.doi.org/10.1080/00357520903272231.

2 Evans HT, Mrose ME. The crystal chemistry of the hydrous copper silicates, shattuckite and planchéite. The American Mineralogist. 1977;62(5-6):491-502.

3 Anthony JW, Bideaux RA, Bladh KW, Nichols MC, editors. Handbook of mineralogy. Arizona: Mineral Data Publishing; 2003. (vol. 2).

4 Sarma KBN, Reddy BJ, Lakshman SVJ. Absorption spectra of Cu^{2+} in shattuckite and plancheite. Physics Letters. [Part A]. 1982;92(6):305-308. http://dx.doi.org/10.1016/0375-9601(82)90093-7.

5 Frost RL, Xi Y. Raman spectroscopic study of the mineral shattuckite $Cu_5(SiO_3)_4(OH)_2$. Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy. 2012;87:241-244. http://dx.doi.org/10.1016/j.saa.2011.11.046. PMid:22177220.

6 Koshelev AV, Zvereva EA, Chareev DA, Volkova OS, Vymazalova A, Laufek F, et al. The long-range magnetic order and underlying spin model in shattuckite Cu5(SiO3)4(OH). Physics and Chemistry of Minerals. 2016;43(1):43-49. http://dx.doi.org/10.1007/s00269-015-0772-7.

7 Kawamura K, Kawahara A. The crystal structure of synthetic copper sodium silicate: Cu_3Na_2 (Si_4O_{12}). Acta Crystallographica. 1976;B32(8):2419-2422. http://dx.doi.org/10.1107/S0567740876007887.

8 Tur'yanskiĭ AG, Aprelov SA, Gerasimenko NN, Pirshin IV, Senkov VM. Relative X-ray reflectometry of discrete layered structures. Technical Physics Letters. 2007;33(3):224-227. http://dx.doi.org/10.1134/S1063785007030121.

9 Kudryashov SI, Lyon K, Allen SD. Near-field thermal radiative transfer and thermoacoustic effects from vapor plumes produced by pulsed CO_2 laser ablation of bulk water. Journal of Applied Physics. 2006;100(12):124908. http://dx.doi.org/10.1063/1.2402388.

10 Vodop'yanov LK, Kozlov PS, Kucherenko IV, Maksimovskii SN, Radutskii GA. Studying the possibility of applying the light-hydraulic effect to digital printing. Instruments and Experimental Techniques. 2003;46(4):549-553. http://dx.doi.org/10.1023/A:1025102703697.

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