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Ceramic materials made of CdTe and Cd-Zn-Te nanocrystalline powders

Research Article

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Abstract: In the present study newly produced semiconductor ceramic nanopowder materials made of CdTe and $Cd_{1-x}Zn_xTe$ (CZT) are considered. Common features and differences in microstructures, phase transformations, grain growth and properties of the ceramic materials of the binary and ternary compositions are studied.

Keywords: *AIIBVI semiconductors • Nanomaterials • Ceramics • Phase transformation • Grain growth*

1. Introduction

Cadmium telluride and cadmium-zinc tellurides are widely used in IR optics, ionizing radiation detectors [1,2]. Bulk semiconductor materials are conventionally grown from melt by Brigdman and similar techniques [2-4]. However, new technologies are being developed and new ideas of production of these materials are implemented. One of them is the production of ceramic materials. They seem to be promising, because production of optical elements from ceramics in many cases should be easier and less expensive than a multi-staged process including melt growth, cutting and polishing of the elements. However, numerous attempts to make ceramic semiconductor materials have failed. Only experiments with ZnS, ZnSe ceramics were more or less successful [5]. These ceramics were produced from CVD microcrystals by sintering in combination with high-pressure treatment at elevated temperatures. So far, no telluride ceramics have ever been produced.

We have developed the technique for production of cadmium telluride and cadmium zinc telluride nanopowders [6] and fabrication of dense ceramics from these nanopowders [7,8]. We have previously studied some properties of CdTe [6,7] and CZT [8-10] ceramics.

The aim of this study is to compare microstructures, textures, phase compositions of the ceramics made of binary and ternary nanopowders and to study an effect of the third component, zinc, on the phase transformation and grain growth of the CdTe and Cd-Zn-Te ceramics.

2. Experimental Procedure

The CdTe and $Cd_{1-x}Zn_xTe$ nanopowders consist of nanocrystals deposited from vapor. These powders with a definite chemical composition were obtained directly from the vapor phase. The following steps are involved: evaporation of the initially synthesized polycrystalline materials, complete decomposition of the compounds, reaction in the vapor phase, and deposition of the particles [6]. Neither impurities nor side products appear in the process, so the powders are pure. The particles are small, and have an almost spherical shape. This makes it possible to compact the materials at room temperature without bindings, lubricants and under relatively low pressure. As a result, density of the bulk ceramic materials is 95-97% of the single crystal density.

The ceramics from CdTe, Cd-Zn-Se nanopowders were fabricated at room temperature in air by compression on a TT-CM-L Instron machine under constant pressure in the range of 400-650 MPa. The loading time ranges from 1 to 30 min [7,8]. Samples of the ceramics were annealed in a furnace in a sealed tube under pressure about 0.1 mbar.

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To compare some properties of the ceramics and the traditionally produced crystals, CdTe and $Cd_{1-x}Zn_xTe$ single crystals were grown from melt by High Pressure Vertical Zone Melting [4].

X-ray powder diffraction (a Siemens D500) and X-ray texture analysis (a DRON 3) were used to analyze phase composition and crystallographic structure of the compacted ceramic samples. X-ray electron probe microanalysis (a Vega Tescan) was used to study chemical composition of the samples. Vickers microhardness was measured on a PMT-3 setup, the loads applied were in the range of 50-100 g. A Neophot-2 was used to conduct metallographic studies. Grain size distribution was measured by Saltykov random line method.

3. Results and Discussion

Figs. 1a, b shows the microstructure and grain size distribution of the CdTe ceramics, which consists of quite uniformly distributed grains with prevailing diameter of 8 µm. These almost equiaxial small grains is a substructure of a larger elongated grain. The grain structure consists of these coarse elongated grains, which in fact are deformation bands, with a grain boundary in <110> direction. This microstructure has a two-component crystallographic texture: sharp cubic texture {100}<110> and <100> axial texture, as is shown in the pole figure (Fig. 2). Intensity levels of the relative values 0.3, 0.5, 0.8 are indicated in the figure.

Grain size distribution in $Cd_{1-x}Zn_xTe$ (CZT) ceramics is less uniform, it has bimodality, which becomes even more pronounced after short time annealing at T_{an} = 300 °C for t_{an} = 10-30 min (Figs. 3a, b). Microstructure of CZT ceramics after compression and annealing is shown in Figs. 3c, d. In this case the textural components are the same as in CdTe ceramics, but the texture is weaker (Fig. 4).

The cubic component of the texture disappears during the annealing. After 2 hours of annealing at T_{an} = 300°C the textures become more scattered and disappear completely (Fig. 5).

In both cases, the ceramics made of nanopowders have binary or ternary composition. Annealing in vacuum after compaction brings to grain growth. However, for CdTe, where grain structure is rather uniform after compaction, annealing at T_{an} = 300°C for 0.5—2 h brings to coarsening of grains, while for CZT ceramics having bimodality in grain size distribution after compaction, annealing under the same conditions leads to gradual increase in uniformity of grain size distribution as the annealing time increases.

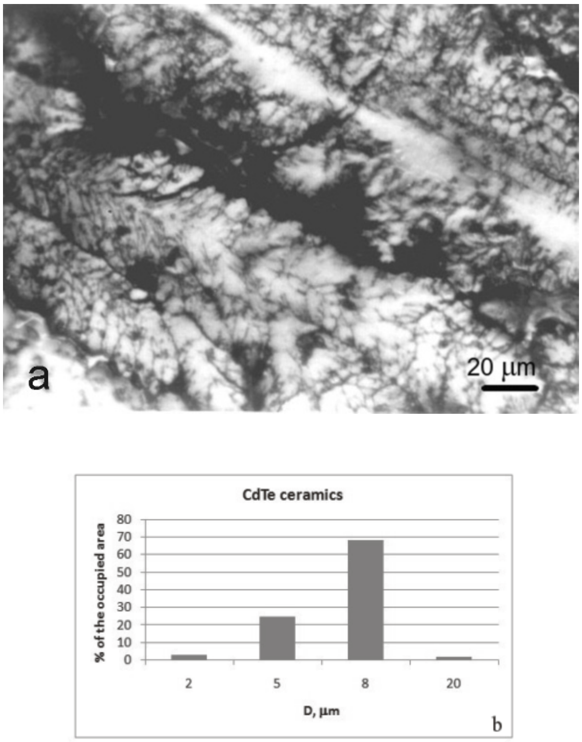

Figure 1. CdTe ceramics after compression at T = 25°C, p = 600 MPa: (a) microstructure; (b) grain size distribution.

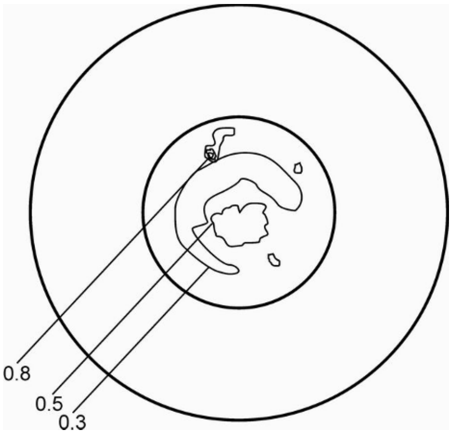

Figure 2. Pole figure {220} of CdTe ceramics after compression at T = 25°C, p = 600 MPa.

In the initial state the nanopowders contain hexagonal (wurtzite) and cubic (sphalerite) phases (Figs. 6a,7a). During compaction the hexagonal phase transforms into the cubic. In CdTe ceramics the transition is complete during pressing, only traces of hexagonal phase remains (Fig. 6b). Whereas in CZT ceramics about 10% of hexagonal phase remains after compressing (Fig. 7b). Further annealing of the samples at T_{an} = 300°C for 2 h results in complete transformation into the stable cubic phase (Fig. 7c).

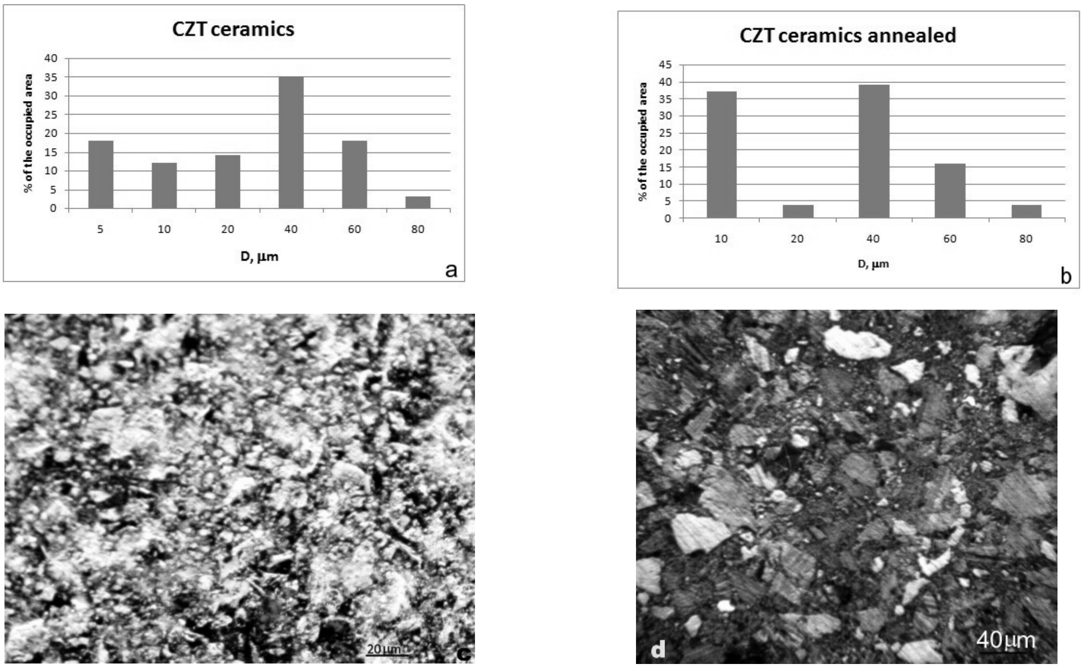

Figure 3. Cd-Zn-Te ceramics after compression at T = 25°C, p = 400 MPa: (a, b) grain size distribution; (c, d) microstructure before and after annealing at T_{an} = 300°C, t_{an} = 10 min.

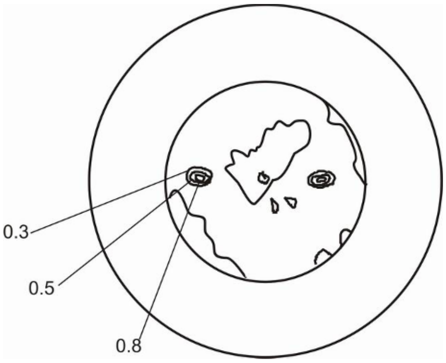

Figure 4. Pole figure {220} of CZT ceramics after compression at T = 25°C, p = 400 MPa.

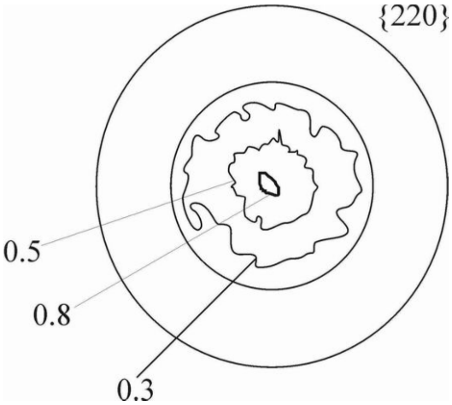

Figure 5. Pole figure {220} of CZT ceramics after compression at T = 25°C, p = 400 MPa and annealing at T_{an} = 300°C, t_{an} = 120 min.

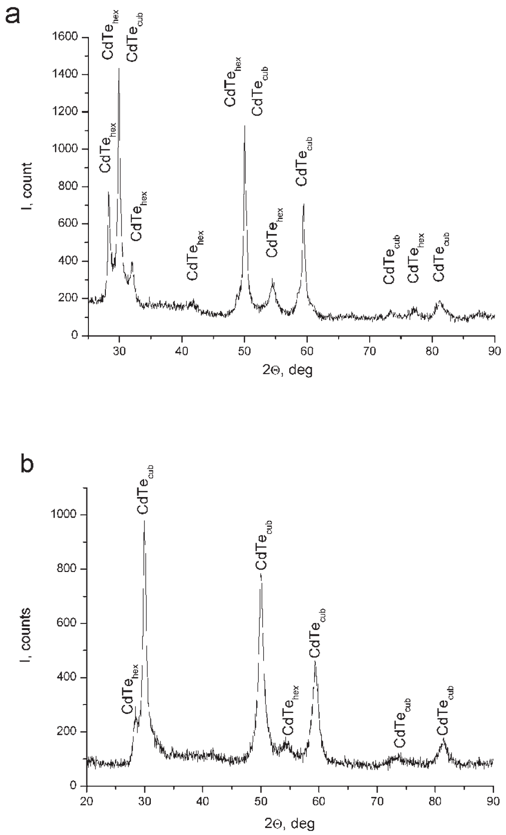

Figure 6. Diffractograms of CdTe: (a) nanopowder; (b) ceramics produced by compaction of the powder at T = 25°C, p = 600 MPa.

Table 1. Microhardness of ceramics and single crystals

Material	Treatment	H_v, MPa
CdTe single crystal	As grown	450
CdTe ceramics from nanopowder	T_d = 25°C, 10 min, P = 600 MPa	1400
CdTe ceramics from nanopowder	T_d = 200°C, 30 min, P = 600 MPa	1460
CdTe ceramics from micropowder	T_d = 25°C, P = 600 MPa, 10 min	850
$Cd_{0.9}Zn_{0.1}Te$ single crystal	As grown	830
$Cd_{0.9}Zn_{0.1}Te$ from nanopowder	T_d = 25°C, 5 min, P = 400 MPa	1550
$Cd_{0.9}Zn_{0.1}Te$ from nanopowder	T_d = 25°C, 5 min, P = 400 MPa, T_{an} = 300°C, t_{an} = 30 min	1160
$Cd_{0.9}Zn_{0.1}Te$ from nanopowder	T_d = 25°C, 5 min, P = 400 MPa, T_{an} = 25°C, storage at room temperature for 1.5 year	717
ZnTe single crystal	As grown	788
$Cd_{0.96}Zn_{0.04}Te$	As grown	640
$Cd_{0.9}Zn_{0.1}Te$ single	As grown	710

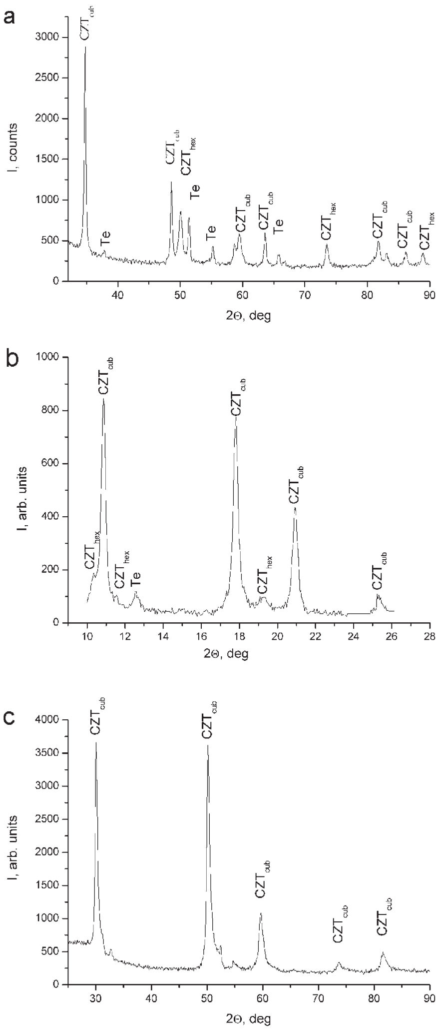

Figure 7. Difftactograms of CZT: (a) nanopowder; (b) ceramics produced by compaction of the powder at T = 25°C, p = 450 MPa; (c) ceramics annealed at T = 300°C for t = 2 h.

Microhardness of CdTe and $Cd_{0.9}Zn_{0.1}Te$ ceramics is at least three times higher than that of the respective single crystals (see Table 1). Both the $Cd_{0.9}Zn_{0.1}Te$ ceramics and the single crystals have higher microhardness than the CdTe ceramics. Most probably, solid solution hardening causes an increase in hardness of CZT single crystals and ceramics as compared to the respective CdTe materials.

Binary CdTe has a chemically stoichiometric composition, whereas $Cd_{1-x}Zn_xTe$ compositions are continuous solid solutions of the pseudo-binary CdTe—ZnTe system. This may cause a difference in kinetics of phase transition in the ceramic materials made of these compounds: if hexagonal zinc is accumulated on stacking faults embedded in the cubic matrix, it should cause a decrease in the stacking fault energy, and impeding of the polymorphic transition from wurtzite to sphalerite in CZT ceramics as compared to the ceramics made of CdTe nanopowder. Annealing after deformation provides additional energy for completion of the transition in the ceramics made of Cd-Zn-Te powder. Presence of Zn in these compounds may also influence uniformity of deformation, grain growth and grain size distribution in the considered ceramics.

4. Conclusions

The effect of the third component - zinc on the phase transformation and grain growth during compaction of the CdTe and CZT nanopowders and annealing of the ceramics after deformation was found. It has been shown that transition from the hexagonal to the cubic phase is impeded by presence of Zn. The conditions which provide complete phase transition into the stable cubic phase in the nanopowder-based CdTe and Cd-Zn-Te ceramics have been found. The effect of zinc on the increase of microhardness of the ceramics is considered.

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