Functional Materials 11, No.3 (2004)

Preparation of high-purity charge for growth of $Cd_{1-x}Zn_xTe$ crystals

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Possibilities have been studied to prepare high-purity charge for growth of $Cd_{1-x}Zn_xTe$ crystals of high perfection and spectrometric quality. Studies have been carried out of deep purification of Cd, Zn and Te using the installation developed by us, which comprised a rotating container of optical quartz, by distillation and recrystallization. This installation is polyfunctional, allowing distillation, zone purification, recrystallization in horizontal (at a small angle) or vertical direction. It has been shown that horizontal zone purification is efficient for most admixtures, with exception of carbon. For carbon removal from Cd, Zn and Te, a vertical variant of zone purification was additionally used, which allowed reduction in carbon content from 10^{-3} to ~10^{-6} %.

Работа посвящена исследованию возможности получения высокочистой шихты для выращивания кристаллов $Cd_{1-x}Zn_xTe$ высокого структурного совершенства и спектрометрического качества. Приведены результаты изучения процессов глубокой очистки Cd, Zn и Te при использовании разработанной нами установки с вращающимся контейнером из оптического кварца путем их дистилляции и перекристаллизации. Эта установка является многофункциональной и позволяет проводить дистилляцию, зонную очистку, перекристаллизацию как в горизонтальном (под небольшим углом), так и в вертикальном направлениях. Показано, что горизонтальная зонная очистка является эффективной для большинства примесей, за исключением углерода. Для очистки Cd, Zn и Te от примеси углерода дополнительно использован вертикальный вариант зонной очистки, который позволил снизить содержание углерода с 10^{-3} до ~10^{-6} %.

It has been shown [1] that for preparation of perfect $Cd_{1-x}Zn_xTe$ crystals of spectrometric quality the charge used should contain constituents (Cd, Zn, Te) of high purity. Negative effects of carbon inclusions have been specially noted [2]. The presence of carbon can give rise to low-resistivity regions and conducting channels leading to detector breakdown [3]. Contamination of the growing crystal by equipment materials (especially by carbon) is a natural process, but the purity degree of the initial raw material plays a major role.

A complex of different purification methods is generally used for preparation of pure substances [4–8].

Efficiency of zone melting processes depends upon the dopant effective distribution coefficient k_{eff}, which is the ratio of the dopant concentration in the solid phase near the moving phase boundary surface to its concentration in the liquid phase at a certain distance from the interface. In processes of zone recrystallization or crystal growth, a region (layer) with higher or lower dopant concentration can be formed at the solid/liquid phase boundary due to a limited molecular diffusion. The presence of this layer lowers the purification degree and, in certain conditions, can completely nullify the effects of purification. The effective distribution coefficient is determined according to the expression:

$$k_{eff} = \frac{k_0}{k_0 + (1 - k_0)e^{-\frac{V_{cr}\delta}{D}}}, \quad (1)$$

where k_0 — is the equilibrium distribution coefficient determined by the solution diagram of state; V_{cr} is the crystallization rate, δ — thickness of the boundary layer; D — diffusion coefficient in the melt.

It is known that at $k_{eff} > 1$ a dopant-depleted layer is formed near the crystal surface, and at $k_{eff} < 1$ — an enriched one. Dopant capture in the process of crystal growth or material purification by melt crystallization methods are controlled by this layer. To decrease its effects upon the final purification result, various methods of melt mixing are generally used: ampoule vibration, magnetic [9] or ultrasonic techniques.

The objective of the present work was to study possibilities of increasing the purification degree of Cd, Zn and TeZn in an installation equipped with a rotating container made of optical quartz [10], ensuring rotation in the vertical plane from 0° to 180°.

In a container that does not rotate, mixing is carried out due to natural convection; the container rotation ensures forced mixing, leading to higher purification degree of the initial compound.

As initial compounds, we used Cd, Zn and Te with main substance content of 99.99...99.999 %. Purification of the initial components was carried out in an installation developed by us [10]. Its schematic drawing is shown in Fig. 1. The material purification method used is based on double distillation for separation of heavy and volatile admixtures with subsequent zone recrystallization.

At the first stage of this work, distillation of the initial material was carried out in the following temperature conditions: evaporation temperature $T_{ev} = T_m +$ (50...60)°C, condensation temperature $T_c = T_m -$ (30...40)°C, where T_m is the melting point of the substance.

High separation efficiency in distillation, as a rule, is manifested at large boiling temperatures of the purified substance and the dopant [11]. One of the main quantitative characteristics of the efficiency of separation of the main material from the admixture is the partition coefficient:

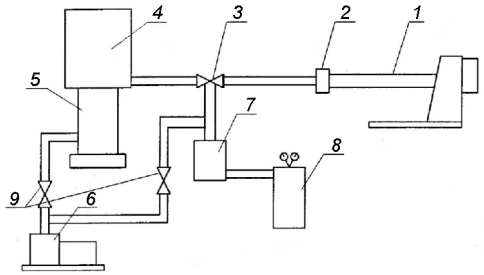

Fig. 1. Schematic design of the rotating container installation: 1 — container, 2 — vacuum seal, 3 — three-way valve, 4 — nitrogen trap, 5 — diffusion pump, 6 — forevacuum (roughing down) pump, 7 — filter, 8 — gas vessel, 9 — vacuum valve.

$$\alpha = \frac{P_1^0}{P_2^0}, \quad (2)$$

where P_1^0 and P_2^0 are saturated vapor pressures of individual basic and admixture components, respectively.

Distillatin was carried out in a sealed vacuum container installed at an angle of 3–5° to the horizon loaded with initial Cd, Zn or Te. After final distillation, the purified material yield with respect to the initial load was 90–95 %.

At the second stage of our work, additional purification was carried out by zone melting in the argon atmosphere (for Cd and Zn) and in hydrogen atmosphere for Te by both horizontal and vertical methods (Figs. 2,3, respectively). Gas pressure in the container was 0.7–0.8 atm; container rotation speed was 80–100 rpm; crystallization speed 3–4 cm/h; variable inclination angle. After each run, the melt residues were poured onto the container bottom. The purified material yield was 80–85 %.

The final purification was carried out by vertically directed recrystallization. It is primarily aimed at purifying the substance from carbon admixtures, for which the horizontal directional crystallization was shown to be of low efficiency. The vertical crystallization was carried out in vacuum-sealed and argon-filled (up to 0.7–0.8 atm) container installed at < 90° to the horizon, with heaters being varied: the narrow one — downward, the wide one — upward. After crystallization completed, directional crystallization was carried out from bottom to top changing the container rotation to the opposite after each run. In the melted layer of the material, the Archimedes force operates, pushing these particles to the

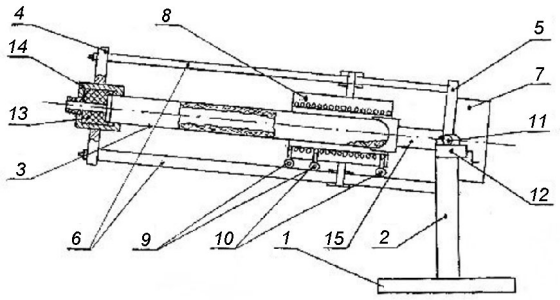

Fig. 2. General view of the horizontal purification container: 1 — base, 2 — pillar, 3 — container, 4 — forward support, 5 — back support, 6 — guides, 7 — electrical drive, 8 — two-zone heater, 9 — narrow zone, 10 — broad zone, 11 — axis, 12 — rotation device, 13 — vacuum input, 14 — clamp, 15 — clip.

upper part of the layer, thus favoring carbon removal. The final yield of the purified material was 65–70 %.

Analysis of the initial and purified products was carried out using laser mass-spectrometry with recording by a UF-4 film (a Mattauch-Hertzog MS 3101 high resolution laser mass-spectrometer with double focusing). The relative standard deviation for all the analyzed elements was within 0.15–0.30.

Analyses were carried out for 24 purification experiments with Cd, Zn, Te and $Cd_{1-x}Zn_xTe$ with determination of 78 impurity elements. The results obtained show that in the initial zinc, the most important contaminants were (in mass %): Ca — $1{\cdot}10^{-5}$, Cr — $6{\cdot}10^{-5}$, Fe — $1.3{\cdot}10^{-4}$, Cd — $2.5{\cdot}10^{-4}$, Te — $3.2{\cdot}10^{-4}$. Concentrations of other admixtures was either below $1{\cdot}10^{-5}$ % or below their detection limits. After distillation and horizontal purification of the initial zinc, the concentration of carbon was reduced by ~ 2 times, Cd — by 10 times, Cr — by 30 times, Fe — by 200 times. Te concentration remained essentially unchanged. After vertical zone purification, carbon concentration was reduced down to $1{\cdot}10^{-6}$%.

Results for cadmium after and before distillation and horizontal purification were the following. For the initial Cd, the largest concentration (in mass %) was noted for C — $7{\cdot}10^{-5}$, O— $3{\cdot}10^{-4}$, Ag — $1.3{\cdot}10^{-4}$, Sn — $1.2{\cdot}10^{-4}$, Tl — $1.8{\cdot}10^{-4}$, Pb — $4.4{\cdot}10^{-4}$. As a result of purification, the concentration of oxygen decreased by 3 times, and that of Ag, Sn, Tl and Pb ~ by 10 times. However,

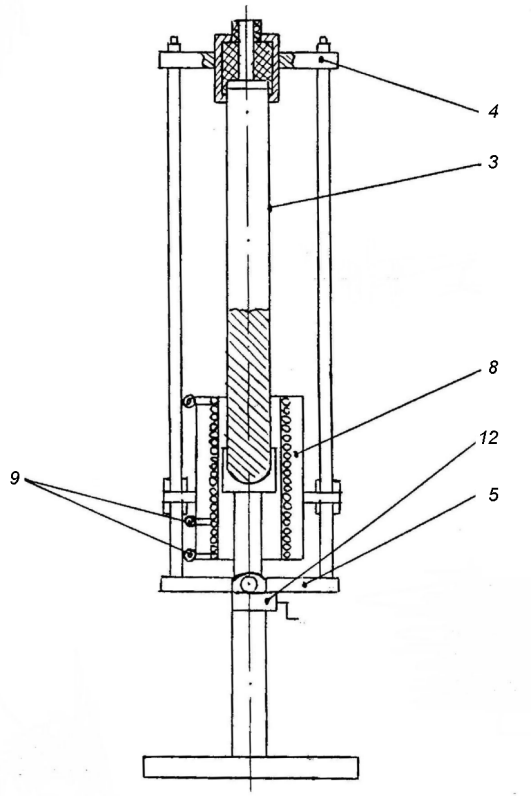

Fig. 3. General view of the container for vertical purification (designations are the same as in Fig. 2).

for carbon admixtures the purification appeared to be inefficient. After vertical zone purification, carbon concentration was decreased down to $1{\cdot}10^{-6}$%.

In the initial tellurium, the most important admixtures were (in mass%): C — $1{\cdot}10^{-4}$, Cl — $3{\cdot}10^{-4}$, Ni — $2{\cdot}10^{-3}$, Cu — $1{\cdot}10^{-3}$, Se — $3.5{\cdot}10^{-4}$, Mo — $2{\cdot}10^{-4}$, Ru — $8{\cdot}10^{-4}$, Rh — $2{\cdot}10^{-4}$, Pd — $6{\cdot}10^{-4}$, Ag — $2.4{\cdot}10^{-3}$, Pt — $5.8{\cdot}10^{-2}$, Pb — $4{\cdot}10^{-2}$. After distillation and horizontal purification, concentrations were decreased: Cl — by 150 times, Ni ~ by 400 times, Cu ~ by 200 times, Mo — by 10 times, Ru ~ by 30 times, Rh ~ by 200 times, Pd ~ by 20 times, Ag ~ by 200 times, Pt — by more than ~ 100 times, Pb — by more than 300 times. This purification was inefficient for C and Se. After vertical zone purification, carbon concentration was decreased by 100 times.

It should be noted that after horizontal purification of Cd, Zn and Te concentration of carbon admixture remained rather high (~ 10^{-4}%). It could be substantially reduced (to 10^{-6}%) only after vertical zone purification.

Table. Total content of admixture elements in Cd, Zn, Te and $Cd_{1-x}Zn_xTe$ in the initial state and after distillation, horizontal and vertical zone purification

Material	Total admixture content in the initial material, mass.%	Total admixture content in the material after distillation and horizontal purification, mass.%	Carbon content in the material after vertical zone purification, mass.%
Cd	$1.2 \cdot 10^{-2}$	$7.0 \cdot 10^{-4}$	~ 10^{-6}
Zn	$2.1 \cdot 10^{-2}$	$1.7 \cdot 10^{-3}$	~ 10^{-6}
Te	$1.1 \cdot 10^{-1}$	$1.5 \cdot 10^{-3}$	~ 10^{-6}
$Cd_{1-x}Zn_xTe$	–	$5.5 \cdot 10^{-3}$	~ 10^{-6}

Composition was also analyzed of $Cd_{1-x}Zn_xTe$ crystals grown by the Bridgman-Stockbarger method from the charge prepared from the purified elements. The level of admixtures was (in mass %): C — $4 \cdot 10^{-6}$, O — $1 \cdot 10^{-5}$, Al — $1 \cdot 10^{-5}$, Si — $4 \cdot 10^{-5}$, Fe — $7 \cdot 10^{-5}$, Mo, Ru, and Pd — $1 \cdot 10^{-5}$, and Se — $2 \cdot 10^{-4}$. Concentration of other controlled admixtures was either below $1 \cdot 10^{-5}$%, or below the analysis sensitivity.

In Table 1, results are presented on the total content of admixture elements (including carbon) in Cd, Zn, Te and $Cd_{1-x}Zn_xTe$ before and after distillation, horizontal and vertical purification.

1. It has been shown that the installation used, equipped with a rotating container, is multifunctional and can be used for distillation, zone purification, recrystallization in horizontal (at small angles), or vertical position. It can also be used for synthesis of materials.

2. Analysis of [4] shows that the method of horizontal purification in a rotating container does not ensure removal of carbon down to acceptable concentrations. In our work, carbon concentration decrease to 10^{-6} % was achieved only after vertical purification (which as used as a supplementary stage to the horizontal purification), after which the carbon concentration was ~ 10^{-4} %.

3. After certain improvements, our installation can be used for growth of $Cd_{1-x}Zn_xTe$ crystals of high spectrometric quality, with content of main controlled admixtures at the level of ~ $5 \cdot 10^{-3}$ %, and of carbon ~ 10^{-6} %.

The research described in this publication was made possible in part by Award No.UE-2481-KH-02 of the US Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF).

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Одержання шихти високої чистоти для вирощування кристалів $Cd_{1-x}Zn_xTe$

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Робота присвячена дослідженню можливості одержання шихти високої чистоти для вирощування структурно досконалих кристалів $Cd_{1-x}Zn_xTe$ спектрометричної якості. Приведено результати вивчення процесів глибокого очищення Cd, Zn та Te при використанні розробленої нами установки з обертовим контейнером із оптичного кварцу шляхом їх дистиляції і перекристалізації. Ця установка є багатофункціональною і дозволяє проводити дистиляцію, зонну очистку, перекристалізацію як у горизонтальному (під невеликим кутом), так і у вертикальному напрямках. Показано, що горизонтальна зонна очистка є ефективною для більшості домішок, за винятком вуглецю. Для очищення Cd, Zn та Te від домішки вуглецю додатково використаний вертикальний варіант зонної очистки, що дозволив знизити вміст вуглецю з 10^{-3} до ~10^{-6} %.