

Influence of ion implantation on the phase transitions in Cu_6PS_5I superionic conductors

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Received September 29, 2009

Ion implantation with sulfur as well as the structural studies by scanning electronic microscopy have been performed for Cu_6PS_5I superionic crystals. Using temperature isoabsorption examinations of the optical absorption edge, the influence of ion implantation and annealing on the phase transitions have been studied. Dependences of the temperature and the temperature interval of the superionic phase transition on the fluence value have been obtaineds.

Выполнены ионная имплантация серой и структурные исследования методом сканирующей электронной микроскопии для суперионных кристаллов Cu_6PS_5I. С использованием температурных изоабсорбционных исследований края оптического поглощения изучено влияние ионной имплантации и отжига на фазовые переходы. Получены зависимости температуры и температурного интервала суперионного фазового перехода от величины флюенса.

1. Introduction

Cu_6PS_5I compounds with the argyrodite structure are characterized by high ionic conductivity due to the features of crystal lattice structure [1–3]. At room temperature, Cu_6PS_5I crystals belong to the cubic syngony ($F\bar{4}3m$ space group) [1]. As the temperature decreases, two phase transitions (PT) occur, one of which at T_{II} = (269±2) K is the structural second-order PT (accompanied by the symmetry change $F\bar{4}3m \rightarrow F\bar{4}3c$), while the second at T_I = (144±1) K is simultaneously a superionic and ferroelastic first-order PT (accompanied by the symmetry change $F\bar{4}3c \rightarrow Cc$) [4, 5]. As a result of previous investigations, it is shown that the argyrodite structure crystals are characterized not only by high ionic conductivity but also possess ferroelastic and nonlinear optical properties [7–13]. At present, their structural, electrical, acoustic, calorimetric and some optical properties have been studied in detail [4, 5, 7–12]. Electrochemical sensors, solid electrolyte energy sources, optical temperature and hydrostatical pressure relays using these crystals have been developed [13].

Ion implantation as a method of impurity atoms incorporation became long ago the traditional and high-effective method to vary the properties of solid state materials, that, in turn, has provided fast development of micro- and optoelectronics. Both from the fundamental and applied point of view, it is of interest to investigate the structure modification under external factors, namely, the effects of implantation on fundamental characteristics of superionic conductors. In this connection, the aim of this paper is to study the influence of ion implantation on phase transitions in Cu_6PS_5I superionic crystals.

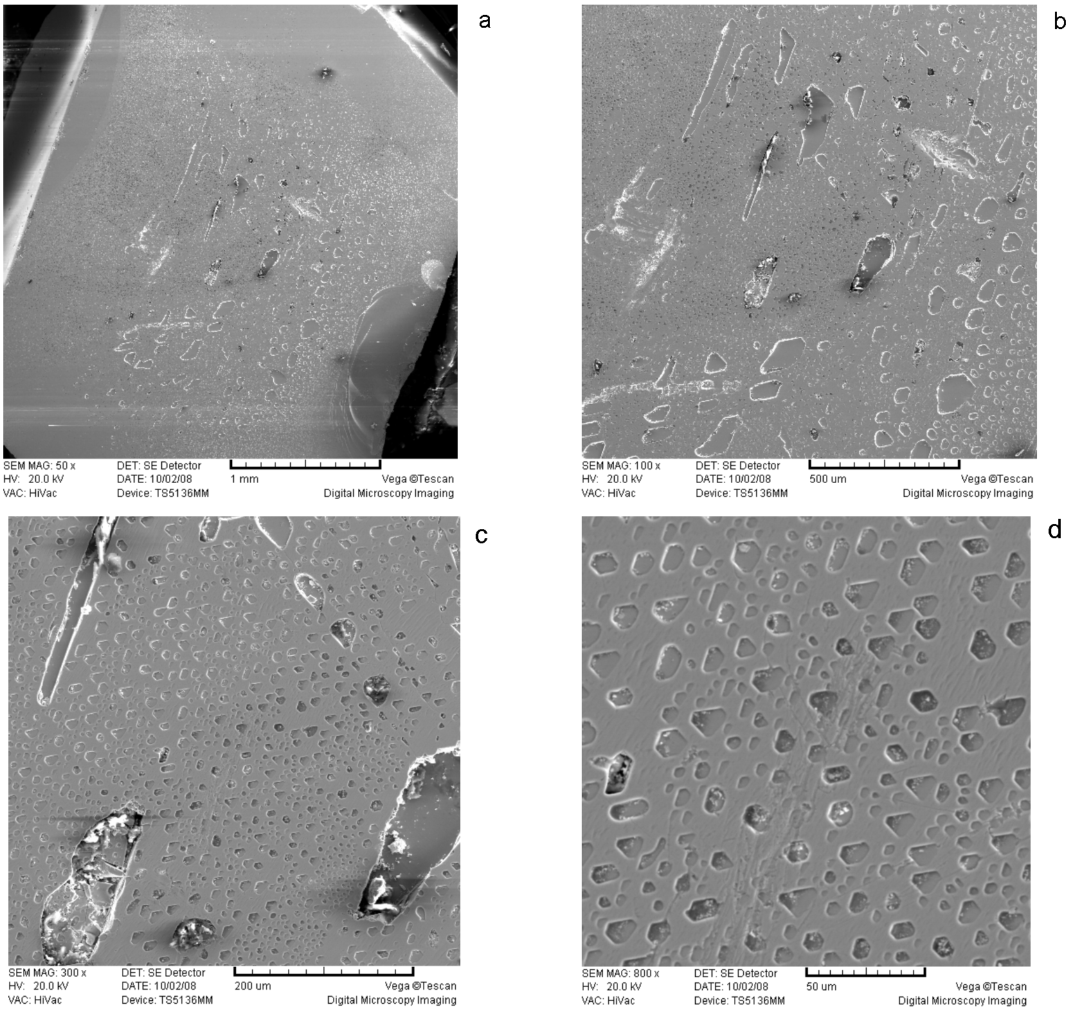

Fig. 1. SEM image of the implanted Cu_6PS_5I crystals (at 1×10^{15} ions/cm^2 fluence) in different scales at different magnifications: a) ×50; b) ×100; c) ×300; d) ×800.

2. Experimental

The synthesis of Cu_6PS_5I compound was carried out as follows [2, 12]. Special purity Cu, P, S, and CuI were charged into a quartz ampoule that was then pumped out down to 10^{-2} Pa, heated at 600 K during 12 hours, then the temperature was elevated up to 973 K and maintained during 24 hours. Further, Cu_6PS_5I single crystals were grown in those ampoules using chemical vapor transport method. CuI in an amount of 10–20 mg per 1 cm^3 of the ampoule free volume was used as the transporting agent. The temperatures of evaporation zone and crystallization zone were kept at 973 K and 923 K, respectively. The grown Cu_6PS_5I single crystals have the shape of plane-parallel plates (5×5×2 mm^3) or distorted tetrahedrons (4×4×4 mm^3).

For implantation, the experimental set-up with magnetic separation and regulative accelerating voltage from 25 kV to 180 kV (9.6×10^{-6} Torr) was used. The incidence angle was 10°, the ion energy 149 keV. Implantation of Cu_6PS_5I crystals was performed using the $^{32}S^+$ isotope obtained in a gaseous state from sulfur powder heated above 400°C and entered into the ionic source. Following the implantation, the samples were annealed in vacuum for 1 h at 200, 400, and 600°C. A TESCAN REM VEGA TS5136MM scanning electron microscope (SEM) was used for the morphological examinations. The isoabsorption studies of optical absorption edge which consisted in determination of the energy position of optical absorption edge $E_g^{\alpha}(T)$ at fixed values of absorption coefficient α and temperature T, were performed using a MDR-3 grating monochromator in the 77–320 K tempera-

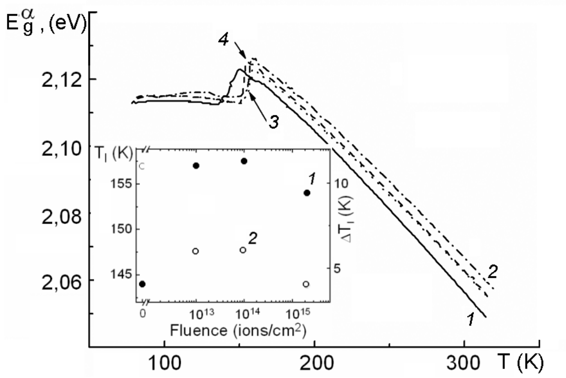

Fig. 2. Temperature dependences of E_g^α (α = 250 cm^{-1}) for the unimplanted (*1*) and implanted Cu_6PS_5I crystals at the different fluence values (ions/cm^2): *2* – $1\cdot10^{13}$, *3* – $1\cdot10^{14}$, *4* – $2\cdot10^{15}$. The inset shows the fluence dependences of the temperature (*1*) and of the temperature interval (*2*) of superionic PT for the implanted Cu_6PS_5I crystals.

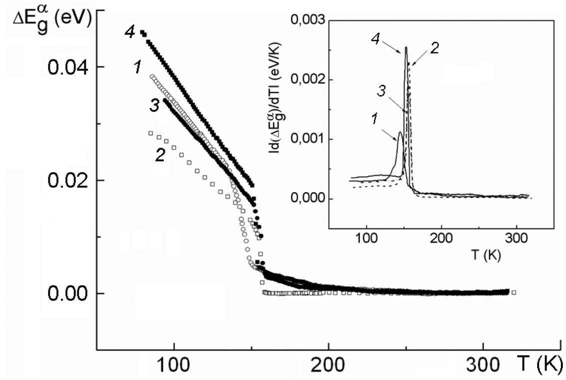

Fig. 3. Temperature dependences of ΔE_g^α at the PT for unimplanted (*1*) and implanted Cu_6PS_5I crystals at different fluence values (ions/cm^2): *2* – $1\cdot10^{13}$, *3* – $1\cdot10^{14}$, *4* –$2\cdot10^{15}$. The inset shows the temperature dependences $|d(\Delta E_g^\alpha)/dT|$ for the unimplanted and implanted Cu_6PS_5I crystals.

ture range; an "UTREX" cryostat was used for low-temperature investigations [12].

3. Results and discussion

The structure of implanted Cu_6PS_5I crystals was studied using the SEM technique. The microcrystals of 5 to 15 μm size were found to be formed on the sample surface as a result of Cu_6PS_5I crystal implantation at $1\cdot10^{15}$ ion/cm^2 fluence (Fig. 1). The so formed induced structural defects can be distinguished from the proper growth defects being microcrystals of 50 to 250 μm size. The X-ray studies of unimplanted and implanted Cu_6PS_5I crystals have shown that a crystal structure typical of the unimplanted Cu_6PS_5I compound is presented in the implanted samples. A good agreement between the X-ray study results of the cubic lattice parameters and reference data [14] was found.

The temperature isoabsorption studies of optical absorption edge allowed us to study the ion implantation effect on the temperature of superionic PT at $T = T_I$ (which simultaneously is ferroelastic) as well as on the realization of superionic and ferroelastic state. At the temperature increase in the 77–139 K range, the energy position of optical absorption edge E_g^α remains almost unchanged; in the range of first-order PT (in the 139–150 K temperature interval), a step of E_g^α is observed ($dE_g^\alpha/dT > 0$); at $T > 150$ K, a nonlinear decrease of E_g^α is observed; in the range of the second-order PT, a slight variation in the nonlinearity slope of the $E_g^\alpha(T)$ being revealed (Fig. 2). In the range of the first-order superionic PT at $T = T_I$, the temperature hysteresis is observed; the PT temperature was determined in the heating mode.

Basing on the experimental data, we have constructed temperature dependences of the ΔE_g^α variation at the PT (Fig. 3) determined as the E_g^α increment in the low-temperature phase ($T < T_{II}$) with respect to the high-temperature one ($T > T_{II}$):

$$\Delta E_g^\alpha(T) = E_{g,l}^\alpha(T) - E_{g,h}^\alpha(T), \qquad (1)$$

where $E_{g,l}^\alpha(T)$ is the absorption edge energy position in the low-temperature phase; $E_{g,h}^\alpha(T)$, the similar value obtained by the extrapolation of the experimental values for the high-temperature phase to the low-temperature range. The $E_{g,h}^\alpha(T)$ values in the low-temperature phase were calculated using the known relation [15]

$$E_g^\alpha(T) = E_g^\alpha(0) - S_g^\alpha k\theta_E\left[\frac{1}{\exp(\theta_E/T) - 1}\right], \qquad (2)$$

where $E_g^\alpha(0)$ is the absorption edge energy position at zero temperature; S_g^α, a dimensionless constant of interaction; θ_E, the Einstein temperature corresponding to the average frequency of phonon excitations in a system of non-interacting oscillators.

Fig. 3 also presents the temperature dependences of the temperature deriva-

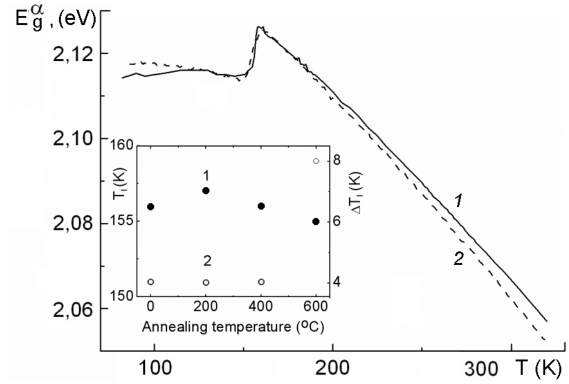

Fig. 4. Temperature dependences of E_g^{α} (α = 250 cm^{-1}) for implanted (at the fluence value $1\cdot10^{13}$ ions/cm^2) non-annealed (*1*) and annealed at 600°C (*2*) Cu_6PS_5I crystals. The inset shows the annealing temperature dependences of the temperature (*1*) and the temperature interval (*2*) of superionic PT for Cu_6PS_5I crystal implanted at the fluence of $1\cdot10^{13}$ ions/cm^2.

tive of the absorption edge energy position variation induced by the PT order parameter which corresponds to the temperature behavior of the anomalous part of specific heat capacity. The temperature dependences of $|d(\Delta E_g^{\alpha})/dT|$ reveal a maximum at the first-order PT which are narrowed with fluence increasing.

The ion implantation of Cu_6PS_5I crystals is shown to result at first in a temperature increasing of the first-order superionic PT at $T = T_I$ from 144 K to 157 K (for the crystal implanted at the fluence of 1×10^{13} ions/cm^2) (Fig. 2). As the fluence increases up to $1\cdot10^{14}$ ions/cm^2, the PT temperature remains almost unchanged, and then decreases to 153 K at the fluence value of $2\cdot10^{15}$ ions/cm^2. Meanwhile, the PT temperature interval becomes narrowed from 11 K to 4 K thus evidencing a structural ordering of the crystal lattice due to the ion implantation.

The influence of isochronous annealing on the PT in Cu_6PS_5I single crystals implanted at the fluence of $1\cdot10^{13}$ ions/cm^2 has been studied. It is shown that as the annealing temperature increases the temperature of first-order PT at $T = T_I$ remains essentially constant while its temperature interval at the annealing temperatures lower than 400°C is unchanged but at those exceeding 400°C, increases sharply. The latter indicates that at the annealing temperatures above 400°C, the disordering of crystal lattice is observed which is accompanied by expanding temperature interval of abovementioned PT.

4. Conclusion

To conclude, Cu_6PS_5I single crystals were grown using chemical vapor transport method. The implantation of Cu_6PS_5I single crystals was carried out at different fluence values using $^{32}S^+$ isotope, ion energy being 149 keV. The structure investigations using scanning electronic microscopy allowed us to find out on the surface of implanted samples the induced structural defects, namely, 5 to 15 μm size microcrystals. The variations of the superionic PT temperature as well as its temperature interval due to the ion implantation have been studied. Within the framework of Einstein model, the changes in the energy position of absorption edge ΔE_g^{α} and its temperature derivative $d(\Delta E_g^{\alpha})/dT$, induced by the PT order parameter have been calculated. It should be noted that the maximum observed in the the first-order PT range in the temperature dependences $|d(\Delta E_g^{\alpha})/dT|$ corresponds to the temperature behavior of the specific heat capacity anomalous part. The implantation of Cu_6PS_5I superionic conductors by sulfur ions results in the structural ordering of crystal lattice, while the isochronous annealing causes its disordering.

Aknowledgments. This work was supported by the Slovak Research and Development Agency under the contract No.SK-UA-001407 and Ministry of Education and Science of Ukraine under the contract No.M/35-2008.

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Вплив іонної імплантації на фазові переходи у суперіонних провідниках Cu_6PS_5I

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Виконано іонну імплантацію сіркою та структурні дослідження методом скануючої електронної мікроскопії суперіонних кристалів Cu_6PS_5I. З використанням температурних ізоабсорбційних досліджень краю оптичного поглинання вивчено вплив іонної імплантації та відпалу на фазові переходи. Отримано залежності температури та температурного інтервалу суперіонного фазового переходу від величини флюенса.