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EVALUATION OF CZT CRYSTALS FROM THE FORMER SOVIET UNION

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ABSTRACT

Vertical high pressure Bridgman (VHPB) $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($0.04 < x < 0.24$) detector crystals grown in the Ukraine and Russia have been evaluated and compared to U.S.-grown materials. Various analytical techniques were used to study the materials for trace impurities, precipitates, crystallinity, and electrical transport properties. Relatively high concentrations of carbon and trace impurities such as Se, Nd and Si have been detected in the crystals. In most cases, the crystals showed lower resistivity than U.S.-grown CZT. However, recent crystals grown in Russia exhibited better detector performance than those grown in prior years, and good response to an ^{241}Am radioactive source was found. Electron lifetimes below $1\ \mu\text{s}$ were measured in crystals having significant numbers of micro-defects, compared to lifetimes of 5-15 μs found in spectrometer grade materials produced in the U.S. Furthermore, the zinc composition along the growth axis showed better homogeneity in comparison with the U.S. material.

1. INTRODUCTION

The present need for CZT spectrometers with better electrical properties requires crystals having higher purity of the starting materials and higher crystalline perfection of the final product. The widespread desire for portable gamma-ray spectrometers based on solid-state detectors has triggered the present investigation of CZT grown by different suppliers. In each case the crystals were grown using the vertical high pressure Bridgman. Crystals grown in the U.S., Russia, and the Ukraine were compared in terms of their ability to

produce high-quality detectors [1-10]. The results have shown that better understanding of the growth parameters is essential for improving the material quality. It is also clear that microstructural defects, such as grain boundaries, affect the total performance of the CZT. Some of the major causes for poor detector response are related to microstructural defects, crystallinity and uniformity, and significant improvements are expected by modifying the growth process [1].

Alpha particle spectroscopy is one of the most common methods used to evaluate electrical properties associated with electron transport in wide band gap semiconductors; however, highly imperfect regions of the detectors do not respond to alpha radiation. In order to evaluate the electrical properties of those regions and to study the hole transport, a much more intense source of energy is required to produce detectable current pulses. In this study a 3-ns laser pulse, which produces many orders of magnitude more charges, is used. In parallel, we have focused on the evaluation of the elemental impurities in the bulk CZT as well as the microstructures. Carbon was found to be one of the main impurities in CZT. We suspect that it originates from the graphite-deposited growth crucible. In an earlier publication [10], it was shown that carbon could be found as separate precipitates and also aligned along grain boundaries. These impurities could, in turn, lower the resistivity and increase the leakage currents, thus deteriorating the electrical properties. Carbon was also measured by electron microprobe elemental analysis and observed within numerous precipitates and along some grain boundaries. These results will be presented in a future publication and will provide further support to the hypothesis of carbon contamination during growth.

The present paper summarizes some recent results obtained on VHPB-grown CZT from Russia and the Ukraine. Data are reported using triple axis diffraction (TAD), X-ray diffraction (XRD), scanning particle-induced X-ray emission (PIXE), low temperature photoluminescence (PL), inductively coupled plasma mass spectrometry (ICP/MS), and transient charge technique (TCT) measurement methods. Although the results show a large number of defects, it is believed that these new results will enrich our data-base on the growth defects management and understanding of the growth process, which ultimately will lead to the production of homogeneous large volume CZT spectrometers.

2. DEFINITION OF p-AND n-TYPE CZT

The difference between U.S. and Russian VHPB-CZT is that the U.S. material has always been prepared with an excess of Cd. Based on PL spectra, the U.S. material has a much larger amount of recombination associated with donor sites. Consequently, we label the U.S. material as n-type, although electrical properties must be performed to clearly determine the dominant electrical carrier at room temperature. On the other hand, Russian CZT has been prepared with both Te-deficient and Te-rich starting materials. For the Te-deficient material, the PL spectra are dominated by defects associated with acceptor states; hence, we label this material as p-type. The p-type material from Russia has proved to be much more uniform along the axial direction than any of the n-type material (Russian or U.S.). However,

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the crystallinity and nuclear radiation response of the p-type CZT was much poorer than the U.S. produced n-type material [8].

One should note that the typical dimensions of the Russian and Ukrainian CZT boules are 120 mm in length and 50 mm in diameter. The pulling rates are about 1 mm/hr for the Russian grown CZT, about 0.5 mm/hr for the Ukrainian CZT, and about 0.1 mm/h for the U.S. grown material. Other details on the methods of preparations and some previous results obtained on the homogeneity and stoichiometry of the U.S. and Russian CZT have been published elsewhere [6-10].

3. CHARACTERIZATION

3.1. Triple axis Diffraction

The Zn composition in CZT samples has been measured by TAD [11] and PIXE [12]. The nominal Zn content had typical values of x between 0.1 and 0.2 for U.S. grown material, 0.1, 0.2, 0.3 or 0.4 for the Russian material and 0.2 for the Ukrainian CZT. TAD results of Russian samples with a nominal composition of $x=0.2$ showed values ranged from 23.1% Zn for the first to freeze end, to 13.9% for the last to freeze end of the n-type samples. For the most recent Ukrainian samples provided for analyses, the variation is 26-28% over a distance of 2 cm. Unfortunately at a distance of 8 cm from the bottom of the boule, the CZT becomes a polycrystalline mixture with excess Te. For U.S. material with $x=0.1$, a typical variation of the value of x from bottom to top is 3.5-14% over a length of 7 cm. The first homogeneous Russian samples with $x=0.1, 0.2, 0.3$ and 0.4 were prepared from presynthesized CdTe and ZnTe and yielded p-type material [7-10]. The VHPB material grown in the U.S. is n-type material [1,10] and, when the Russian lab synthesized CZT directly from Cd, Zn and Te, the zinc uniformity was reduced to a value comparable to the U.S. material (i.e., 13.9-23.1%). The Ukrainian material was also grown from CdTe and ZnTe and in some cases did produce CZT with fairly uniform Zn composition of 26-28%. Additionally, Table I and Fig. 1 show the mosaicity of one of the latest Ukrainian samples, which is beginning to approach that of the U.S. produced CZT.

3.2. Particle-Induced X-ray Emission

Particle-induced x-ray emission (PIXE) provides a convenient way to map the stoichiometry of Russian and Ukrainian n-type CZT crystals. The samples were mounted onto an aluminum sample holder before they were placed in the analysis chamber of the nuclear microprobe. A 3-MeV proton beam was focused to a 1 x 1 mm spot size and electronically scanned to different locations on a sample in order to collect the PIXE data. At each location, the emitted characteristic x-ray spectrum was recorded using a high purity germanium detector, which was fitted with a Mylar absorber to eliminate backscattered particles and reduce the low energy Bremsstrahlung background. The proton beam dwelled on each spot until a total charge of about 0.4 C was collected. The resulting set of PIXE spectra was analyzed [12,13] and the corresponding stoichiometric ratios computed from the x-ray yields. Fig. 2-4 show PIXE mapping results of the (Cd + Zn)/Te ratio for sample 61974 (Russian) and samples K03-15 and K0-40 (Ukrainian),

respectively. The data indicate the overall stoichiometry in each of the three samples is fairly uniform, although there appears to be a small gradient in the stoichiometry across sample 61974. Some of the compositional variations between adjacent spots could be due to localized defects, precipitates, and/or statistics. Also of note is that selenium was observed in the PIXE analysis of sample K03-15 at approximately the 0.1 wt% level.

3.3. Photoluminescence

Low temperature photoluminescence (PL) measurements were performed on the CZT samples from Russia and the Ukraine [7-11]. Analyses of the recombination centers were also made for these CZT crystals. The crystals were immersed in liquid helium at 4.2K and illuminated with the 514.5 nm line of an Ar⁺ laser, which was chopped at 500 Hz. The average incident power density was approximately 500 W/cm². The luminescence was dispersed by a double-pass spectrometer with the slits adjusted for 2.5 nm resolution and detected by a liquid nitrogen cooled Ge diode detector. The signal was analyzed using a lock-in amplifier. The low temperature PL results of the Ukrainian samples K02-14 and K02-75 are shown in Fig. 5. The last two numbers of the sample identifications indicate the distance (in mm) from the tip of the ingot (first to freeze).

It was found that the sample K02-14 has a better overall crystal quality, since its spectrum is dominated by a shallow bound exciton luminescence, while K02-75 has stronger donor acceptor and A-center luminescence. Both samples also show weak luminescence in the 1.1 eV band due to vacancies. In both cases, the acceptor bound exciton is more prominent than the donor bound exciton. From the low temperature PL measurements, it is difficult to assign a clear-cut dopant to the PL lines. They are different from the Russian p-type where the acceptor band is very prominent and the U.S. n-type where the donor band is prominent.

Room temperature PL was used for mapping purposes. Typical mapping data of two Ukrainian samples, K02-75 and K02-14 is shown in Fig. 6. In the first sample there is a substantial standard deviation of about 1.5% of the Zn composition. The second sample depicts a line trace over an area of 10 mm in the horizontal direction and 1 mm in the vertical direction. There is a uniform composition with a standard deviation of 0.8% over 6 mm of the scanned area, followed by a sudden increase of the Zn composition from $x=0.133$ to $x=0.144$ for the next 2 mm, decreasing again to $x=0.134$ in the next 2 mm.

3.4. Laser ablation ICP/MS

Ultra-trace element analyses were conducted using ICP/MS and ICP/OES methods, both of which involve dissolution of the CZT sample in an acidic aqueous solution. As a result, their sensitivities were limited by the dissolution ratio, the presence of non-soluble substances, and optical or mass interferences. Additional impurities could also be introduced from the solvent itself. To avoid the latter problems, laser ablation ICP/MS was used for trace element analysis because it is sensitive to minor impurities and to low Z elements such as carbon.

Laser ablation with ion coupled plasma mass spectroscopy, LA-ICP/MS, is a relatively new improvement over ICP/MS. Rather than dissolving the sample and evaporating the liquid solution into the plasma, the basic idea behind the LA-ICP/MS method is the use of a pulsed laser to provide enough energy to directly ablate material from the solid sample. Argon or helium gas is used to sweep the ablated particles into the ICP torch. By directly analyzing the solid, one can increase the sensitivity by a few orders of magnitude over the common wet ICP/MS dilution method, thereby enhancing the statistics of the results. However, the drawback of this method is that the results are very dependent on the nature of the ablated particles, such as the reaction with other substances existing in the ablated media and the ionization efficiency and volatility rates, each of which is poorly known. The calibration and optimization of the process is still under further research.

Currently, the procedure for the ablation involves ablating a series of spots, which are approximately 30 μ m apart and 5-30 μ m in diameter. Each ablated spot is created from three sets of ten laser hits each. The penetration depth after each set of hits is 10, 20 and 30 μ m respectively with about 60 seconds elapsed time between each set of hits. Table II summarizes some of the data obtained on three Ukrainian KO-50, KO-20, and KO2-75 samples and one RO-2 CZT grown in U.S. Table II reveals that there are no significant differences in the impurity analysis between the Ukrainian and U.S. produced CZT.

3.5. TCT measurements

Electrical transport properties such as mobility (μ) and trapping lifetimes (τ) have been obtained using pulsed laser transient charge technique (TCT). This method has been used previously to study the electrical transport properties in mercuric iodide [14]. The TCT system is equipped with a 3 ns pulsed, 337 nm nitrogen laser and a laser dye, LN₂ cold temperature stage, vacuum test chamber with an optical window on top, fiber optic cable and an oil-free vacuum pump. The pulsed laser with attached dye module was tuned to a wavelength of 525 nm. The pulse width is 3 ns with energy of 120 mJ per pulse. Theoretically, each pulse produces about 1.5×10^{14} electron hole pairs in the near-surface region of the CZT. A transmission IR micrograph is obtained prior to testing in order to locate the grain boundaries within the bulk. The most common method to observe the grain boundaries is by rough polishing of the surface until the grains are visualized. The IR transmission and reflection images are taken and recorded by a CCD camera. The setup also allows transport properties measurements with no contacts deposited on the surface, using a spring-loaded conductive hollow probe which allows light at a spot size of 0.8 x 0.8 mm².

No additional amplification is required since the pulses are intense enough for direct reading from the detector. This enables recording the original transients (in case of high enough bias), or the trapping times (in low bias conditions). Recording transients at low temperature range can be used to obtain the detrapping times and hence the trapping energy levels related to the studied impurities. A typical waveform resulting from the electron trapping process is shown in Fig. 7. More details on low temperature TCT are given elsewhere [14].

The trapping lifetimes, τ , measured near and along an identified grain boundary in a commercial 5 x 5 mm² CZT detector did not change. This evidence could indicate that some grain boundaries might, in some cases, be insignificant to the total transport properties. The preliminary results show that τ for electrons of a Russian sample in the IR transparent region is 0.5-2.0 μ s, whereas in the more defective region it is consistently <0.5 μ s. Note that in detector grade material supplied by U.S. manufacturers, electron-trapping lifetimes are typically on the order of 10 μ s.

4. CONCLUSIONS

Crystals originating from Russia and the Ukraine have more microstructural defects, such as precipitates, inclusions, bubbles, pipes and larger mosaicity than U.S. produced material. These defects greatly deteriorate the detector electrical transport properties, as can be seen by the reduced life times measured for both electrons and holes. Impurity levels for many contaminants are comparable to those in U.S. grown material. However, in addition to the carbon in FSU-grown CZT crystals, other trace impurities such as Ca, Si, Fe, Ba, Ni, Al, Se, and Pb were also found. The more recent Russian grown CZT yields detectors capable of measuring alpha spectra.

5. REFERENCES

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Table I. Comparison Summary of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ Crystallinity Determined by Triple axis X-ray Diffraction (TAD) ω -Scans.

	Ukraine	Russia	USA
FW@1%M; Range	80 - 340 arcsecs (8 samples)	160 - 2000 arcsecs (15 samples)	30 - 50 arcsecs (typical)
FW@1%M; Average	177 arcsecs	760 arcsecs	~ 40 arcsecs

Table II. Bulk Elemental Analyses by LA-ICP/MS of Four Different CZT materials (Sorted by decreasing mass concentration)

Element Name	Element Symbol	CZT: KO-50 Relative Mass Ratio (ppb)	CZT: KO2-75 Relative Mass Ratio (ppb)	CZT: RO-2 Relative Mass Ratio (ppb)	CZT: KO-20 Relative Mass Ratio (ppb)
Tellurium	Te	50018917	50014603	50767629	56072470
Cadmium	Cd	44115127	47010913	46645133	39313233
Zinc	Zn	5860309	2972947	2584118	4600889
Europium	Eu	312	358	289	220
Nickel	Ni	253	200	218	185
Boron	B	510	183	1512	7289
Selenium	Se	2174	135	391	4648
Iron	Fe	910	135	70	60
Lead	Pb	344	111	114	143
Thallium	Tl	52	59	52	58
Caesium	Cs	43	57	56	49
Bismuth	Bi	35	35	27	45
Manganese	Mn	42	32	28	21
Uranium	U	24	29	30	20
Thorium	Th	22	29	31	16
Barium	Ba	667	27	55	95
Scandium	Sc	12	23	22	26
Rubidium	Rb	24	23	32	26
Gold	Au	78	21	23	17
Chromium	Cr	79	20	102	437
Lanthanum	La	17	20	31	23
Strontium	Sr	12	14	15	8
Cobalt	Co	10	12	10	6
Vanadium	V	26	11	11	10
Lithium	Li	1	2	2	3
Beryllium	Be	1	1	1	3

* note: aggregated data of 12 mass spectral sets for each sample from 4 runs at 3 ablation levels

Figure captions

- Fig. 1. Typical triple axis x-ray diffraction (TAD) ω -scans of a Russian-grown $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystal, where $x=0.22$ measured by TAD lattice parameter measurements.
- Fig. 2. Locations and measured values of $(\text{Cd}+\text{Zn})/\text{Te}$ stoichiometric ratios obtained by PIXE, spot analyses on Russian center slice of sample 61974.
- Fig. 3. Locations and measured values of $(\text{Cd}+\text{Zn})/\text{Te}$ stoichiometric ratios obtained by PIXE on Ukrainian sample KO3-15.
- Fig. 4. Locations and measured values of $(\text{Cd}+\text{Zn})/\text{Te}$ stoichiometric ratios obtained by PIXE on Ukrainian sample KO-40.
- Fig. 5. Low temperature PL measured on Ukrainian grown KO2-14 and KO2-75 CZT samples.
- Fig. 6. PL mapping of two Ukrainian CZT samples, showing the deviation of the Zn composition.
- Fig. 7. Typical TCT waveform obtained from high-grade CZT spectrometer.

Figure 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7