Functional Materials 19, No.3 (2012)

Symmetry peculiarities of the intracrystalline fields layered semiconductor crystals $(PbI_2)_{(1-x)}(BiI_3)_x$

O.I.Barabash, I.G.Vertegel, E.D.Chesnokov, O.I.Ovcharenko, L.S.Ivanova

Institute of Physics, National Academy of Sciences of Ukraine,
46 Nauki Ave., 03680 Kyiv, Ukraine

Received December 25, 2011

The results of our study deal with the NQR spectra of ^{127}I at 77 K in mixed layered semiconductor crystals $(PbI_2)_{(1-x)}(BiI_3)_x$ in a wide range of content PbI_2 and BiI_3 $0 \le x \le 1$. It is shown that in the range of content $0 \le x \le 0.02$ the crystal $(BiI_3)_{(1-x)}(PbI_2)_x$ has the properties of the impure crystal PbI_2, which contains intralayer BiI_3 clusters, and in the range $0.8 \le x \le 1$ it contains intralayer clusters PbI_2. Under the concentration $x = 0.10$ and $x = 0.80$ the crystal $(PbI_2)_{(1-x)}(BiI_3)_x$ undergoes a phase transition and in the concentration range $0.1 \le x \le 0.8$ there is a new crystal $(PbI_2)_{(1-x)}(BiI_3)_x$, in which groups of atoms PbI_2 and PbI_3 are intercalants fully or partially ordered in the crystal system.

Представлены результаты исследований спектров ЯКР ^{127}I при 77 К полупроводниковых смешанных слоистых кристаллов $(PbI_2)_{(1-x)}(BiI_3)_x$ в широком интервале содержания PbI_2 и BiI_3 $0 \le x \le 1$. Показано, что в диапазоне содержания $0 \le x \le 0.02$ кристалл $(BiI_3)_{(1-x)}(PbI_2)_x$ имеет свойства примесного кристалла PbI_2, содержащий внутрислоевые кластеры BiI_3, а в диапазоне $0{,}8 \le x \le 1$ содержит внутрислоевые кластеры PbI_2. При содержании $x \sim 0{,}10$ и $x \sim 0{,}80$ кристалл $(PbI_2)_{(1-x)}(BiI_3)_x$ испытывает концентрационный фазовый переход и при $0{,}1 \le x \le 0{,}8$ существует новый кристалл $(PbI_2)_{(1-x)}(BiI_3)_x$, в котором группы атомов PbI_2 и BiI_3 – интеркалянты полностью или частично упорядочены в кристаллической системе.

1. Introduction

Actuality of the investigations of solid solutions of layered semiconductor crystals $(PbI_2)_{(1-x)}(BiI_3)_x$ has been mainly associated with the possibility of cluster structures formation in such crystals that can significantly change their physical properties. It is known [1] that in cluster structures an excitation associated with changes in the configuration of clusters and their sizes may be observed, that can lead to phase transformations and significant changes in the properties of the crystals. Besides, the layered semi-conductor crystals PbI_2, BiI_3, CdI_2 have properties [2, 5], which allow to use them as detectors of high energy resolution of γ-radiation.

In this regard, it may be actual in the current research to investigate the properties of mixed crystals $(PbI_2)_{(1-x)}(BiI_3)_x$ and to determine the concentration dependences of the crystals parameters, which may vary depending on changes in state of the impurities. Nuclear quadrupole resonance spectra (NQR) of ^{127}I nuclei of chemically pure crystals BiI_3 and PbI_2 ($x = 0$ and $x = 1$), as well as mixed layered crystals $PbI_2 \cdot CdI_2$ with isovalent iodine atoms we have studied in [6, 7]. Absorption and reflection spectra, as well as X-ray analysis of the mixed crystals $(PbI_2)_{(1-x)}(BiI_3)_x$ were investigated in [8]. In this paper it was shown that for $0 \le x \le 0.2$ there is a phase similar to that of PbI_2, and for $x \ge 0.80$ the phase is similar to BiI_3

Table. Concentration dependence of ^{127}I NQR spectrum parameters for mixed layered semiconductors $(PbI_2)_{(1-x)}(BiI_3)_x$

x	υ_1, MHz $\pm1/2\leftrightarrow\pm3/2$	υ_2, MHz $\pm3/2\leftrightarrow\pm5/2$	$\Delta\upsilon_1$, MHz	η	e^2Qq_{zz}, MHz
0	4.475	8.95	0.21±0.01	0	29.83±0.02
0.02	4.515	8.952	0.32±0.01	0.01	29.91±0.1
0.1	5.21	10.28	1.4±0.1	0.09±0.03	34.4±0.1

phase. NQR spectra of mixed crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ at ^{127}I nuclei of BiI_3 group we have studied in [7-11]. ^{127}I NQR spectrum of the mixed semiconductor crystal $(PbI_2)_{(1-x)}(BiI_3)_x$ on the group PbI_2 have been studied for the first time. The aim of this study was to investigate an influence of the content of PbI_2 and BiI_3 on the value and symmetry of the electric field gradient of iodine nuclei for solid solutions of semiconductor layered crystals $(PbI_2)_{(1-x)}(BiI_3)_x$.

2. Experimental

127I NQR spectra of these crystals $(PbI_2)_{(1-x)}(BiI_3)_x$ at temperature T = 77 K in the frequency range 2–300 MHz were measured using quasi-coherent spectrometer an ISSH NQR-2-13. We also used a digital storage device required for the detection of weak and broad lines ^{127}I NQR spectrum. Crystals were examined at the following concentrations x: 0, 0.02 and 0.10. υ_1 and υ_2 frequency ^{127}I NQR measurement corresponding to the transitions $\pm1/2\leftrightarrow\pm3/2$ and $\pm3/2\leftrightarrow\pm5/2$, allowed on the basis of tables [10] to determine the concentration dependence of the constants $e^2Qq_{zz}(x)$ of quadrupole interaction and asymmetry parameter $\eta(x)$ of electric field gradient tensor ($\eta = (q_{xx} - q_{yy})/q_{zz}$). The data of our measurements are shown in Table 1. The accuracy of determination of the asymmetry parameter and quadrupole coupling constants were determined by the lines width and were no worse than ±1.5 %±0.1 % of their absolute values.

3. Results and discussion

It was found that for chemically pure crystal PbI_2 (x = 0) at 77 K ^{127}I NQR frequencies υ_1 and υ_2 of the two transitions of electric field gradient tensor are equal respectively to 4.475 and 8.950 MHz. The quadrupole interaction constant e^2Qq_{zz} = (29.83±0.01) MHz and asymmetry parameter of the electric field gradient tensor η = 0 correspond to given values of frequency υ_1 and υ_2 at 77 K. The results are in agreement with those of [6].

With increasing x of BiI_3 content in the basic crystal PbI_2 matrix from 0 to 0.02 the quadrupole interaction constant e^2Qq_{zz} and asymmetry parameter η of the electric field gradient of ^{127}I nuclei vary slightly. The observed change of υ_1 and υ_2 frequencies does not exceed of 1 % of the absolute values (Table).

The width $\Delta\upsilon$ of the line υ_2 of ^{127}I NQR spectrum in the same range of content x increases approximately in half: $\Delta\upsilon|_{x=0}$ ~ 0.2, $\Delta\upsilon|_{x=0.02}$ ~ 0.3 MHz. Note that the value of the constant e^2Qq_{zz} in the same range of content BiI_3 varies slightly. This may indicate that the introduction of BiI_3 for this range of concentrations ($0 \le x \le 0.02$) causes a slight increase of the intralayer symmetry and does not change the interlayer structure of the crystal. In this case, the symmetry of the layered crystals $(PbI_2)_{(1-x)}(BiI_3)_x$ in the range of BiI_3 content ($0 \le x \le 0.02$) remains the same D_{3d}. This assumption is based on the fact that the axes x and y of components q_{xx} and q_{yy} of the electric field gradient tensor lie in the crystal lays plane and the axes z — are perpendicular to the layers [6]. Therefore, we can also assume that for the concentration range $0 < x < 0.02$ the layered structure of the crystals $(PbI_2)_{(1-x)}(BiI_3)_x$ is preserved and BiI_3 groups locate within the crystal layers. In addition, BiI_3 groups may form intralayer clusters of the "islanding" type whose sizes increase with increasing x content.

For PbI_2 crystals with BiI_3 content 0.10 we detected at 77 K a new line in the NQR spectrum of ^{127}I. Thus, for x = 0.10 line υ at 77 K is characterized by the following parameters: υ_1 = 5.2, υ_2 = 10.28 MHz, e^2Qq_{zz} = 34.4 MHz, η = 0.09. It is important to note that for the given new line υ of ^{127}I NQR spectrum asymmetry parameter η is increased on 9 %: η^{II} = 0.09 and η^{I} = 0. In this case the value of electric field gradi-

ent constant e^2Qq_{zz} on ^{127}I nuclei increases on 15 %: $e^2Qq_{zz}^{I} = 29.83$ and $e^2Qq_{zz}^{II} = 34.4$ MHz. This allows to conclude that with x increasing intralayer symmetry of the crystal decreases. It should be noted that line υ of ^{127}I NQR spectrum with parameters $e^2Qq_{zz}^{I} = 29.83$ MHz and $\eta = 0$ in the interval $x \geq 0.1$ is no longer observed.

It is known [10] that the product of width and intensity values of the NQR line is proportional to the number of resonant nuclei that form a given line. Therefore, the fact that in the concentration range $x \geq 0.1$ υ^{I} line of ^{127}I NQR spectrum with parameters $e^2Qq_{zz}^{I} = 29.83$ MHz and $\eta^{I} = 0$ is no longer observed, may indicate a substantial reduction of the number of resonant nuclei ^{127}I which form the line υ.

In [7, 11] during investigating the concentration dependence of the asymmetry parameter as well as the line width of NQR spectrum on I^{127} nuclei of BiI_3 group in $(PbI_2)_{(1-x)}(BiI_3)_x$ crystal at the concentration $x \sim 0.80$ we discovered the so-called "concentration" phase transition. In this case on the basis of the results analysis we showed that when PbI_2 content is larger than 0.8 in the structure of $(PbI_2)_{(1-x)}(BiI_3)_x$ islet impurity or clusters PbI_2 are formed which are located within the layers of the crystal BiI_3. At the same time, at the concentration of $x \leq 0.80$ investigated crystal $(PbI_2)_{(1-x)}(BiI_3)_x$ has the properties of a solid solution of substitution type.

Analysis of the obtained in this work experimental concentration dependences of the asymmetry parameter as well as the line width υ_1 indicates that at the concentration $x \sim 0.10$ in crystal $(PbI_2)_{(1-x)}(BiI_3)_x$ a "concentration" phase transition takes place. Taking into account that the total number of resonant nuclei ^{127}I in $(PbI_2)_{(1-x)}(BiI_3)_x$ crystal must be constant it may be concluded that a new line υ^{II} in ^{127}I NQR spectrum for $x \geq 0.10$ is formed by the previous line. These results indicate that in BiI_3 content range $0 \geq x \geq 0.02$ in the structure $(BiI_3)_{(1-x)}(PbI_2)_x$ the islet clusters or impurity of BiI_3 can be formed which are located within the layers of PbI_2 crystal. It is shown that in the concentration range $x \geq 0.10$ the investigated crystal $(PbI_2)_{(1-x)}(BiI_3)_x$ has the properties of a solid solution of substitution type. In this case the formed virtual crystal BiI_3 PbI_2 is characterized by isotropic glassy properties.

4. Conclusions

Thus, these results indicate that in the layered mixed semiconductor $(PbI_2)_{(1-x)}(BiI_3)_x$ for the content of BiI_3 and PbI_2 $0 \geq x \geq 0.02$ and $x \geq 0.80$ the islet clusters of PbI_2 and BiI_3 are formed which are located within the layers of the crystal. In the concentration range of $0.10 \geq x \geq 0.80$ the synthesized crystals are glassy solid solutions of substitution type in which groups of atoms of PbI_2 and BiI_3 are intercalants which are wholly or partially ordered in the crystalline semiconductor PbI_2 BiI_3 system both within the crystalline layers and between them.

References

1. B.M.Smirnov, *Uspehi Fiz. Nauk*, **177**, 369 (2007).
2. V.F.Aghekyan, *Fis.Tverd.Tela*, **40**, 1724 (1998).
3. M.Schluter, M.L.Cohen, *Phys.Rev.B*, **14**, 424 (1976).
4. K.G.Konopleva, N.U.Venskovsky, A.Tupolev et al., *Koord.Khim.*, **23**, 505 (1999).
5. A.S.Abyzov, L.N.Davydov, V.E.Koutny, *Tekhnol.Konstr.Electron.Apparat.*, No.3, (2004).
6. A.I.Barabash, I.G.Vertegel, E.D.Chesnokov et al., *Functional Materials*, **15**, 175 (2008).
7. A.I.Barabash, I.G.Vertegel, E.D.Chesnokov et al., *Functional Materials*, **17**, 24 (2010).
8. I.Gorban, V.Donets, S.N.Rudko, T.N.Sushkevich, *Ukr.Fiz.Zn.*, **26**, 495 (1981).
10. G.K.Semin,T.A.Babushkina, G.G.Jacobson, Nuclear Quadrupole Resonance in Chemistry, Wiley, New-York (1975).
11. O.I.Barabash, I.G.Vertegel, E.D.Chesnokov et al., *Ukr.Fiz.Zn.*, **56**, 159 (2011).

Особливості симетрії внутрішньокристалічних полів шаруватих напівпровідникових кристалів $(PbI_2)_{(1-x)}(BiI_3)_x$

О.І.Барабаш, І.Г.Вертегел, Є.Д.Чесноков, О.І.Овчаренко, Л.С.Іванова

В роботі приводяться результати досліджень спектрів ЯКР ^{127}I при 77 К напівпровідникових змішаних шаруватих кристалів $(PbI_2)_{(1-x)}(BiI_3)_x$ в широкому интервалі вмісту PbI_2 і BiI_3 $0 \le x \le 1$. Показано, що в диапазоні вмісту $0 \le x \le 0.02$ кристал $(BiI_3)_{(1-x)}(PbI_2)_x$ має властивості домішкового кристалу PbI_2, який має внутрішньошарові кластери BiI_3, а в діапазоні $0.8 \le x \le 1$ має внутрішньошарові кластери PbI_2. При вмісті $x = 0.10$ і $x = 0.80$ в кристалі $(PbI_2)_{(1-x)}(BiI_3)_x$ відбувається концентраційний фазовий перехід і при $0.1 \le x \le 0.8$ утворюється новий кристал $(PbI_2)_{(1-x)}(BiI_3)_x$, в якому групи атомів PbI_2 и BiI_3 — інтеркалянти повністю або частково впорядковані в кристалічній системі.