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The Features of the Temperature Dependence of Photoconductivity in Ferroelectrics-Semiconductors of the System Sb_2S_3-Sb_2Se_3

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Abstract: In this paper the temperature dependence of photoconductivity in ferroelectric-semiconductor crystals of Sb_2S_3-Sb_2Se_3 systems has been investigated. In crystals close to Sb_2S_3 composition except for the intrinsic maximum of photoconductivity appropriate to fundamental absorption, the additional maximum has been observed at low temperatures related to ferroelectric activity of crystals, which disappear at more high temperatures (T>300K). It is established that the forbidden zone width shows anomalous behavior in the temperature range of phase transitions. The ranging of coefficient of temperature dependence of the forbidden zone width has been determined.

Key Words: Photoconductivity, ferroelectric semiconductor, absobtion, forbidon zone

Sb2S3-Sb2Se3 Sisteminin Ferro-elektrik Yarı İletkenlerinde Fotoiletkenliğin Sıcaklığa Bağlı Özellikleri

Özet: Bu makalede ferro-elektrik yarı iletken kristalle sistemler Sb_2S_3-Sb_2Se_3'de sıcaklığa bağlı foto iletkenlik incelendi. Kristallerde yaklaşık temel soğurma foto iletkenliğinin maksimumu hariç, Sb_2S_3 yakın bileşiklere sahiptirler. Kristalin ferro-elektrik aktivitesine bağlı olarak, düşük sıcaklıklarda ortaya çıkan, yüksek sıcaklıklarda (T > 300 K) ise kaybolan ilave maksimum gözlenmiştir. Oluşturulan yasak bant genişliği gösteriyor ki, faz geçişi sıcaklığı aralığında anormal davranış görülmektedir. Yasak bant genişliğinin sıcaklığa bağımlılık sabitinin değişim aralığı belirlenmiştir.

Anahtar Kelimeler: Foto iletkenlik, ferro elektrik yarı iletken, soğurma, yasak bölge

Introduction

The definition of a ferroelectric is a crystal in which a reversible polarization is observed. A member of the group of A^V-B^{VI}-C^{VII} compounds has been widely studied since 1960 due to its semiconducting and ferroelectric properties [Surthi et al., 2003]. The single crystal of the Sb_2S_3-Sb_2Se_3 is in the same group and has the similar properties. The anisotropy of the electric [Aliyev et al. 1967] and dielectric [Aliyev et al., 1968] properties which have been found out in single crystals of the system Sb_2S_3-Sb_2Se_3 has determined an opportunity of the existence of anisotropy of photoelectric and optical properties in the investigated system of crystals. Therefore, for measurement of photoelectric properties of the single crystals of the system Sb_2S_3-Sb_2Se_3 , samples were prepared in the form of rectangular parallelepipeds of two types, allowing to make measurements of photoelectric properties both along an "c" axis and perpendicular to it.

The investigation of photocurrent generation is useful not only for a better understanding of space-charge waves, but also for practical applications, for instance, for the detection of weakly phase modulated laser beams for remote laser testing including laser ultrasonic diagnostics. The effective and actual mobilities of photo-carriers can be estimated from the characteristic resonant frequencies. In this work, experimental setup for measurement of the photocurrent system [Bryushinin and Sokolov, 2001] was used.

Since layered semiconductors, like GaTe, have always been of interests due to their anisotropic properties photoconductivity, low temperature conductivity and magnetoresistivity measurements have been carried out [Bose and Pal, 2001].

In another work, Bratkovsky and Levanyuk [Bratkovsky and Levanyuk, 1999] have investigated ferroelectric phase transitions in ferroelectric-semiconductor film with a space charge which leads some unusual behavior and ferroelectric perovskite materials used in memory applications usually behave as semiconductors (Bryushinin and Sokolov, 2001).

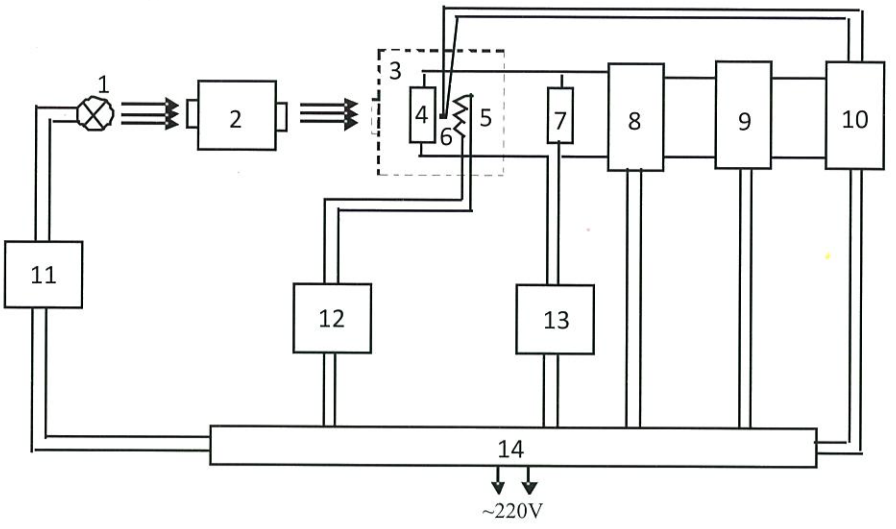

Fig. 1. The flow diagram of the measurement system for Sb_2S_3-Sb_2Se_3 single crystal's fotoconductivity depended on the temperature. 1. Light source, 2. Heater monocromator, 3. Sample handler, 4. Sample, 5. Sample heater, 6. Thermocouple, 7. Load resistance, 8. Constant current regulator, 9. Oscilloscope, 10. Plotter, 11., 12., 13. Current sources, 14. Power supply.

Experimental Results

For the realization of experiment we used single crystals of Sb_2S_3-Sb_2Se_3 system prepared by the method of zone alignment.

As the initial components at synthesis were used antimony (Sb), selenium (Se) and suffer (S) from special cleanliness. The synthesis were made at temperature of 925 K for 45 hour and further cooling with rate of 30 K/h. To grow the single crystals and to clean them an installation was constructed, which has allowed to prepare perfect single crystals of Sb_2S_3-Sb_2Se_3 by the method of zone alignment. The sizes of investigated samples were 5x4x0.6 mm^3 and 1.9x4x6 mm^3. The diagram of the photoconductivity measurement setup is seen in Fig. 1.Temperature dependence of photoconductivity of the single crystals of the system Sb_2S_3-Sb_2Se_3 was investigated in the 100 - 450K temperature range.

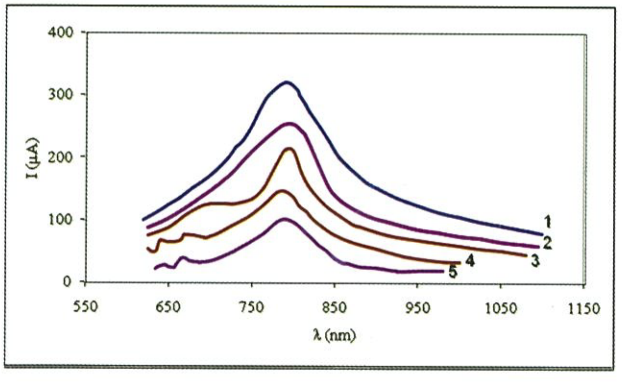

Fig. 2. Temperature dependence of spectral distribution of the photo-conductivity in single crystal of composition of *50%Sb_2S_3* at illumination on the plane (001). Where the numbers represent 1 - 300 K, 2 - 250 K, 3 - 220 K, 4 195 K, 5 150 K temperatures data.

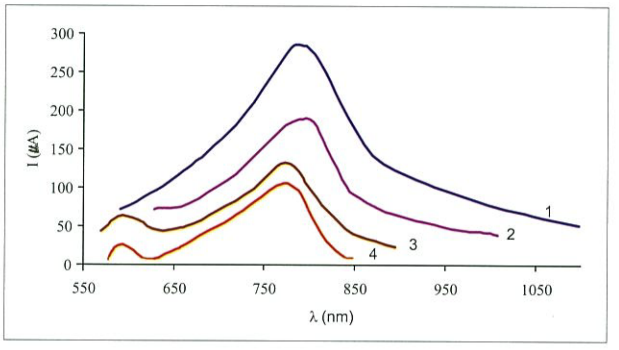

Fig. 3. Temperature dependence of spectral distribution of the photoconductivity in single crystal of composition 90%Sb_2S_3 - 10%Sb_2Se_3 at illumination on the plane (001). Where the numbers represent 1- 300 K, 2 - 260 K, 3 - 200 K, 4 125 K temperatures data.

The measurements have shown that at illumination on non-ferroelectric faces (100) or (010), over all investigated temperatures one maximum of photoconductivity corresponding to fundamental absorption edge is found out. At illumination on ferroelectric faces (001) of the non-polarized crystals in short-wave region at a wide range of temperatures additional maximum of the photocurrent is found out (seen in Fig. 2, 3), whose position does not depend on the temperature. For composition 50% Sb_2S_3 - 50 % Sb_2Se_3 it is revealed two additional maxima at 700 - 775 nanometers (Fig. 3). Temperature dependence of photoconductivity for the faces (001) and (100) is also different. With the increase of the temperature the height of this additional maximum decreases and disappears at $T \geq 300$ K for all compositions, except for composition 50% Sb_2S_3-50% Sb_2Se_3 in which second additional maximum disappears at temperature $T \geq 350$K. It is necessary to assume that in both SbSI [Aliyev et al., 1987] and Sb_2S_3 [Fridkin, 1979] these additional maxima, found out in crystals

of the system Sb_2S_3-Sb_2Se_3, are caused by ferroelectric activity of the crystals. A short-wave maximum of "intrinsic" photoconductivity on the ferroelectric face (001) of the single crystals of the system Sb_2S_3-Sb_2Se_3 is caused by a space-charge layer, shielding spontaneous polarization (P_S) and creating a strong electric field on a surface of a crystal which is similar to Schottky barrier - influences on the non-equilibrium charge carriers lifetime (τ), a quantum yield (β_K), and causes dielectric saturation as well as "intrinsic" photosensitivity in the strong absorption region. In crystals of relatives on structure to Sb_2S_3-Sb_2Se_3 additional maximum is not found out that is connected with weak ferroelectric activity of the crystals [Aghaised et al, 1999].

In the Sb_2S_3-Sb_2Se_3 crystal systems, the second maximum appears on (001) planes by illumination at lower temperatures and there are two main reasons for that appearing. The first reason is that the crystal has the ferroelectric structure, and the second reason is that spontaneous polarisation occurs by the illumination of the (001) plane. The spontaneous polarization, Ps(T), causes screening volume charges which form higher electric field. According to this investigation Ps(T) has constant value at the interval of 200-220 K temperatures. In this interval the magnitudes of the Ps(T) are 13 and 10 $\mu C/cm^2$ between 200 and 275 K respectively. After 275 K degrees the Ps(T) decays gradually and at T > 300 K degrees disappears. In these crystal systems, conductivity measurements were performed in the [001] direction. With the increase of the temperature, the spontaneous polarisation (P_S) decreases and level structure takes place in the Sb_2S_3-Sb_2Se_3 crystal systems and that structure form causes of the disappearing of the second maximum at T > 300 K temperatures.

It can be said that there are some reasons for the temperature dependent of the photo-current conductivity spectrum curves in (001), (100) and (010) planes. At lower temperatures with the illumination of the (010) or (100) planes any physical anomalies cannot take place because Sb_2S_3-Sb_2Se_3 crystals are one dimensional ferro-electric semiconductors and in these systems phase transformation occurs in [001] direction. Thus with the illumination of the (001) plane only, physical anomalies can be observed at the temperature interval of 300 – 450 K.

Investigation has shown that in single crystals of the system Sb_2S_3-Sb_2Se_3 the maximum of the temperature dependence of spectral distribution and photoelectric threshold with the decrease of the temperature shifted to short waves region that specifies growth of the width of the forbidden zone of this system crystals, as seen in Fig. 4, for (100) and (001) planes. Thus a photocurrent of the studied crystals system increases with the increase of the temperature: slowly at low temperatures and sharply from room temperature to 450 K.

At illumination on the non-ferroelectric faces (100) or (010), maximum of photoconductivity displaced to the region of low temperatures that specifies growth of width of the forbidden zone in a direction perpendicular to "c" axes. These data are in a good accordance with the results obtained by other authors [6] and testify the presence of the anisotropy of photoconductivity in single crystals of the system Sb_2S_3-Sb_2Se_3.

The structure of the crystal and its purity were determined by X-ray diffraction (XRD). The crystal structure was orthorhombic with the lattice constants as a : 8.50 Å; b : 10.20 Å and c : 4.15 Å. From XRD patterns the preferred orientation of the crystal was observed as (311). The elemental composition of SbS-SbSe crystal crystals was determined by performing EDS analysis at several points on the sample and the average composition was: Sb-33.4%, S-32.8%, and Se-33.8% (accuracy ±3%). It can be said that the crystal grown by the PLD technique is close to stoichiometric.

At studying of the temperature dependence it is established that the width of the forbidden zone determined at illumination on the non-ferroelectric face (100) varies linearly with temperature (Fig. 4, curves 1 and 2), and the temperature factor depending on the composition of the system Sb_2S_3-Sb_2Se_3 matters $\beta \cong -7.5\times10^{-4}$ eV/K. However, at illumination on the ferroelectric face (001) in the temperature region corresponding to phase transitions [5], anomalies of the width of the forbidden zone (E_{gc}) are found out (Fig. 4, curves $1'$ and $2'$). It is necessary to note that temperature dependence of the width of the forbidden zone E_g of the single crystals of the system Sb_2S_3-Sb_2Se_3 is caused by electron-phonon interaction and expansion of the crystal:

$$\left[\frac{\Delta E_g}{\Delta T}\right]_p = \left[\frac{\Delta E_g}{\Delta T}\right]_V - \frac{\beta^*}{\alpha^*}\left[\frac{\Delta E_g}{\Delta pV}\right]_T \qquad (1)$$

where:

$$\beta^* = \frac{1}{T}\left[\frac{dV}{dT}\right] \;; \quad \alpha^* = -\frac{1}{V}\left[\frac{dV}{dP}\right] \qquad (2)$$

The contribution of temperature expansion is determined as:

$\beta^* = \gamma_g \frac{\lambda^*}{\nu} C_V$, where: γ_g – Grunayzen's constant.

For Sb_2S_3 [Grigas, 1980; Penahov et al., 2000] $\beta = 1.5\times10^{-5}$ K, hence, electron-phonon interaction is strong. Owing to the Kays relationship $\left(\frac{dE_g}{dT}\right)_p C_V$; and hence both ferroelectric and non-ferroelectric phase transitions are accompanied by change of the E_g. Phase transitions of the first kind are accompanied by a jump in the width of the forbidden zone (ΔE_g), and at phase transition of the 2nd kind changes stepwise the temperature factor of width of the forbidden zone $\Delta\beta(\beta = \frac{dE_g}{dT})$.

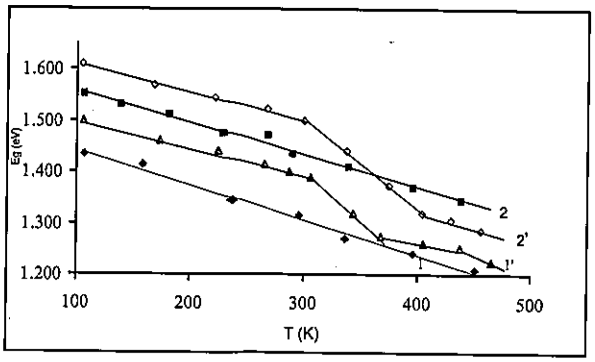

Fig.4. Temperature dependence of the width of the forbidden zone of composition $50\%Sb_2S_3$-$50\%Sb_2Se_3$ and $90\%Sb_2S_3$-$10\%Sb_2Se_3$:1, 2 - at illumination on the plane (100); 1', 2' - at illumination on the plane (001).

In Table 1 temperature dependence of width of forbidden zone E_g of the single crystals of two compositions of the system Sb_2S_3-Sb_2Se_3 is presented. As it is seen in the table temperature dependence of the width of the forbidden zone for single crystals of the system Sb_2S_3-Sb_2Se_3, at illumination on the plane (001) is having sudden changes in values at some temperature intervals. In fact, the cause of the occurring extra maxima at lower temperatures, are related to the ferroelectric peculiarity of the crystals. Because of spontaneous polarization screening surface current come into existence and that forms a high electric field. With increase of the temperature the spontaneous polarization decrease and the SbSeS crystal constitutes layered structures. In figs 2 and 3 all shown occurred between 770 and 820 nm are connected with Eg and the values are between 1.5 2 eV.

Table 1. Temperature dependence of the width of the forbidden zone for single crystals of the system Sb_2S_3-Sb_2Se_3 at illumination on the plane (001)

Temperature	Composition, % $50\%Sb_2S_3$-$50\%Sb_2Se_3$		Temperature	Composition, % $90\%Sb_2S_3$-$10\%Sb_2Se_3$	
T (K)	$\frac{dE_g}{dT}$ (eV/K)	$\frac{dE_{gi}}{dT} - \frac{dE_{gf}}{dT}$	T (K)	$\frac{dE_g}{dT}$ (eV/K)	$\frac{dE_{gi}}{dT} - \frac{dE_{gf}}{dT}$
150-320	-7×10^{-4}	0	100 - 310	6.8×10^{-4}	0
320-375	-18×10^{-4}	11×10^{-4}	310 - 420	-19×10^{-4}	12.2×10^{-4}
375-450	-4×10^{-4}	-14×10^{-4}	420 - 450	-3×10^{-4}	-16×10^{-4}
T> 450	-20×10^{-4}	16×10^{-4}	T> 450	-3.5×10^{-4}	0.5×10^{-4}

Conclusion

Temperature dependence of the width of forbidden zone $E_g(T)$ for the crystals close on composition Sb_2Se_3 it is possible to interpret as sequence of phase transition or change of interactions in various coordination polyhedrons of the anisodecmic crystal, occurring in wide intervals of temperatures.

Hence, even insignificant structural changes result in essential changes in an electronic spectrum.

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YÜZÜNCÜ YIL ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ DERGİSİ YAZIM İLKELERİ

Dergide Fen Bilimleri alanında yapılmış özgün araştırmalar yayınlanır.

Dergide yayınlanacak eserler, Türkçe ve İngilizce olarak yazılabilir.

Dergiye yayınlanmak üzere gönderilen eserin, daha önce hiçbir yayın organında yayınlanmamış veya yayın hakkının verilmemiş olması gerekir. Eser sahibinden makale ile birlikte buna ilişkin yazılı belge (dilekçe) alınır.

Dergiye gönderilen eser, basılmadan önce konunun uzmanı olan 2 hakeme gönderilir. Gönderilen eserin dergide yayınlanabilmesi için hakemler tarafından olumlu rapor gelmesi gerekir. Eserin yayınlanması konusunda, hakemlerden biri olumlu, diğeri olumsuz görüş bildirirse bu durumda eser üçüncü hakeme gönderilir. Yayınlanması uygun bulunmayan eser, yazara (yazarlarına) iade edilir.

Eser, Microsoft Word ' da **Arial** (Arial Tur) yazı karakteri ile yazılarak, 3 nüsha halinde Disketiyle (veya CD ile) birlikte gönderilmelidir.

Eser, A4 boyutunda ve birinci hamur kağıda, 170 x 250 mm lik alana 8.25 cm lik iki sütun halinde ve sütunlar arasında 0.5 cm boşluk olacak şekilde hazırlanmalı ve toplam sayfa sayısı 8'i geçmemelidir.

Eserin başlığı, kelimelerin baş harfleri büyük ("ve", "ile", "veya" vb bağlaçlar hariç) 13 punto, koyu ve sayfayı ortalayacak şekilde olmalıdır.

Eser, bir kurum veya kuruluş tarafından desteklenmiş veya yüksek lisans / doktora tezinden özetlenmiş ise bu durum, başlığın son harfi üzerine yıldız konularak, ilk sayfanın altında dip not olarak belirtilmelidir.

Abstract başlığı, eser başlığı ile aynı şekilde ancak 11 punto büyüklüğünde olmalıdır.

azarların adları, unvan kullanılmaksızın, baş harfleri büyük diğer harfleri küçük, soyadları ise büyük harflerle yazılmalı, yazar adresleri, yazarların soyadlarının son harfi üzerine numara verilerek, ilk sayfada dip not şeklinde belirtilmelidir.

Eser; **Özet, Abstract, Giriş, Materyal ve Yöntem, Bulgular ve Tartışma, Sonuç, Kaynaklar** şeklinde düzenlenmeli. Başlıklar, koyu ve başlıktan bir önce ve bir sonra birer boşluk olacak şekilde yazılmalı. Eğer alt başlıklar kullanılacaksa, (alt başlığın sadece ilk harfi büyük) başlıktan sonra iki nokta üst üste (:) konulup devam edilmelidir.

Eserde; Türkçe ve İngilizce özet (Abstract), 8 punto büyüklüğünde, 200' er kelimeyi geçmeyecek şekilde, 15 cm genişliğinde, tek sütun halinde ve bir aralık (satır aralığı 1) ile yazılmalıdır. En fazla 6 adet anahtar kelime (kendi içerisinde alfabetik sırada ve makale başlığındaki kelimeleri içermeyecek şekilde) verilmelidir.

Metin, paragraflar arası bir boşluk ve paragraf başı 0.5 cm + da çizelgenin üstüne numaralandırılarak 8 punto büyüklüğünde yazılmalıdır. Çizelgelerde dikey çizgi kullanılmamaldır.

Eserde kullanılan kaynaklar metin içerisinde "yazar ve yıl" olarak verilmeli. Eserde yer alan kaynakların hepsi "Kaynaklar" listesinde bulunmalıdır. Doktora ve Yüksek Lisans tezleri dışında yayınlanmamış eserler ve sözlü görüşmeler kaynak olarak belirtilmemelidir.

Kaynak metin içerisinde; tek yazarlı, iki yazarlı, üç ve daha fazla yazarlı olmasına göre paragraf veya satır başında belirtiliyor ise sırası ile: "Kor (2000), Kor ve Ertuğrul (2000), Kor ve ark. (2000) " şeklinde paragraf sonu veya satır sonunda belirtiliyor ise "(Kor 2000) , (Kor ve Ertuğrul 2000), (Kor ve ark. 2000) şeklinde belirtilmelidir. Yabancı kaynaklar da "ve" ve "ark." olarak belirtilmelidir. Anonim kaynak: Türkçe ise "(Anonim 2000)" , Yabancı dilde ise "(Anonymous 2000)" şeklinde belirtilmelidir. Aynı konu için birden fazla kaynak ard ada verilirken araya noktalı virgül (;) konulmalıdır. Örnek: (Kor 2000; Ertuğrul ve ark. 2004). Kaynaklar listesinde yararlanılan eser **Kitap** ise:

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"Kaynaklar" İlk yazarın soyadına göre alfabetik olarak 8 punto büyüklüğünde bir aralık (satır aralığı 1) olarak düzenlenmelidir.

Basımına karar verilen eserde, her hangi bir ekleme ve çıkarma yapılamaz.

Bir yazarın aynı sayıda ilk isim olarak bir (1) , ilk isim olmadan da bir (1) eseri olmak üzere en fazla iki eseri basılabilir.

Yayınlanan eserin tüm sorumluluğu yazarına veya yazarlarına aittir.