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Structural and temperature-related disordering studies of Cu_6PS_5I amorphous thin films

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ABSTRACT

Cu_6PS_5I thin films were deposited onto silicate glass substrates by non-reactive radio frequency magnetron sputtering. Spectrometric and isoabsorption studies of Cu_6PS_5I thin films in the temperature interval 77–500 K were performed. Structural studies were carried out using X-ray diffraction and scanning electron microscopy techniques. Temperature evolution of optical transmission spectra as well as temperature dependences of optical pseudogap and Urbach energy is investigated. The influence of temperature-related and structural disordering on the Urbach tail is studied.

1. Introduction

Cu_6PS_5I crystal belongs to argyrodite family and is well known as a superionic conductor [1–3]. At room temperature it possesses high ionic conductivity and low activation energy what makes it, similarly to the most efficient solid electrolytes, promising for applications as an electrochemical energy source [4–6]. The efficient ion transport is explained by the specific crystalline structure studied in detail in Refs. [2,7,8]. At room temperature the crystal belongs to cubic syngony while at lower temperatures two phase transitions occur [8].

Dielectric permittivity, specific heat, ultrasound velocity and absorption coefficient as well as their temperature variation in the range of the phase transitions have been studied in Refs. [9–11]. Optical properties of Cu_6PS_5I (Raman scattering, optical absorption, luminescence, refractive index dispersion) were extensively studied [3,4,12–14]. Optical absorption edge studies have shown that at room temperature in the near-edge absorption range exciton bands are observed which broaden with temperature and totally smear out at the superionic phase transition. In the superionic phase, the absorption edge is of exponential shape, its temperature dependence being described by the Urbach rule [12]. The Urbach absorption edge is formed by exciton–phonon interaction, and its additional smearing is caused by temperature-related and structural disordering; the latter in superionic conductors consists of static and dynamic components [12].

Thin films based on advanced superionic conductors can find broad applications for the fabrication of supercapacitors. In comparison with traditional capacitors, they are characterised by small size, high capacitance, radiation and thermal stability [15]. These advantages make this type of capacitors extremely important for the production of self-powered nano- and microsystems as well as efficient energy and power devices on their base.

Here we report on the deposition of Cu_6PS_5I amorphous thin films, their structural investigation as well as isoabsorption and spectrometric studies of the optical absorption edge. Besides, we attempt to analyse the temperature behaviour of the optical pseudogap and the Urbach energy as well as disordering processes in the thin films under investigation.

2. Experimental details

Cu_6PS_5I single crystals were grown using chemical vapour transport method [12]. Cu_6PS_5I thin films were deposited onto a silicate glass substrate by non-reactive radio frequency magnetron sputtering; the film growth rate was 3 nm/min. The sputtering was performed using a 2-inch target at a distance of 90 mm from the substrate with the power of 90 W. The target was prepared by pressing of Cu_6PS_5I polycrystalline powder obtained by grinding

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single crystals in an agate mortar. The deposition was carried out at room temperature in Ar atmosphere.

The structure of the deposited films was analysed by X-ray diffraction; the diffraction pattern, obtained using a DRON-3 diffractometer (conventional $\theta-2\theta$ scanning technique, Bragg angle $2\theta \cong 10$–60°, Cu K_α, Ni filtered radiation), shows the film to be amorphous (Fig. 1). Structural studies were performed for the as-deposited films (Fig. 2) using scanning electron microscopy (SEM) technique (Hitachi S-4300). The uniformity of the film chemical composition is confirmed by energy-dispersive X-ray spectroscopy (EDX) studies which enabled us to check the chemical composition in different points of the film surface.

Ellipsometric parameters were measured at room temperature by a LOMO LEF-3M laser ellipsometer ($\lambda = 632.8$ nm). The original ellipsometric software enabled us to calculate refractive indices and extinction coefficients of the substrate and the film as well as the film thickness by solving the main ellipsometric equation numerically [16]. The Cu_6PS_5I film refractive index determined from the ellipsometry is 2.460 and the film thickness is 512 nm.

Optical transmission spectra of Cu_6PS_5I thin films were studied in the interval of temperatures 77–500 K by an MDR-3 grating monochromator, a UTREX cryostat was used for low-temperature studies. From the temperature studies of interference transmission spectra, the spectral dependences of the absorption coefficient (or the extinction coefficient) as well as dispersion dependences of the refractive index were derived [16].

3. Results and discussion

Interferential transmission spectra of a Cu_6PS_5I thin film at various temperatures within 77–300 K are shown in Fig. 3. With temperature, a red shift of both the short-wavelength part of the absorption spectrum (related to the temperature behaviour of the absorption edge) and the interferential maxima is observed. Besides, a typical decrease of transmission in the interferential maxima with temperature is revealed. Fig. 4 shows the temperature isoabsorption dependences of the characteristic energy E_g^α from the short-wavelength part of the absorption spectrum, corresponding to a fixed absorption coefficient value. At low temperatures, a monotonous decrease of E_g^α is observed while in the high-temperature range at $T > 450$ K a sharp decrease of E_g^α by about 0.125 eV is revealed, corresponding to the film darkening, this process being irreversible (Fig. 4). Curve 4 in Fig. 3 corresponds to the film transmission at $T = 300$ K after it having been heated above the darkening temperature ($T > 470$ K) and cooled to $T = 300$ K. After the heating/cooling cycle the film transmission is seen to decrease almost twice, and the interferential maxima as well as the short-wavelength part of the absorption spectrum are strongly smeared. SEM studies show that at $T > 470$ K the film not only darkens, but is also partly destructed and detached from the substrate (Fig. 5). Besides, white spheres 250 nm to 5 μm in diameter appear on the film surface as well as darkened areas with linear size of 200 nm to 2 μm (Fig. 5). Their chemical composition deviates from that of other film areas. The composition of the spheres appears to be deficient in Cu, S, and I atoms (their content decreases by factor of 1.3–1.4) and enriched in P atoms (their content increases by factor of 2.8). Simultaneously, the chemical composition of the darkened areas differs in all chemical elements of the formula unit from the non-darkened area (Cu and P content decreases by factor of 1.3–1.4 while S and I content decreases by factor of 1.5 and 1.7, respectively).

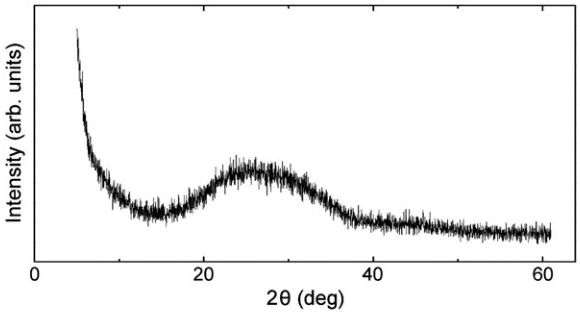

Fig. 1. Diffraction pattern of Cu_6PS_5I thin film at room temperature.

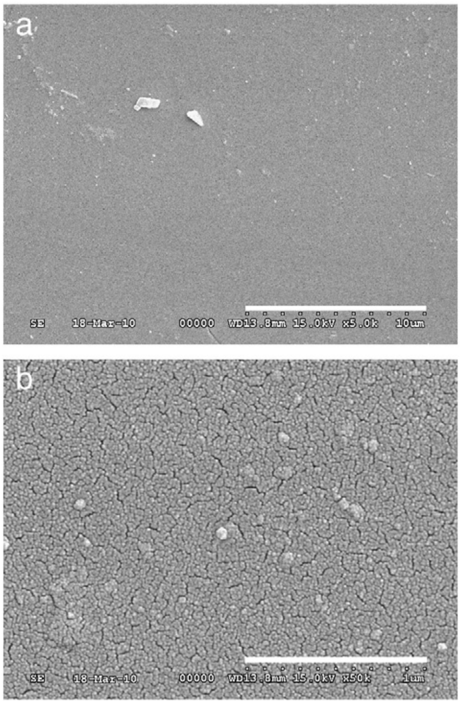

Fig. 2. SEM images of an as-deposited Cu_6PS_5I thin film at different magnification factors. The white bar size is (a) 10 μm, (b) 1 μm.

It is seen (Fig. 6) that the optical absorption edge spectra in the range of their exponential behaviour in amorphous Cu_6PS_5I thin film, similarly to the single crystal, are described by the Urbach rule [17]

$$\alpha(h\nu,\ T) = \alpha_o \cdot \exp\left[\frac{\sigma(h\nu - E_0)}{kT}\right] = \alpha_o \cdot \exp\left[\frac{h\nu - E_0}{E_U(T)}\right] \tag{1}$$

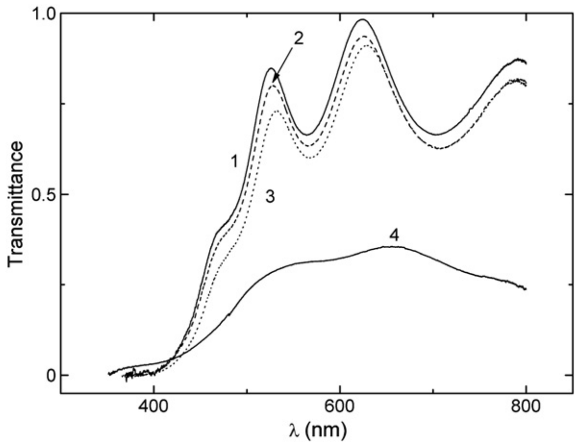

Fig. 3. Spectral dependences of transmission coefficient for Cu_6PS_5I thin film at various temperatures: (1) 77 K, (2) 200 K, (3) 300 K. Curve 4 presents the transmission spectrum at 300 K for the thin film after it being heated above the darkening temperature ($T > 470$ K) and cooled down to 300 K.