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Structure of Cu_6PS_5I Nanoceramics Under the Influence of Sintering Conditions

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Cu_6PS_5I ceramic pellets were produced from a nanocrystalline powder. Different magnitudes of pressure, temperature and time of sintering were used for the samples preparation. Scanning electron microscopy technique was the main instrument of investigations. Hence, SEM-images of fractured surfaces are shown. Relative porosity of the material is also estimated.

Keywords: nanoceramic, superionic, sintering conditions, structure, SEM.

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Introduction

Cu_6PS_5I superionic conductor belongs to the argyrodite family and is promising material for creation of solid-state batteries, electrochemical and optical sensors on their base [1 - 4]. High ionic conductivity at room temperature determines the possibilities of their practical application as solid electrolyte sources of energy, sensors and high-effective capacitors [5, 6]. Bulk Cu_6PS_5I crystals were studied in many papers [1 - 7]. For instance, its structural disordering was investigated in Ref [7]. Nanocrystalline Cu_6PS_5I solid electrolyte and Cu_6PS_5I-based superionic composites were also investigated earlier [8, 9].

The present paper is aimed at the investigations of Cu_6PS_5I nanoceramics structure after sintering in different conditions.

I. Experimental

High-purity Cu, P, S and copper monoiodide, obtained by precipitation from aqueous solutions and distilled in vacuum, were used as initial components for synthesis of Cu_6PS_5I compounds [10]. The nanocrystalline powders were obtained by ball milling the material in a stainless steel cylindrical vial with hardened steel balls. The average grain sizes were determined from the XRD patterns (Fig. 1). Pellets of 8 mm in diameter and 0.2 – 2 mm thick were pressed at certain pressure (up to 250 MPa) and were placed in an evacuated ampoule of quartz glass. The ampoule was heated at a rate 100 K/h to the temperatures up to 600°C and kept at these temperatures during 12 or 24 h. Then the ampoule was cooled to room temperature. Three average grain sizes powders were used for the preparation of ceramic pellets under the different sintering conditions (Table 1).

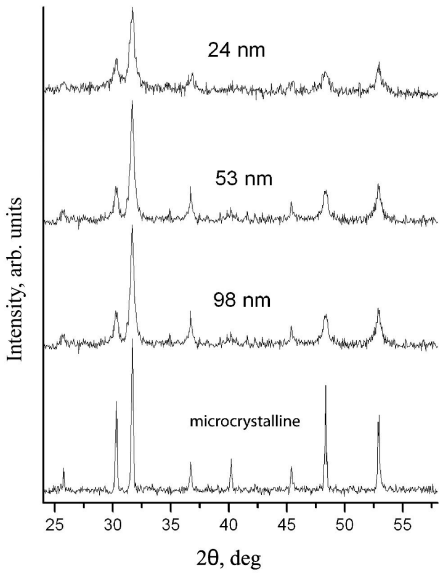

Fig. 1. X-ray diffraction patterns of Cu_6PS_5I: nanocrystalline powders (24, 53 and 98 nm) and the initial microcrystalline powder for the ball milling.

Structural studies were performed using scanning electron microscopy (SEM) technique (Hitachi S-4300), the chemical composition is controlled by energy-dispersive X-ray spectroscopy (EDX) studies which enabled us to check the chemical composition in

Table 1

Sintering conditions for the Cu_6PS_5I nanoceramic preparation

Average grain size, nm	Pressure, MPa	Temperature, °C	Time, hours
98	150, 200, 250	600	24
53	250	400, 500, 600	24
24	250	600	12, 24

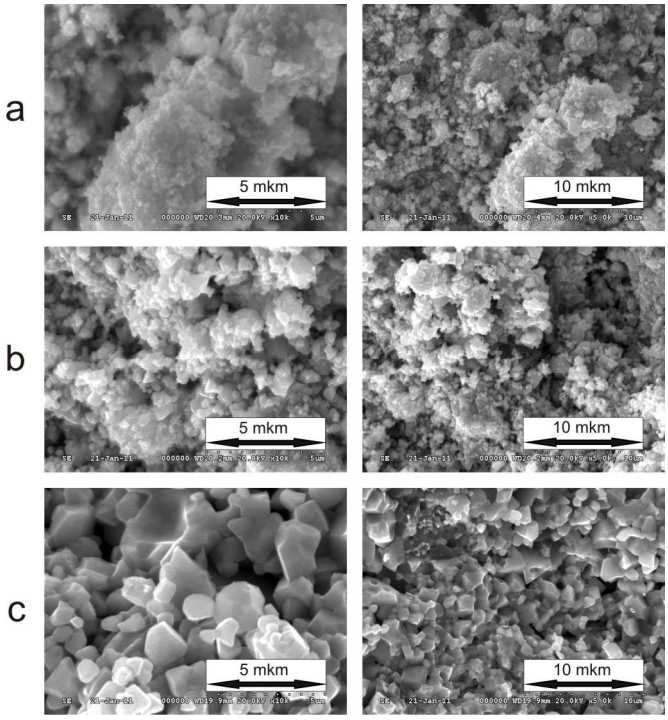

Fig. 2. SEM-images of fractured surfaces on Cu_6PS_5I nanoceramic samples, prepared at different sintering temperatures: 400°C (a), 500°C (b), 600°C (c).

different points of the nanoceramic surface.

II. Results and Discussion

X-ray diffraction analysis has confirmed that Cu_6PS_5I lattice structure is preserved for the nanocrystalline samples, though the diffraction peaks become broader and less pronounced with the decrease in size (Fig. 1).

The structural investigations of ceramical samples sintered in different pressures performed by SEM-technique have revealed almost no significant changes in size of the constituent particles. With sintering temperature increase the size of particles increases. Thus, at 400 °C one can distinguish particles with a size of 50 nm (Fig. 2,a). With further temperature increase the size of particles increases responsibly, becoming of micrometer size (at least 500 nm). Besides, tendency of particles increasing, ordering of a structure and decreasing of porosity is well seen. The structure of a sample, sintered with 600 °C, is more uniform but nevertheless there are some micrometer sized holes in it. A significant change of color with sintering temperature increase is observed (400°C sintered sample has brown color; 500°C sintered sample has orange color; 600°C sintered sample has red color). During the annealing process, nanoparticles of the initial powder become bigger. It is obvious if to compare the SEM-images of the samples, which were annealing for 12 and 24 hours (Fig. 3). After 24 hours of annealing the particles of a sample become of microns order size. The structural investigations of ceramical samples with different

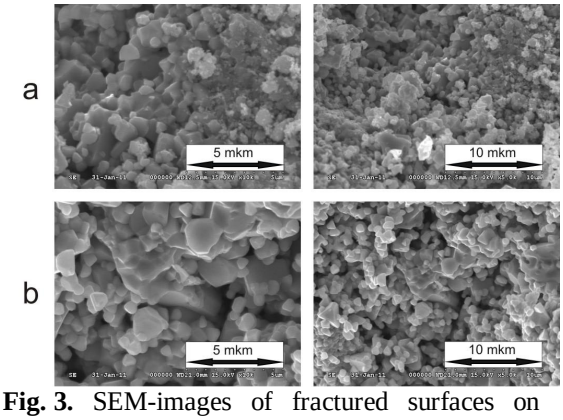

Fig. 3. SEM-images of fractured surfaces on Cu_6PS_5I nanoceramic samples, prepared at different time of sintering: 12 hours (a), 24 hours (b).

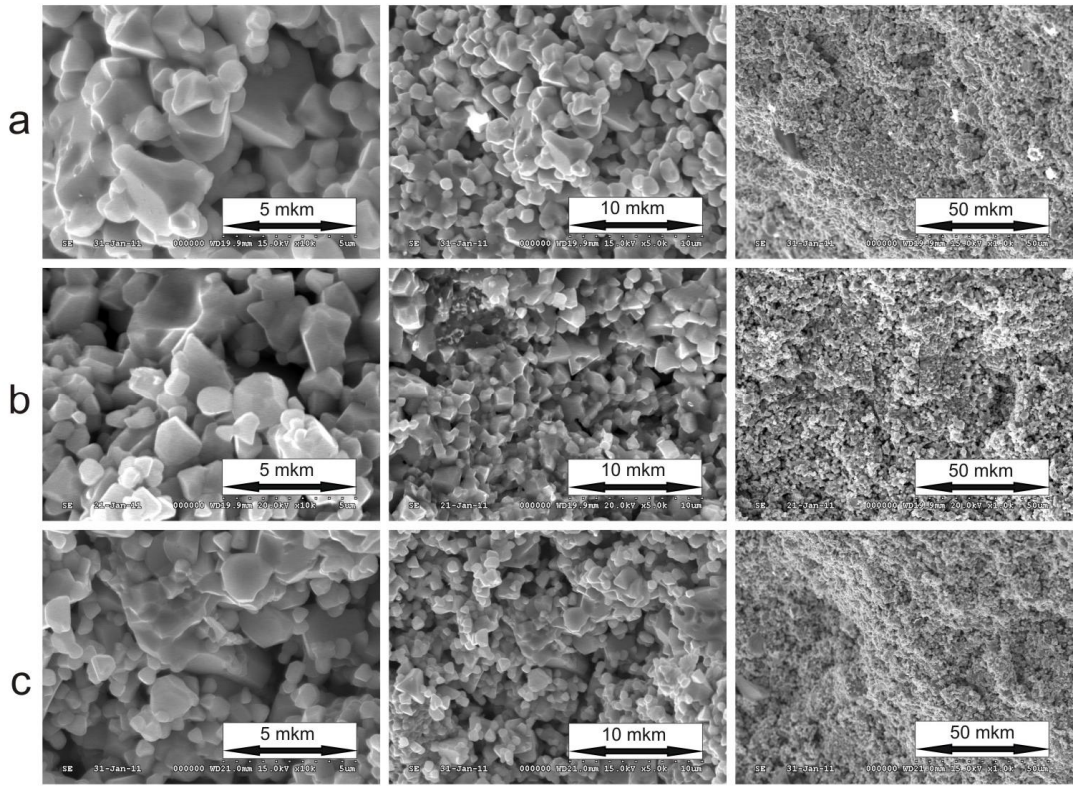

Table 2

Porosity analysis: the area in a color range 0-50 (from 0-255) estimated from SEM-images

Pressure, MPa	150	200	250
Area, %	4.8±0.5	4.9±0.5	4.7±0.5
Temperature, °C	400	500	600
Area, %	13.5±1.4	6.5±0.7	7.0±0.7
Time, hours	12		24
Area, %	6.3±0.6		5.5±0.6
Size, nm	24	53	98
Area, %	5.5+0.6	7.0±0.7	4.7±0.5

average grain size of initial powder sintered in equal conditions performed by SEM-technique have revealed noticeable changes in size of the constituent particles. The SEM-images on ceramic samples sintered in equal conditions with different average grain size of initial powder are shown in Fig. 4.

There is also a black film on the one side of every sample. Its thickness is near 100 micrometer. The EDX measurements showed that the composition of the film includes only Cu and S, which is probably Cu_2S.

Porosity of the material was estimated from the SEM-images. A computer program was used to find the area of an image of a color range from black to dark gray (0-50, where 0 is for black and 255 is for white). The results of such calculations are presented in the Table 2. Results on porosity analysis (estimating accuracy is 10%) show its decrease with the increment of temperature in the range 400-500°C. Initial powder grain size also affects the material porosity (Table 2).

Conclusions

Cu_6PS_5I nanocrystalline ceramic was obtained by ball milling the bulk material and subsequent sintering of the powder. The nano size of grains can be seen on SEM-images. The most significant changes are well seen on the SEM-images of fractured surfaces on Cu_6PS_5I nanoceramic samples, prepared at different sintering temperatures. The dependence on a time of sintering is also obvious. Estimated relative porosity factors (in this case the area of black coloured parts comparatively to the whole area of an SEM-image) help to confirm structural changes in Cu_6PS_5I nanoceramic.

Acknowledgements

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[1] W.F. Kuhs, R. Nitsche, K. Scheunemann. The argyrodites - a new family of tetrahedrally close-packed structures. // *Mater. Res. Bull.*, **14**, p. 241 (1979).

[2] W.F. Kuhs, R. Nitsche, K. Scheunemann. The Crystal Structure of Cu_6PS_5Br, a New Superionic Conductor // *Acta Crystallogr.*, **B34**, p. 64(1978).

[3] I.P. Studenyak, M. Kranjčec, M.V. Kurik. Urbach rule and disordering processes in $Cu_6P(S_{1-x}Se_x)_5Br_{1-y}I_y$ superionic conductors // *J. Phys. Chem. Solids*, **67**, pp. 807-817 (2006).

[4] I.P. Studenyak, R.A. Vaitkus, V.S. Djordjai, A.P. Kežionis, V.F. Mikučionis, V.V. Panko, Gy.Sh. Kovacs, V.A. Stephanovich, A.S. Orliukas, A.N. Borets, V.Yu. Slivka. Phase transitions in Cu_6PS_5I single crystals // ***Fiz. Tverd. Tela,* 28**, pp. 2555-2557 (1986).

[5] I.P. Studenyak, Gy.Sh. Kovacs, A.S. Orliukas, E.T. Kovacs. Temperature variations of dielectric and optical properties in phase transitions regions for $Cu_6PS(Se)_5Hal$ superionic ferroelastics // ***Izv. RAN: ser. fiz.,* 56**, pp. 86-93 (1992).

[6] I.P. Studenyak, V.O. Stefanovich, M. Kranjčec, D.I. Desnica, Yu.M. Azhniuk, Gy.Sh. Kovacs, V.V. Panko. Raman scattering studies of Cu_6PS_5Hal (Hal = Cl, Br, and I) fast-ion conductors // ***Solid State Ionics,* 95**, pp. 221-225 (1997).

[7] I.P. Studenyak, M. Kranjc˘ec, Gy.Sh. Kova´cs, V.V. Panko, V.V. Mitrovcij, O.A. Mikajlo. Structural disordering studies in $Cu_{6+d}PS_5I$ single crystals // ***Materials Science and Engineering,* B97**, pp. 34-38 (2003).

[8] M. Kranjčec, I.P. Studenyak, R.Yu. Buchuk, V.O. Stephanovich, S. Kökényesi, M. Kis-Varga. Structural properties and Raman scattering in Cu_6PS_5X (X=I, Br) nanocrystalline electrolytes // ***Solid State Ionics*, 179**, pp. 218-221 (2008).

[9] A.F. Orliukas, E. Kazakevicius, A. Kezionis, T. Salkus, I.P. Studenyak, R.Yu. Buchuk, I.P. Prits, V.V. Panko. Preparation, electric conductivity and dielectrical properties of Cu_6PS_5I-based superionic composites // ***Solid State Ionics,* 180**, pp. 183-186 (2009).

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Вплив умов спікання на структуру нанокерамік Cu_6PS_5I

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Керамічні таблетки Cu_6PS_5I були виготовлені з нанокристалічного порошку. При виготовленні зразків були використані різні величини тиску, температури і часу спікання. Основним інструментом досліджень був скануючий електронний мікроскоп. Відповідно, показані зображення поверхонь зламу, виконані з допомогою скануючого електронного мікроскопа. Розрахована також і відносна пористість матеріалу.

Ключові слова: нанокераміка, суперіоний провідник, умови спікання, структура, скануючий електронний мікроскоп.