Journal of Solid State Chemistry 183 (2010) 2813–2817

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Lithium ions in the van der Waals gap of Bi_2Se_3 single crystals

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ARTICLE INFO

Article history:
Received 6 March 2010
Received in revised form
15 September 2010
Accepted 19 September 2010
Available online 24 September 2010

Keywords:
Intercalation
van Der Waals gap
Bi_2Se_3 crystals

ABSTRACT

Insertion/extraction of lithium ions into/from Bi_2Se_3 crystals was investigated by means of cyclic voltammetry. The process of insertion is reflected in the appearance of two bands on voltammograms at ~1.7 and ~1.5 V, corresponding to the insertion of Li^+ ions into octahedral and tetrahedral sites of the van der Waals gap of these layered crystals. The process of extraction of Li^+ ions from the gap results in the appearance of four bands on the voltammograms. The bands 1 and 2 at ~2.1 and ~2.3 V correspond to the extraction of a part of Li^+ guest ions from the octahedral and tetrahedrals sites and this extraction has a character of a reversible intercalation/deintercalation process. A part of Li^+ ions is bound firmly in the crystal due to the formation of negatively charged clusters of the ($LiBiSe_2.Bi_3Se_4^-$) type. A further extraction of Li^+ ions from the van der Waals gap is associated with the presence of bands 3 and 4 placed at ~2.5 and ~2.7 V on the voltammograms as their extraction needs higher voltage due to the influence of negative charges localized on these clusters.

1. Introduction

Bi_2Se_3 crystals rank among the group of layered semiconductors of tetradymite structure (space group D_{3d}^5—$R3m$). The crystal lattice of Bi_2Se_3 is formed by a periodic arrangement of layers aligned perpendicular to the trigonal *c*-axis. Each layer is composed of five atomic planes arranged according to the following pattern:

$$\cdots Se^1{-}Bi{-}Se^2{-}Bi{-}Se^1 \cdots Se^1{-}Bi{-}Se^2{-}Bi{-}Se^1 \cdots$$

Between Se^1 atomic planes of neighbouring atoms there is a van der Waals gap, which consists of unoccupied octahedra and tetrahedra.

Considerable attention has been paid to Bi_2Se_3 crystals, in particular to mixed $Bi_2Te_{3-x}Se_x$ crystals, due to their transport and thermoelectric properties, with the aim to apply these materials in the construction of solid state thermogenerators and coolers [1,2]. Physical properties of semiconducting Bi_2Se_3 crystals were studied in detail [3–7]. The attention was also focused on their band structure [8–10] and the mechanism of scattering of free charge carriers [11–13]. Moreover, the issue concerning incorporation of foreign atoms into the Bi_2Se_3 crystal structure has been looked into. Specifically, in Li-doped crystals the effect of Li incorporation on the transport thermoelectric properties of Bi_2Se_3 crystals [14–17] was investigated. In paper [15] the electrochemical insertion/extraction of Li ions into/from Bi_2Se_3 crystals was studied and the process of intercalation/deintercalation was explained by the application of a suitable lattice gas model. Nevertheless, a possible interaction of incorporated Li^+ ions in Bi_2Se_3 with the defects of the host Bi_2Se_3 single crystals has not been considered yet. In this paper, we suggest a new model of defects in Li-doped Bi_2Se_3 single crystals based on the idea of the creation of a new irreversible phase. Our study is based on the investigation of insertion/extraction of Li^+ ions from/into the Bi_2Se_3 single crystal by cyclic voltammetry characterized by an anomalous course of the extraction curve.

2. Experimental

2.1. Preparation of Bi_2Se_3 single crystals

The starting polycrystalline Bi_2Se_3 was synthesised from Bi and Se elements of 5 N purity. N-type single crystals of Bi_2Se_3 were grown using a modified Bridgman technique; the details of preparation were reported previously [18]. The resulting single crystals were 50–60 mm long, approximately 10 mm in diameter, well cleavable, and their trigonal axis was always perpendicular to the pulling direction, i.e. the (0001) plane was always parallel to the ampoule axis. The orientation of the cleavage planes was checked by means of the Laue back diffraction technique.

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doi:10.1016/j.jssc.2010.09.026

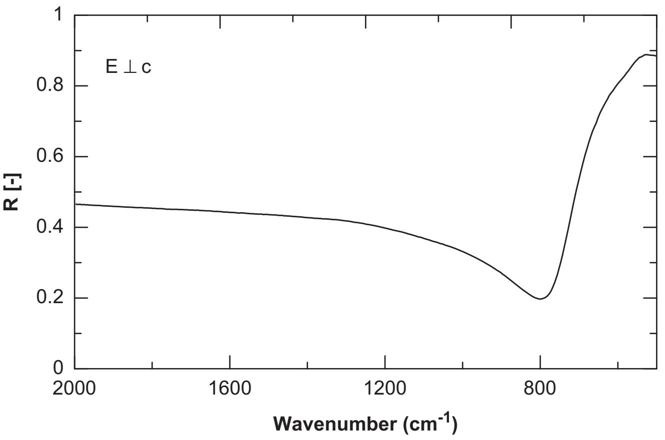

Fig. 1. Specular reflectance spectrum of a Bi_2Se_3 single crystal in the area of the plasma resonance frequency ($E \perp c$—the electric field vector of the electromagnetic radiation perpendicular to the crystallographic c-axis).

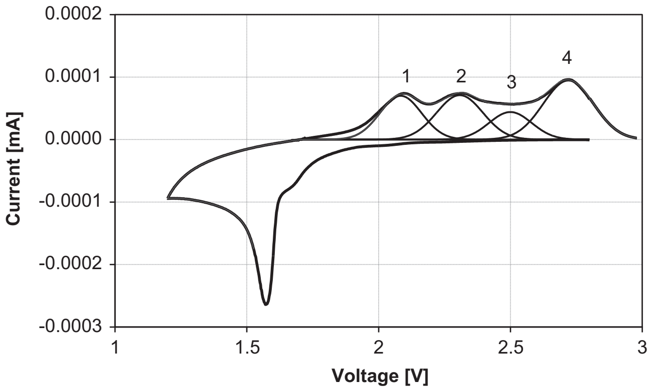

Fig. 2. Cyclic voltammogram of Bi_2Se_3 in 1 M propylen carbonate. The upper and lower curve describes deintercalation/extraction and intercalation/insertion, respectively. Band 1 corresponds to octahedral sites, band 2 corresponds to tetrahedral sites and bands 3, 4 correspond to tetrahedral sites at higher potentials.

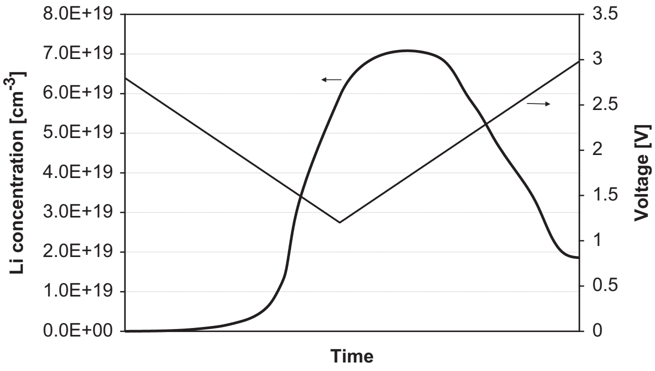

Fig. 3. Time dependence of potential on Li concentration during the insertion/extraction process.

2.2. Characterization of the undoped n-Bi_2Se_3 crystal

Bi_2Se_3 single crystal used for electrochemical insertion of lithium was characterized by the electrical conductivity measured in the direction perpendicular to the trigonal c-axis, $\sigma_\perp = 2.3 \times 10^5\,\Omega^{-1}\,m^{-1}$, and by the Hall effect measured with the current in the basal plane and the magnetic field oriented parallel to the c-axis, i.e., $R_H(B||c) = -0.245\,m^3/C$. Both quantities were determined at 300 K. High crystalline quality of the single crystal is documented by measurements of reflectivity on the natural cleavage face in the plasma resonance region (see Fig. 1).

2.3. Electrochemical insertion of lithium

The sample for electrochemical experiments was cleaved from the Bi_2Se_3 single crystal; it was sliced perpendicularly to the cleavage planes, connected to a collector, and isolated in a glass holder so that only the desired face was exposed to the electrolyte. The area of this electrode was determined to be $0.079\,cm^2$ from a digitised microshot by integration.

Electrochemical intercalation of Li into Bi_2Se_3 was investigated by means of cyclic voltammetry in the potential range 1.2–3.0 V against Li/Li^+ at room temperature.

A three-electrode cell containing 1 M $LiClO_4$ in dry propylene carbonate as an electrolyte and lithium rods as both the reference and counterelectrodes was used for the experiments. The water content in the electrolyte was checked carefully and was never higher than 20 ppm.

A potentiostat (PAR model 263) controlled by a computer was used for electrochemical measurements. Experimental data were recorded in the form of j–E curves (cyclic voltammograms)

3. Results

Insertion and extraction of lithium into/out of a Bi_2Se_3 crystal was investigated by means of cyclic voltammetry. A voltammogram recorded on the measured crystal during the first cycle in the voltage range from 3.0 to 1.2 V is shown in Fig. 2. A band corresponding to the onset of Li intercalation at about 1.7 V and another band around 1.55 V appeared on the descending part of the voltammogram (lower curve). Their counterparts, ascribed to the deintercalation process manifested themselves as two prominent bands at about 2.1 and 2.3 V (bands 1 and 2), a weak band at about 2.5 V (band 3) and a prominent band at about 2.75 V (band 4), appear on the ascending part of the voltammogram (upper curve). For a better presentation of the insertion/extraction process, changes of lithium concentrations in time corresponding with the course of the electrochemical potential, are shown in Fig. 3. To determine the number of Li^+ ions released in the course of the extraction process from positions characterized by the bands on the ascending part of the voltammogram, this part of the curve was fitted combining the current density measurement by four waves as it is demonstrated in Fig. 2 and by

$$j = \sum_{k=1}^{4} j_k \tag{1}$$

Current is given from the definition

$$I = jS = \frac{dQ}{dt} = \frac{d(evnSh)}{dt}, \tag{2}$$

where S and h are the sample cross section and depth, respectively, v is valence, e is elementary charge and n is Li concentration in sample volume.

The distribution of Li^+ ions in the region of the observed bands 1–4 (Fig. 2) can be calculated according to the equation

$$n = \int_{V_{\min}}^{V_{\max}} \frac{j}{evh} \left(\frac{\partial V}{\partial t}\right)^{-1} dV \approx n_{\mathrm{fit}} = \sum_{k=1}^{4} \int_{V_{\min}}^{V_{\max}} \frac{j_k}{evh} \left(\frac{\partial V}{\partial t}\right)^{-1} dV. \tag{3}$$

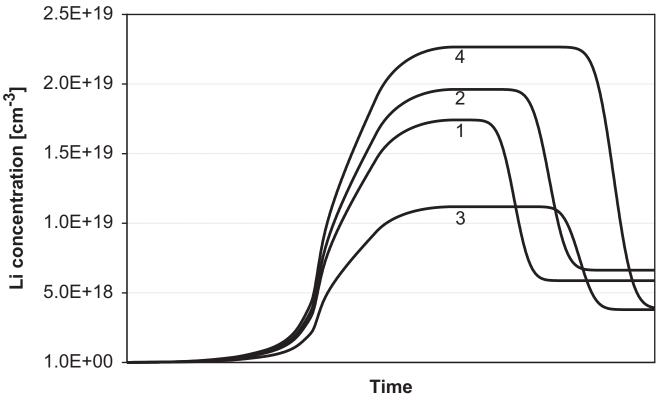

Fig. 4. Concentration of Li^+ ions in the octahedral and tetrahedral positions during the extraction process. 1—octahedral position, 2—tetrahedral position, 3, 4—tetrahedral position at higher potentials.

Table 1
The results of cyclic voltammetry.

$Li_{incaltot}$ (cm^{-3})	72.0×10^{18}	100%
$Li_{octa\ dein}$	11.2×10^{18}	15.6%
$Li_{octa\ in}$	12.8×10^{18}	17.8%
$Li_{tetra\ dein}$	12.7×10^{18}	17.6%
$Li_{tetra\ in}$	10.6×10^{18}	14.7%
$Li_{hp\ 3}$	6.7×10^{18}	9.3%
$Li_{hp\ 4}$	18.0×10^{18}	25.0%
$Li\text{-}cls^{-1}$	23.4×10^{18}	32.5%

During the extraction the amount of escaped Li^+ ions from the region of the band 1 was $Li_{octa\ dein} = 11.2 \times 10^{18}$ Li^+ cm^{-3}, from the region of the band 2 $Li_{tetra\ dein} = 12.7 \times 10^{18}$ Li^+ cm^{-3}, from the region of the band 3 $Li_{hp\ 3} = 6.7 \times 10^{18}$ Li^+ cm^{-3} and from the region of the band 4 $Li_{hp\ 4} = 18.0 \times 10^{18}$ Li^+ cm^{-3} (see Fig. 4). The total amount of intercalated Li^+ ions was $Li^+_{incaltot} = 72.0 \times 10^{18}$ Li^+ cm^{-3} (see Table 1). The process of insertion/extraction of Li^+ ions has a good reproducibility. The position of maxima of bands 1–4 on the extraction curve is in a good agreement with the experimental results published in paper [15].

4. Discussion

Van der Waals gap in the Bi_2Se_3 crystal structure is composed of empty octahedrons and tetrahedrons in the ratio 1:2, respectively; dimensions of the polyhedrons allow an incorporation of Li^{+1} ions. We assume that from the total amount of inserted Li^+ ions $Li_{incaltot}$ approximately one-third of them are incorporated at the octahedral sites and the other two thirds occupy the tetrahedral sites.

As shown in our previous papers, the intercalation of Cu into a Bi_2Te_3 crystal produces, beside intercalates, also lamellae of $CuBiTe_2$ and $Bi_3Te_4^{-1}$[19]. Furthermore, the incorporation of Pb atoms into Bi_2Te_3 gives rise to a lamellae structure of $PbBi_2Te_4$ [20] together with seven-layer-lamellae $Bi_3Te_4^{-1}$. With regard to a similar nature of Bi_2Te_3 and Bi_2Se_3, we assume a similar course of insertion/extraction in Li-doped Bi_2Se_3 crystals and the formation of similar clusters created during the insertion of Li into the crystals.

For the verification of the formation of proposed defects in Li-doped Bi_2Se_3 crystal we have applied the analysis of the insertion/extraction process of Li^+ ions from/into Bi_2Se_3 crystals investigated by cyclic voltammetry. In spite of the fact that this process was described and explained in Ref. [15], the intercalation process characterized by the formation of four bands on the extraction curve (see Fig. 2), when we follow the extraction of Li^+ ions from the van der Waals gap towards higher potentials, has not been considered yet. Insertion of Li^+ ions into the van der Waals gap at first has a character of an intercalation process. Li^+ ions first enter the octahedral sites and then fill tetrahedral sites in the van der Waals gap forming thus an intercalate ($Li^+Bi_2Se_3 + e^-$). The reverse process of extraction of a Li^+ ions is characterized on the extraction curve by the bands 1 and 2 (see Fig. 2) and we ascribe these bands with the maxima at ~2.1 and ~2.3 V to the deintercalation of Li^+ ions from octahedral and tetrahedral positions, respectively.

For a more detailed characterization of the process of intercalation/deintercalation in the Li-Bi_2Se_3 system an approximate values of site energies of octahedral and tetrahedral positions were evaluated using the lattice gas model [21]. This model takes into account the fact that Li^+ ions are released from two positions with a different energy—octahedral and tetrahedral sites in the van der Waals gap. Assuming the equality of chemical potentials of Li^+ ions in the studied system, we can write

$$\mu = E_1 + kT\ln(x_1/(x_{max1} - x_1)) = E_2 + kT\ln(x_2/(x_{max2} - x_2)), \tag{4}$$

where E_1 and E_2 are site energies of the octahedral and tetrahedral sites, respectively, and x_1 and x_2 are mean values of concentration of Li^+ ions extracted from the octahedral and tetrahedral sites, respectively. Here x_{max1} and x_{max2} are numbers representing maximum occupancy of the octahedral and tetrahedral sites in the structure; the following approximate values were taken for the studied system: $x_{max1} = 1.2 \times 10^{20}\ cm^{-3}$, $x_{max2} = 2.4 \times 10^{20}$ cm^{-3}. Inserting these values in Eq. (4) we obtain approximate values of the site energies $E_1 \doteq -2.0$ and $E_2 \doteq -2.2$ eV (Fig. 5).

These results support an idea that the extraction of Li^+ ions from the regions corresponding to the bands 1 and 2 approaches the character of a deintercalation process and thus, this process could be described by the reversible equation

$$(Li^+ + e^-) + Bi_2Se_3 \Leftrightarrow (Li^+Bi_2Se_3 + e^-) \tag{5}$$

Further extraction of Li^+ ions from the van der Waals gap is characterized by the bands 3 and 4, which could be associated with a possible interaction of Li^+ ions with the atoms in the structure of the Bi_2Se_3 crystals. To account for such a process one needs to consider the defect structure of non-stoichiometric Bi_2Se_3 and interactions of Li^+ ions with the atoms forming the lattice of the host crystal.

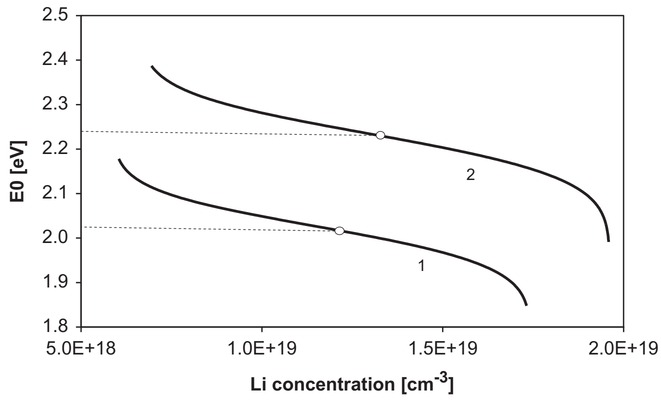

Fig. 5. The determination of site energies for the octahedral (E_1) and tetrahedral (E_2) configuration.

In a similar way as we carried out the analysis of point and structural defects of tetradymite crystals in our previous works [20,22], we describe briefly the defect structure of a Bi_2Se_3 crystal and the interaction of these defects with Li atoms introduced into the crystal lattice. As mentioned before, Bi overstoichiometry is typical for Bi_2Se_3 single crystals prepared from stoichiometric melts of Bi and Se. The presence of overstoichiometric Bi atoms can induce the following defects:

- vacancies in selenium sublattice (V_{Se}^{+2}) carrying two positive charges,
- anti-site (AS) defects (Bi_{Se}^{-1}) carrying one negative charge,
- vacancies in Bi sublattice (V_{Bi}^{-3}), which are supposed to carry three negative charges,
- complex defects of the type $Bi_3Se_4^{-1}$, $Bi_4Se_5^{-2}$ that correspond – as for the charge – to one or two anti-site Bi_{Se}^{-1} defects.

The defect structure of Bi_2Se_3 crystals can be characterized as a hybrid of the Schottky and antistructure disorder [23]; therefore we can formulate the process of creation and interaction of native defects by means of the following equation:

$$\mathrm{Bi}_{\mathrm{Bi}}^{\times} \Leftrightarrow \mathrm{Bi}_{\mathrm{Se}}^{-1} + (1+2/3)\mathrm{V}_{\mathrm{Bi}}^{-3} + 6\mathrm{h}^{+}. \tag{6}$$

Using an equivalence relation, $(2V_{Bi}^{-3}+3V_{Se}^{+2})=0$, an equilibrium of native point defects can be characterized as

$$\mathrm{Bi}_{\mathrm{Bi}}^{\times} + \mathrm{V}_{\mathrm{Se}}^{+2} + 2\mathrm{e}^{-} \Leftrightarrow \mathrm{Bi}_{\mathrm{Se}}^{-1} + \mathrm{V}_{\mathrm{Bi}}^{-3} + 4\mathrm{h}^{+}. \tag{7}$$

For the determination of concentrations of $[Bi_{Se}^{-1}$ anti-site defects, $[V_{Bi}^{-3}]$ and $[V_{Se}^{+2}]$ vacancies in Bi_2Se_3 we use a similar model as used previously [20,22]. The details of the applied model and the determination of the concentration of point defects in an undoped Bi_2Se_3 crystal are given in the Appendix.

According to Kroeger [23] the process of incorporation of lithium into the crystal proceeds in accordance with the following equation:

$$\mathrm{Bi}_{\mathrm{Bi}}^{\times} + \mathrm{V}_{\mathrm{Se}}^{+2} + 2\mathrm{e}^{-} + (\mathrm{Li}^{+1} + \mathrm{e}^{-}) = \mathrm{Li}_{\mathrm{Bi}}^{-2} + \mathrm{Bi}_{\mathrm{Se}}^{-1} + 3\mathrm{h}^{+}. \tag{8}$$

Eq. (8) shows that the embedding of lithium leads to the creation of substitutional defects Li_{Bi}^{-2} and shifts the equilibrium in favor of anti-site defects. The incorporation of point defects given by Eq. (8) into the structure of Bi_2Se_3 can be expressed by the following equation:

$$\begin{aligned}
&(\mathrm{Li}_{\mathrm{Bi}}^{-2} + \mathrm{Bi}_{\mathrm{Se}}^{-1} + 3\mathrm{h}^{+}) + (4\mathrm{Bi} + 6\mathrm{Se}) + (4\mathrm{V}_{\mathrm{Bi}}^{-3} + 6\mathrm{V}_{\mathrm{Se}}^{+2}) \\
&\quad = (\mathrm{Li}_{\mathrm{Bi}}^{-2} + \mathrm{Bi}_{\mathrm{Bi}} + 2\mathrm{Se}_{\mathrm{Se}}) + (\mathrm{Bi}_{\mathrm{Se}}^{-1} + 2\mathrm{Bi}_{\mathrm{Bi}} + 4\mathrm{Se}_{\mathrm{Se}}) + 3\,\mathrm{h}^{+} + \mathrm{Bi}_{\mathrm{Bi}} \\
&\quad = [\mathrm{Li}^{+1}(\mathrm{BiSe}_2)^{-1}\mathrm{Bi}_3\mathrm{Se}_4^{-1}) + \mathrm{h}^{+} + \mathrm{Bi}_{\mathrm{Bi}}] \\
&\quad = \mathrm{LiBiSe}_2.\mathrm{Bi}_3\mathrm{Se}_4]^{-1} + \mathrm{h}^{+} + \mathrm{Bi}_{\mathrm{Bi}}.
\end{aligned} \tag{9}$$

Eq. (9) describes an increase in the number of anti-site defects, as well as the incorporation of Li^+ ions into the crystal with the formation of a negatively charged cluster ($LiBiSe_2.Bi_3Se_4^{-1}$). An apparent discrepancy – the formation of Bi_{Bi} in Eq. (9) – is associated with the fact that the Li^+ ion, entering the crystal from the van der Waals gap, had no lattice position before the reaction described by Eq. (8).

Resulting clusters become an integral part of the crystal lattice. Concentration of the clusters is referred to below as $[\text{Li-cls}^{-1}]$. We now compare this model with the results of cyclic voltammetry.

During the insertion into the van der Waals gap one-third of $Li_{incaltot}$ occupies octahedral sites while two-thirds occupy tetrahedral sites. A fraction of Li^+ ions inserted in the octahedral and tetrahedral positions, i.e. $Li_{octa\ in}+Li_{tetra\ in}$ interacts with crystal lattice defects and forms clusters Li-cls^{-1} incorporated into the crystal structure according to Eqs. (8) and (9).

Whereas the insertion into the octahedral and tetrahedral sites proceeds in two steps, the deintercalation/extraction process from these two sites goes in four steps due to the formation of the above mentioned clusters. The ratio $Li^+/\text{Li-cls}^{-1}$ decreases during the deintercalation process and after the release of a part of Li^+ ions from the octahedral and tetrahedral positions (those ions that are not bonded in clusters $Li_{octa\ dein}+Li_{tetra\ dein}$, we come to a point of equality where $Li^+=\text{Li-cls}^{-1}$; this point is located at the minimum between the 2nd and 3rd bands of the extraction curve (see Fig. 2) at the potential of ~2.4 V. The remaining Li^+ ions in the van der Waals gap are also extracted in a two step process at higher potentials above 2.4 V. These ions are marked as $Li_{hp}=Li_{hp\ 3}+Li_{hp\ 4}$. Based on the experimental data we can claim that $Li_{octa\ in}+Li_{tetra\ in}=Li_{hp}$ (see Table 1). These results also show that the extraction of remaining positively charged Li_{hp} ions, associated with the bands 3 and 4, requires an increased potential due to the increased Coulomb forces associated with the negative charge of clusters.

The proposed description of the extraction curve makes it possible to describe the extraction process by the following relation:

$$\mathrm{Li}_{\mathrm{incaltot}} - (\mathrm{Li}_{\mathrm{octa\ dein}} + \mathrm{Li}_{\mathrm{tetra\ dein}} + \mathrm{Li}_{\mathrm{hp}}) = \text{Li-cls}^{-1} \tag{10}$$

The corresponding concentrations of all types of intercalated Li ions and clusters are summarized in Table 1.

The described extraction process can be qualitatively explained in the following way: the first part of the extraction of Li^+ ions in the region of the bands 1 and 2 approaches the deintercalation process; a further extraction of Li_{hp} ions at an increasing potential is associated with the presence of a cluster formed according to Eq. (9); the negative charge localized on the clusters Li-cls^{-1} incorporated in the crystal structure affects the extraction process in such a way that the extraction of $Li_{hp\ 3}+Li_{hp\ 4}$ species takes place at higher magnitudes of the potential above the value of the site energy E_2 ($\cong -2.2$ eV). The existence of bands 3 and 4 on the voltammograms therefore arises from the presence of a negative charge on clusters Li-cls^{-1} and its effect on the extracted positively charged $Li_{hp\ 3}+Li_{hp\ 4}$ species. The obtained experimental results make it possible to explain qualitatively the complex character of the obtained voltammograms characterized by 4 bands during the extraction of Li^+ ions from the van der Waals gap of tetradymite crystals having only two crystallographic sites—octahedral and tetrahedral.

From the data presented in Table 1, we deduce that upon completion of deintercalation/extraction of Li, almost 1/3 of all intercalated $Li_{incaltot}$ ions remain in the host lattice in the form of clusters of $\text{Li-cls}^{-1}=Li_{octa\ in}+Li_{tetra\ in}$. The proposed formation of Li-cls^{-1} clusters is in agreement with the statement in the conclusion of Ref. [15] that by the electrochemical incorporation of Li atoms into Bi_2Se_3 a Li-intercalated Bi_2Se_3 compound is formed.

We can also compare our model of insertion/extraction of Li^+ ions with the results of a detailed study of intercalation/deintercalation of Cu into/from the Bi_2Se_3 [24] single crystal: the measurements of electrical conductivity and the Hall coefficient during a long-time intercalation of Cu showed that the time evolution of the resistivity and the Hall coefficient during the deintercalation can be explained only when we suppose the presence of both free electrons and holes in the semiconducting crystal during the intercalation process. Such a finding is in agreement with the results of this paper showing that a part of incorporated Li^+ ions is embedded in the van der Waals gap (which generate free electrons), whereas a part of Li^+ interacts with structural defects creating (Li-cls^{-1}) negatively charged clusters.

5. Conclusions

Insertion/extraction of lithium ions into/from tetradymite-type Bi_2Se_3 crystals is interpreted as a coupled chemical reaction which consists of a reversible reaction, $(Li^+ + e^-) + Bi_2Se_3 \Leftrightarrow Li^+Bi_2Se_3 + e^-$, and an irreversible side reaction, $(Li^+Bi_2Se_3 + e^-) + Bi_2Se_3 \Rightarrow (LiBiSe_2.Bi_3Se_4^-) + h^+$. The formation of such a cluster can be expressed by the total formula $(LiBi_4\ Se_6)^{-1} + h^+$. The course of the extraction indicates that a part of Li^+ ions localized in octahedral and tetrahedral sites of the van der Waals gap is bound more firmly than one would expect for a situation corresponding to a mere occupation of these sites. This fact gives rise to a notion of the formation of $LiBiSe_2.Bi_3Se_4^-$ defect structure that has features of a hybrid consisting of the Schottky and antistructure disorder.

In addition to bands 1 and 2, corresponding to the extraction of Li^+ guest ions from the octahedral and tetrahedral sites in the van der Waals gap of the host crystal, the extraction curves of voltammograms reveal the presence of another two bands 3 and 4. Their existence is not in a contradiction with the mechanism of the embedding of Li^+ ions into the crystal; waves 3 and 4 are observed on the ascending part of the extraction curve and correspond to the release of Li^+ ions from the tetrahedral sites under the influence of negative charges localized on the $(LiBiSe_2.Bi_3Se_4^-)$ clusters.

Acknowledgments

The financial support of the Academy of Sciences of the Czech Republic (Research Plan AV0Z40320502) is gratefully acknowledged.

Work at the University of Michigan is supported as part of the Center for Solar and Thermal Energy Conversion, an Energy Frontier Research Center funded by the US Department of Energy, Office of Basic Energy Sciences under Award no. DE-SC0000957.

Appendix

The model described above respects Eq. (8) and is characterized by the idea that overstoichiometric Bi atoms (Bi_{over}) enter both the cation sublattice (on regular sites as Bi_{Bi}) and the anion sublattice as anti-site (AS) defects (Bi_{Se}^{-1}). The latter Bi atoms occupy sites in the anion sublattice in Se^2-sites. The formation of each AS defect is accompanied by the formation of a cation vacancy V_{Bi}^{-3} as follows from Eq. (2). Further, this model satisfies the condition that the ratio of the number of the cation sublattice sites to the anion sublattice ones is equal to 2/3. It also follows from Eq. (2) that the number of incorporated overstoichiometric Bi atoms influences the balance in Eq. (2) and determines the concentration of free charge carriers. In this model we do not concede an existence of Bi atoms in interstitial sites or inside of the van der Walls gap. The presented model is determined by the following relations:

$$\text{(a)}\ [Bi_{over}] = [Bi_{Bi}] + [Bi_{Se}^{-1}]$$

$$\text{(b)}\ [Bi_{Se}^{-1}] = [V_{Bi}^{-3}]$$

$$\text{(c)}\ 2[V_{Se}^{+2}] = [e^-] + [Bi_{Se}^{-1}] + 3[V_{Bi}^{-3}]$$

$$\text{(d)}\ ([Bi_{Bi}] + [V_{Bi}^{-3}])/([V_{Se}^{+2}] + [Bi_{Se}^{-1}]) = 2/3 \qquad 11(a,b,c,d)$$

These relations were used for the calculation of concentrations of considered point defects. The following concentrations of point defects were calculated using relations [5 a, b, c, d], measured electron concentration $[e^-] = 2.5 \times 10^{19}\ cm^{-3}$ in undoped Bi_2Se_3 and the value of $[Bi_{over}] = 1.05 \times 10^{19}\ cm^{-3}$ taken from [25]: $[V_{Bi}^{-3}] = 1.08 \times 10^{18}\ cm^{-3}$, $[V_{Se}^{+2}] = 14.7 \times 10^{18}\ cm^{-3}$, $[Bi_{Se}^{-}] = 1.08 \times 10^{18}\ cm^{-3}$, $Bi_{Bi} = 9.4 \times 10^{18}\ cm^{-3}$. It is necessary to note, that with respect to the validity of relation $(2V_{Bi}^{-3} + 3V_{Se}^{+2}) = 0$ only $13.0 \times 10^{18}\ cm^{-3}$ of $[V_{Se}^{+2}]$ are electrically active.

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