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Effects of tellurium concentration on the structure of melt-grown ZnSe crystals

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Abstract

It has been shown that isovalent doping by tellurium positively affects the structural perfection of ZnSe crystals related to the completeness of the wurtzite–sphalerite phase transition. The optimum concentration range of tellurium in ZnSe crystals is 0.3–0.6 mass %. X-ray diffraction studies have shown that in $ZnSe_{1-x}Te_x$ crystals at tellurium concentrations below 0.3 mass % twinning and packing defects occur, while tellurium concentrations above 0.6 mass % lead to formation of tetragonal crystal lattice.

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1. Introduction

It is known that crystals $A^{II}B^{VI}$ are distinguished by their polymorphism and polytipism, which become more probable when the wurtzite lattice parameter ratio c/a approaches the ideal value of 1.633. This feature is characteristic for undoped ZnSe crystals, which can crystallize into the wurtzite (W) or sphalerite (S) structure depending on specific conditions of their preparation [1]. ZnSe crystals grown from the melt normally have the sphalerite structure. However, packing defects are always present, which are due to incompleteness of the $W \rightarrow S$ phase transition in the process of cooling of the grown crystal. Such crystals are characterized by anisotropy of their optical and mechanical properties.

Doping of zinc selenide with different admixtures leads to changes in the crystal structure and redistribution of the structure defects.

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Tellurium-doped ZnSe crystals ($ZnSe_{1-x}Te_x$), are an efficient scintillation material for dosimetry and radiation monitoring, non-destructive testing, industrial and medical introscopy, equipment for security and customs inspection, etc. [2,3]. However, data on peculiar crystal structure features of tellurium-doped ZnSe crystals as compared with undoped crystals are scarce. Specifically, it is not clear what concentration of tellurium introduced into the melt would be optimum for the structural perfection of these crystals as scintillation materials.

As practically all physico-chemical properties of $A^{II}B^{VI}$ depend upon structural perfection and inperfection, studies of their crystal structure are of great interest and importance.

The aim of the present work was studying a possibility to prepare ZnSe crystals from the melt which would be of sphalerite structure without packing defects by means of doping the crystal with isovalent tellurium.

2. Experimental

$ZnSe_{1-x}Te_x$ crystals were grown from the melt in graphite crucibles under an inert gas (argon) pressure by the Bridgman–Stockbarger method in vertical compression furnaces. In the process of growth, the melt overheating value ΔT was varied (30–200 κ), as well as the inert gas pressure P_{Ar} (5×10^5–3×10^6 Pa) and crystallization speed V_κ (1–10 mm/h).

As initial material, we used ZnSe–ZnTe solid solution in the form of powder, with Te content from 0.5 to 3 mass %. The concentration of Te (C_{Te}) in the crystals was determined using X-ray fluorescence analysis on an VRA-30 installation, with lower determination limit of 0.01 % and relative error not more than 5 %. Local elemental composition was determined using a Link AN10185S scanning electron microscope (EMPA—electron-probe microanalysis); the analysis sensitivity was $\pm$0.3–0.5 mass %. The highest concentration of Te in the grown crystals was 7 mass %.

The presence of twinning and block structure in $ZnSe_{1-x}Te_x$ crystals was determined using X-ray diffraction method by the presence of additional reflexes in scanning the inverse space of the crystal along directions parallel to $<1\,1\,1>$. Diffractograms for samples of about 1 mm^3 size taken from different parts of the crystal were obtained using a two-crystal spectrometer with Cu $K_{\alpha 1}$ emission and (4 0 0) reflection of silicon monochromator.

The presence of packing defects was checked using powder X-ray patterns from $ZnSe_{1-x}Te_x$ samples with different tellurium concentration by systematic shift if specified reflexes. To obtain the X-ray patterns, Cu K_β radiation was used, which allowed avoiding the line asymmetry that distorted the shape of the curve.

Microstructure defects were studied with an optical microscope using polarized light and phase contrast.

3. Results and discussion

The melt-grown ZnSe crystals have the sphalerite structure at room temperature, but there are packing defects related to non-completeness of the phase transition wurtzite–sphalerite (W → S). The temperature of this phase transition is 1420 °C (heating) and 1410 °C (cooling) for crystals grown in crucibles of ultra-high purity graphite [4]. Both structures are characterized by tetrahedral coordination of atoms and are distinguished by the sequence of filling of the densely packed layers (0 0 0 1) in structure W and (1 1 1) in structure S. Violation of this sequence leads to the formation of packing defects. They create in ZnSe crystals a system of stripes and boundaries oriented in plane $(1\,1\,1)_W$, which had been transformed from plane (0 0 0 1) of the high-temperature wurtzite phase.

In polarized light, on planes (1 1 0) of ZnSe crystals birefringence bands can be observed, parallel to planes $(1\,1\,1)_W$. It was established [5,6] that birefringence in ZnSe crystals is of piezo-optical nature and is directly related to mechanical stresses that appear in polysynthetic twinning during the phase transition. The boundary line between the light and the dark stripes corresponds to the growth packing defect. Such defects cause one-dimensional disordering of the lattice S of the crystal due to violation of the ordered sequence of