PROC, 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 757–759

THE PHASE TRANSITION IN SINGLE CRYSTALS OF α-$AgSbS_2$ INDUCED BY THE EXTERNAL ELECTRIC FIELD

V. Valiukenas, A. Brilingas, A. Orliukas, V. Samulionis and A. Sakalas

Vilnius V. Kapsukas State University
Vilnius, USSR

The results of the investigation of the structural phase transition induced by the external electric field have been presented. It has been established that single crystals of α-$AgSbS_2$ at $E \geqslant 2$ kV·cm^{-1} undergo the S-change from the low-conductive state into the high-conductive one at 300 K. Such variation of σ leads to the low energy absorption edge shift, to the change of the acoustic properties, and also of the intensities of (hkl) reflexes. The phase transition induced by the electric field is due to the disorder of cation sublattices α-$AgSbs_2$.

In recent years, the mechanism of temperature phase transition in superionic conductors has been intensively investigated [1-3]. It is theoretically shown [4] that the phase transition can be induced by the action of the external electric field but no experimental confirmation is known yet. We present the evidence, which confirms the theoretical predictions of the paper [4] quite well. We report data of the influence of external electric field to the conductivity, absorption edge, acoustic properties, and structural parameters in α-$AgSbS_2$. According to the data of spectral analysis there are following concentrations of noncontrol impurities in samples of α-$AgSbS_2$ investigated: As-10^{-2}%, Cu-3.10^{-3}%, Mn-10^{-4}%, Mg-10^{-4}%, Pb-$2 \cdot 10^{-3}$ and Fe-5.10^{-3}. These single crystals of α-$AgSbS_2$ are of monoclinic system at 300 K (space group C_2^3h or C_c). X-ray diffraction studies have shown that at T=300 K lattice parameters are as follows: a=13,2269±1,3·10^{-3} Å, b=4,4112±5·10^{-4} Å, c=12,8798±1,1·10^{-3} Å, β =98,48±0.01. Optical measurements lead to the energy band gap E_g of 1,73±0,01 eV [5]. Temperature dependence of the structure parameters [5] and of electrophysical properties [6,7] has shown, that there exists temperature phase transition α-$AgSbS_2 \rightarrow \beta$-$AgSbS_2$ in the temperature range of 653-676 K.

Using the method suggested in [8] it has been established that this compound possesses a mixed electrical conduction $\sigma = \sigma_e + \sigma_i$. At T=300 K, ionic conductivity is extremely small, if compared to electronic one $\sigma_e = 6,3 \cdot 10^{-9}$ $\Omega^{-1}.m^{-1}$ along the crystallographical axis [010] at E=10 V.cm^{-1}. At the same temperature the Hall mobility μ_H is $2,4 \cdot 10^{-5}$ m^2.V^{-1}.s^{-1} and charge carrier concentration N is equal to $1,6 \cdot 10^{15}$ m^{-3}. Ionic conductivity increases with the temperature and at T=570 K $\sigma_i/\sigma = 0,28$. Diffusion coefficient of ions obtained at the latter temperature $D_i = 3,5 \cdot 10^{-9}$ m^2.s^{-1} is comparable with the diffusion coefficient of Ag^+ions in AgI[9] and in Ag_2S[10,11] compounds.

The investigations of σ versus electric field strength E at 300 K have shown that σ does not depend on field until it reaches the value E_k=280 V.cm^{-1} in Fig.(1). σ increases with the further increassing of E and at E_p=2,2 kV.cm^{-1} (here E_p is transition field strength) the S-change from the low-conductive into the high-conductive

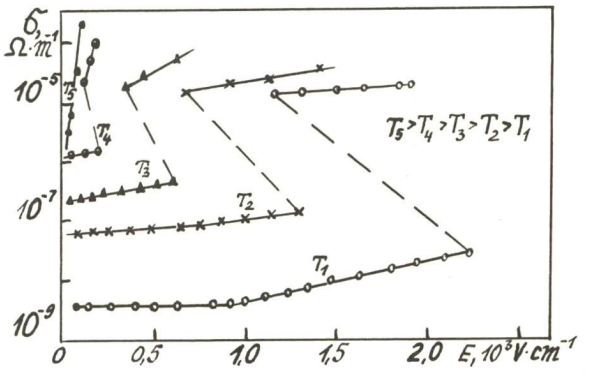

Fig.1 σ' vs E in α-$AgSbS_2$ at T=300 K

state undergoes. Such a change of σ' is due to the disorder of the cation sublattice. The electric conductivity increases 620 times when the S-change in the crystal occurs at room temperature. The latter value, E_k and E_p decrease with the increasing of temperature. Figure (2) presents the absorption edge of crystal at low-conductive state (curve E=0) and after transition to high-conductive state at $E > E_p$. From these data we conclude that S-shape transition induced

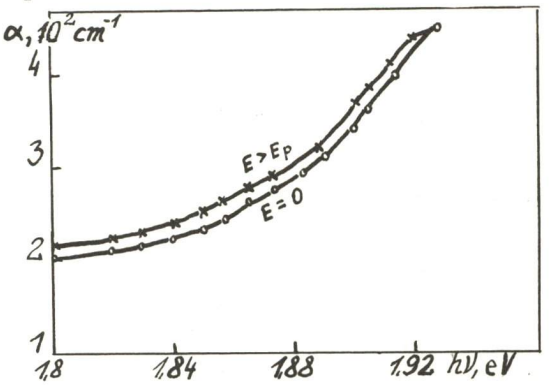

Fig.2 Absorption edge in α-$AgSbS_2$ at T=300 K

by the external electric field is accompanied by absorption edge shift to the low energy side. This phenomenon can be explained by the increased concentration of interstitial Ag^+ions, what leads to the band distorsion and to appearance of the state tails.

It is known [12,13] that temperature phase transitions in superionic conductors are accompanied by the anomalous behaviour of their acoustic properties.

We investigated the dependence of damping coefficient $\mathcal{H}$ and velocity v of longitudinal acoustic waves (LAW) on E, by using the pulse method described in [14]. The data obtained at room temperature and 30 MHz frequency are shown in Fig.(3) (here E is applied in the direction of LAW propagation). $\mathcal{H}$ increases and v decreases with increasing E, and the largest changes of these parameters are obtained at $E=E_p$.

X-ray diffraction studies using Cu K_α radiation have shown that the transition of the sample into the high-conductive state by the external electric field is accompanied by the decrease of the intensities of (hkl) reflexes.

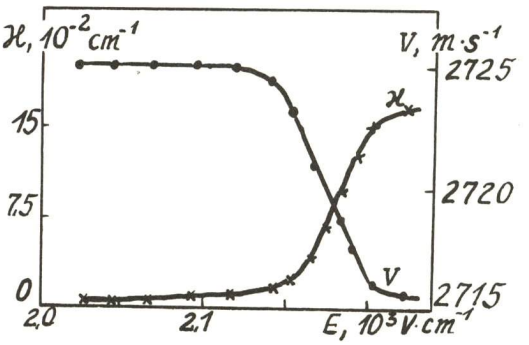

Fig. 3 $\mathcal{H}$ and v of LAW vs external electric field strength

Thus the experimental evidence of σ , E_g, $\mathcal{H}$ and v dependence on the external electric field and also x-ray diffraction studies indicate the possibility to induce the phase transition in single crystals of α-$AgSbS_2$ by the external electric field. It is believed that the phase transition is due to the disorder of cation sublattices in this compound. Consequently, the presumption of theory [4] concerning phase transitions induced by the external electric field in such ionic compounds is experimentaly confirmed.

References

1) M.J. Rice, S. Strassler, G.A. Toombs: Phys. Rev. Lett. 32 (1974) 596.
2) Y.Ya. Gourevich, G.V. Reznik, Yu.I. Kharkats: Solid State Phys. 20 (1978) 1661.
3) D. Brinkmann, W.Freudenreich: Solid State Comm. 25 (1978) 625.
4) Yu.Ya. Gourevich, Yu.I. Kharkats: Dokl. Akad. Nauk SSSR 236 (1977) 332.
5) P. Bohac, A.Orliukas, A. Gaumann, K. Girgis: Helvetica Phys. Acta 50 (1977) 853.
6) A. Orliukas, V. Valiukenas, V. Kalesinskas, J. Grigas: Eleventh International Congress and General Assembly of the International Union of Crystallographys, 1978, Warszawa, Poland, 357.
7) A.S. Orliukas, V.J. Valiukenas, V.A. Kalesinskas, V.J. Samulionis: IX vsesoyouznoie soveshtanie po segnetoelektritchestvu (24-26 sentiabria 1979, Rostov-na-Donu). Tezisy dokladov (tchast I),98.
8) I. Yokota: J. Phys. Soc. Japan 16 (1961) 2213.
9) A. Kvist, R. Tarneberg: Z. Naturforsch. 25a (1970) 983.
10) R. Allen, W. More: J. Phys. Chem. 63 (1959) 223.
11) I. Bartkowicz, S. Mrowec: Phys. Stat. Sol. (b) 49 (1972) 101.
12) N. Kostadinov: Phys. Lett. 64A (1977) 85.
13) M. Nagao, T. Kaneda: Phys. Rev. 11 (1975) 2711.
14) E. Garska, V. Samulionis, I. Vaivada, K. Sakalauskas: Trudy vysshei shkoly Lit. SSR, seria Ultrazvuk 1 (1969) 65.