On some physical properties of InSe and GaSe semiconducting crystals intercalated by ferroelectrics

1997 J. Phys.: Condens. Matter 9 L191

(http://iopscience.iop.org/0953-8984/9/12/001)

J. Phys.: Condens. Matter **9** (1997) L191–L195. Printed in the UK PII: S0953-8984(97)80985-X

LETTER TO THE EDITOR

On some physical properties of InSe and GaSe semiconducting crystals intercalated by ferroelectrics

I I Grigorchak, V V Netyaga and Z D Kovalyuk

Institute of Materials Science, Academy of Sciences of Ukraine, Chernivtsi Branch, Iryna Vilde Street 5, Chernivtsi 274001, Ukraine

Received 15 January 1997

Abstract. Physical mechanisms of intercalation of semiconductors are determined, establishing the main laws of intercalation, and the physical nature of new phenomena and effects induced by intercalation are explained; general statements for obtaining intercalates with characteristics assigned in advance are also developed.

The possibility of In and Ga monoselenide intercalation by $NaNO_2$ and KNO_2 was established earlier [1, 2]. The study of intercalation allowed us to determine the main laws of InSe$\langle NaNO_2\rangle$, InSe$\langle KNO_2\rangle$ and GaSe$\langle NaNO_2\rangle$ intercalate formation as well as kinetic parameters of intercalation. The purpose of the work presented here is the study of physical properties of the compounds obtained. We are interested first in transport phenomena, photoelectric processes and polarizability properties.

The target materials were monocrystalline ingots of InSe and GaSe prepared by the Bridgman method of which samples 5 mm $\times$ 5 mm $\times$ 0.1 mm were taken for further research with further intercalation by direct exposure to $NaNO_2$ or KNO_2 salt. The resistances of the samples were tested on standard equipment with direct current. Contacts were discovered to be ohmic.

In tested samples the effect in figure 1 was observed: the temperature dependences of specific resistance perpendicular to the layers of the materials under consideration are given. It is clearly seen that not only does intercalation by $NaNO_2$ or KNO_2 lead to quantitative change, but a cardinal change in the character of the function $\rho_\perp(T)$ also takes place. For example, although in the temperature range of 233–333 K in GaSe nonintercalated samples the specific resistance is changed not more than tenfold, after intercalation with $NaNO_2$ $\rho_\perp(233\ \mathrm{K})/\rho_\perp(333\ \mathrm{K})$ reaches a value of 1000. For the monoselenide InSe the absolute value of temperature coefficient of specific resistance before and after intercalation is not changed essentially as for GaSe, but in the latter case it has more nonmonotonic character. It should be noted that in both cases (for InSe and GaSe) intercalation induces a change of sign for the temperature coefficient of electric resistance. This is a new phenomenon which is not observed in the initial crystals.

For Ga the corresponding special point is around 323 K, for InSe around 313 K, in the latter case for intercalation either by $NaNO_2$ of KNO_2. We have not managed to obtain GaSe due to the instant intercalation which releases a great quantity of heat and is followed by full breakdown of a sample.

It should be noted that the detailed analysis of the transport phenomena is rather difficult to perform because of the experimental obstacles in correct determination of Hall effect

0953-8984/97/120191+05$19.50

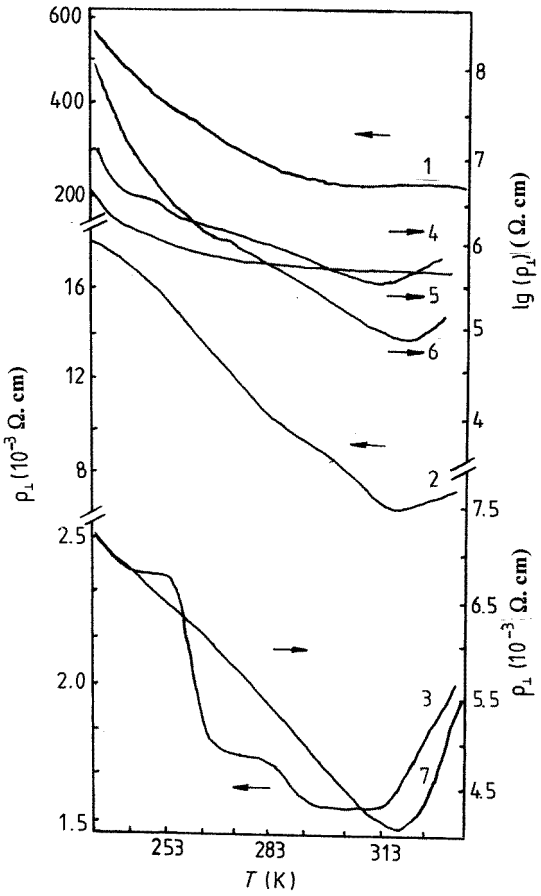

Figure 1. The temperature dependences of resistance perpendicular to the layer plane. 1, InSe; 2, InSe⟨KNO_2⟩; 3, InSe⟨$NaNO_2$⟩; 4, GaSe⟨NaNO + $CuSO_4$⟩; 5, GaSe; 6, GaSe⟨$NaNO_2$⟩; 7, InSe⟨KNO_2 + $CuSO_4$⟩.

parameters for the obtained materials; moreover the standard approximations, which are good for traditional materials, are not quite suitable in our case. Nevertheless, we are able to suppose some principles:

(i) Taking into account that InSe and GaSe are semiconductors of n and p types of conductivity respectively, the intercalated $NaNO_2$ and KNO_2 are of donor character [3].

(ii) Intercalation by $NaNO_2$ and KNO_2 not only increases the number of donor levels near the conductivity band, but also changes their density (topology of energy bands) [3].

(iii) Interlayer combination on the molecular level of semiconducting properties of the 'host' crystal and ferroelectric properties of the 'guest' material induces nonlinearity of polarizability characteristics and leads to formation of the 'soft' mode responsible for electron–phonon interaction [3].

Within the band 233–333 K we obtained the effect of temperature on dielectric penetration shown in figure 2. It is seen that besides an essential increase in $\varepsilon_\perp(T)$ (almost 10^2-fold for InSe and sevenfold for GaSe) after intercalation, sections characteristic of

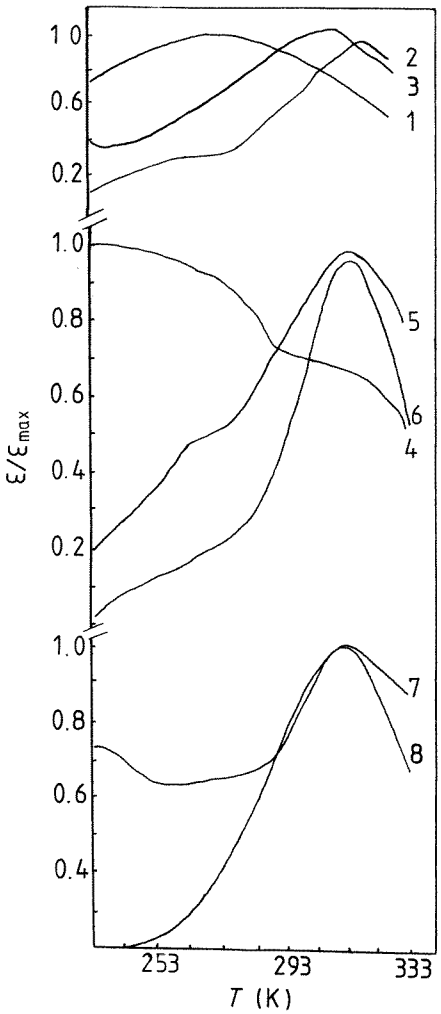

Figure 2. The temperature dependences of dielectric susceptibility ε, perpendicular to the layer plane. 1, GaSe; 2, GaSe$\langle NaNO_2\rangle$; 3, GaSe$\langle NaNO_2 + CuSO_4\rangle$; 4, InSe; 5, InSe$\langle KNO_2\rangle$; 6, InSe$\langle NaNO_2\rangle$; 7, InSe$\langle NaNO_2 + CuSO_4\rangle$; 8, InSe$\langle KNO_2 + CuSO_4\rangle$.

dielectric constant behaviour in the vicinity of Curie points have appeared. Comparing the measurement results of $\rho_\perp(T)$ and $\varepsilon_\perp(T)$ we can see excellent coincidence of the special points of the indicated curves. It should be noted that the value of special points 'forms' the 'host' crystal, since for the 'guest' components $T_c = 397$ K (KNO_2) and $T_c = 433$ K ($NaNO_2$).

Taking into account the great scientific and practical interest in photoelectric phenomena of ferroelectric semiconductors, the photoconductivity spectral dependence of GaSe$\langle NaNO_2\rangle$ intercalate was measured. The contacts were soldered on the sample surface, coinciding with the chipping plane (see the inset of figure 3) and then blacked out to protect the contact region from radiation. From figure 3 it is seen that first photoconductivity is increased tenfold after intercalation by $NaNO_2$ and second the spectral distribution is changed radically. One may suppose that three factors are responsible for the increase of photoconductivity: an increase

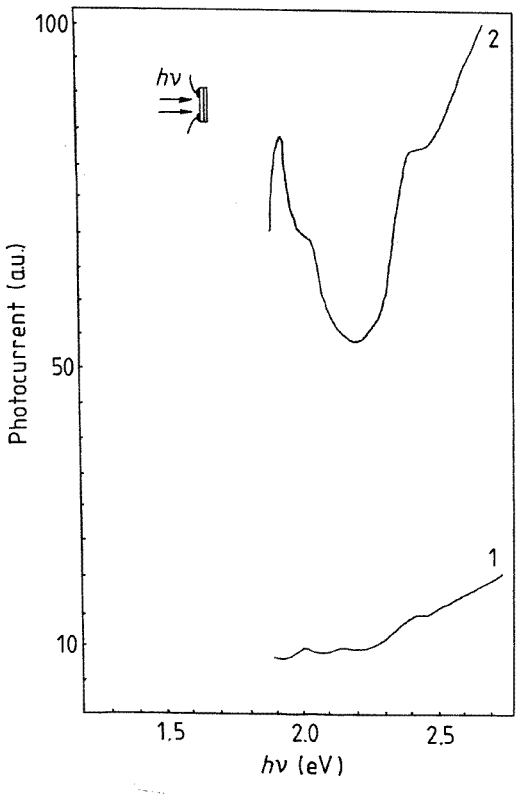

Figure 3. The spectral dependences of photocurrent: 1, GaSe; 2, GaSe⟨$NaNO_2$⟩.

of absorption coefficient due to the impurity levels which intensify sensitivity of the material, the quantum yield and lifetime of nonequilibrium carriers. The latter may be due to the strong surface bending of bands, induced by screening of spontaneous polarizability [3]. The nonmonotonic character of spectral distribution may be caused by surface recombination mechanisms competing with space separation of electron–hole pairs.

As reported previously [4] an attempt at final intercalation of monoselenides InSe and GaSe by other guest substances was not a success but during the test an important and interesting effect was achieved. If any material A can not be directly intercalated into InSe or GaSe, it is possible to insert it by means of intercalation combined with $NaNO_2$ of KNO_2. As a result we obtain biintercalates of formula InSe(GaSe)⟨$NaNO_2$ + A⟩ or InSe(GaSe)⟨KNO_2 + A⟩.

$CuSO_4$ has been chosen as material A. It is seen from figures 1 and 2 that adding $CuSO_4$ to a certain extent neutralizes the 'action' of $NaNO_2$ on InSe properties, reducing at the same time the critical point T_c by 10 K into the low-temperature range. In InSe the position of the critical point after biintercalation is not changed either at $\rho_\perp(T)$ or at $\varepsilon_\perp(T)$, but, unlike GaSe, $CuSO_4$ intensifies the 'action' of KNO_2 on electrical resistivity perpendicular to the layers.

It should be said in conclusion that the results obtained point out the necessity of further investigation in order to enrich and better our knowledge in such an important field as crystal engineering, which deals with giving desirable properties to the initial materials.

References

[1] Grigorchak I I, Netyaga V V, Kozmic I D, Tovstyuk K D, Kovalyuk Z D, Bakhmatyuk B P and Golyb S J 1989 *Pis. Z. Tekh. Fiz.* **15** 87
[2] Kozmic I D, Netyaga V V, Bakhmatyuk B P, Grigorchak I I and Kovalyuk Z D 1992 *Fiz. Tekh. Poluprov.* **26** 1992
[3] Fridkin V M 1976 *Ferroelectric–semiconductor* (Moscow: Nauka) (in Russian)
[4] Netyaga V V, Grigorchak I I and Kovalyuk Z D 1993 *Fiz. Tekh. Poluprov.* **27** 1220