

Micro-Raman Characterization of Effects of Zn Alloying and of In Doping to CdTe

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Abstract Cadmium telluride(CdTe) is unique among II–VI compounds which makes it important and quite suitable for several applications as it may exhibit both n- and p-types conductivity. It is one of the few II–VI compounds that are usually used as absorbers for photovoltaic devices. In this research work we studied In-doped CdTe and CdZnTe after annealing using for investigation the technique of micro-Raman spectroscopy.

Keywords CdTe, Micro-Raman, CdZnTe, Optical Properties

1. Introduction

In general, infrared optical materials are insulators or semiconductors as judged by their band-gaps and resistivity. Photons of light corresponding to energy greater than the band-gap of the solid are strongly absorbed at the surface. [1-2] As the wavelength is increased and the photon energy is decreased below the band-gap, light is transmitted through the solid. The beginning of light transmission of a solid occurs at the wavelength that corresponds to the band-gap energy. The absorption of the photon is a very strong, quantized electronic transition.

One may think of this energy as representing the average ionization energy for the primary chemical bonds formed between the atoms that make up the solid. If the required ionization energy is large enough, transmission begins in the ultraviolet region of the spectrum, as in the case for alkali halides or alkaline earth halides. Then the solid appears water-clear or colorless. If it occurs in the visible region, the solid appears colored. If the absorption edge occurs in the infrared region, the solid appears metallic because all visible light is strongly absorbed and reflected.

2. Experimental

Considerable change in optical, electrical, and mechanical properties of CdTe thin films is produced by doping and annealing conditions [3]. Moreover p-type and n-type doping of CdTe is easy to achieve. All samples we studied are CdTe doped with Indium and CdZnTe. All samples were grown by

the Vertical gradient freeze method directly from the melt [3], where In doping was added to the samples. The doping concentration was $5 \times 10^{15} \text{ cm}^{-3}$. Electrical conductivity – mobility was measured using the Van der Paw method. The data tabulated in Table 1 shows the electrical properties of the samples and the annealing conditions of each sample.

Raman spectroscopy can give information on the composition, the stress-strain state, crystal symmetry and orientation, and crystalline defects in a material. Raman spectroscopy is commonly used to determine the molecular structure of organic and inorganic compounds for contamination analysis, material classification, and stress measurements. Also, to characterize carbon polymorph layers (graphitic vs diamond) or for sense covalent bonding (complexes, metal bonding).

Additionally, to classify material orientation (random vs organized structure) and to identify organic functional groups and often specific organic compounds [4-6]. It requires very little sample preparation and is generally non-destructive. We used the Renishaw Ramascope RM 1000 with an He-Ne laser of 632.8nm excitation wavelength to reduce the fluorescence signature in samples that show strong fluorescence at shorter wavelengths [7, 8]. The laser spot on the surface had a diameter of approximately 1 μm and a power of $\sim 4\text{mW}$. The spectral resolution of about 0.5cm^{-1} was determined by measuring the Rayleigh line of the He-Ne laser.

The laser is focused on the sample and viewed simultaneously through the lens with our USB camera. The advantage is the ideal solution when sample molecules or trace impurities emit fluorescence a condition which can overshadow the effectiveness of Raman spectroscopy. Eliminating or reducing fluorescence emission requires a laser excitation wavelength that does not have the energy to excite molecular fluorescence.

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It uses a He-Ne laser of 632.8nm excitation laser to reduce the fluorescence signature in samples that show strong fluorescence at shorter wavelengths.

Spectra can be saved with an automated baseline correction algorithm or in raw form. All spectra are referenced with the laser off to subtract ambient light. The spectral viewer allows users to interpret the most recently acquired spectrum. Spectra may be zoomed or expanded and

peak heights and frequencies are reported on the screen.

In Fig. 1-5, the micro-Raman spectra of each sample acquired in the spectral range from 180 to 2000 cm^{-1} , 10sec X 10 accumulations are presented. In addition we did micro-Raman measurements for all the samples in the range of 180-2000 cm^{-1} , 20sec X 2 accumulations and in the range of 180-500 cm^{-1} , 20sec X 10 accumulations and of 180-500 cm^{-1} , 50sec X 10 accumulations.

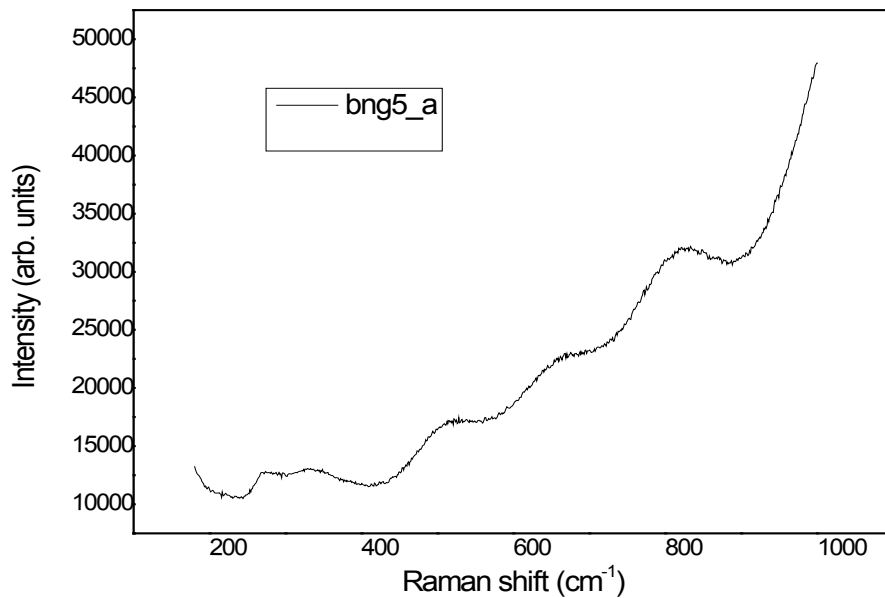


Figure 1. A micro-Raman spectrum of CdZnTe 15%Zn, undoped, as-grown

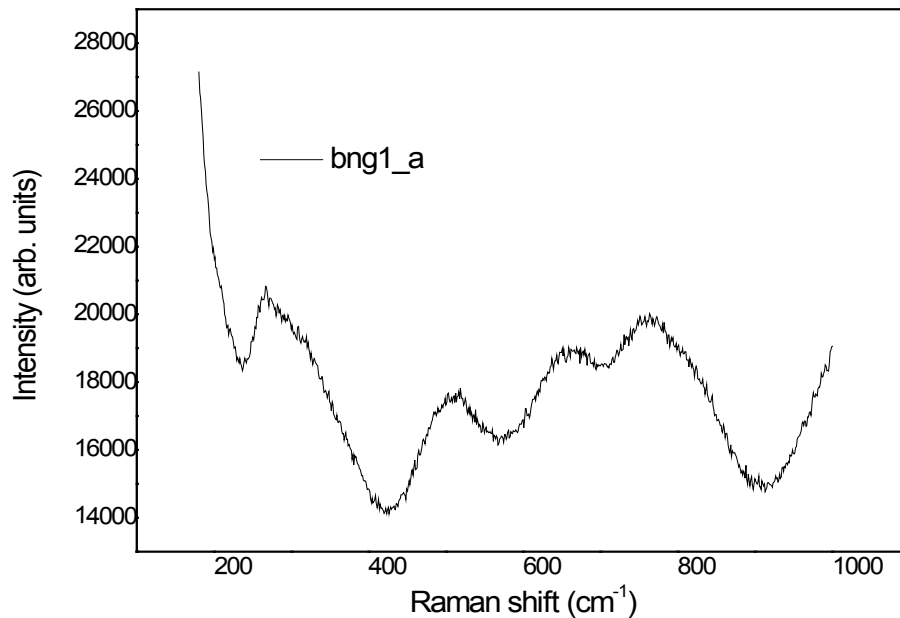
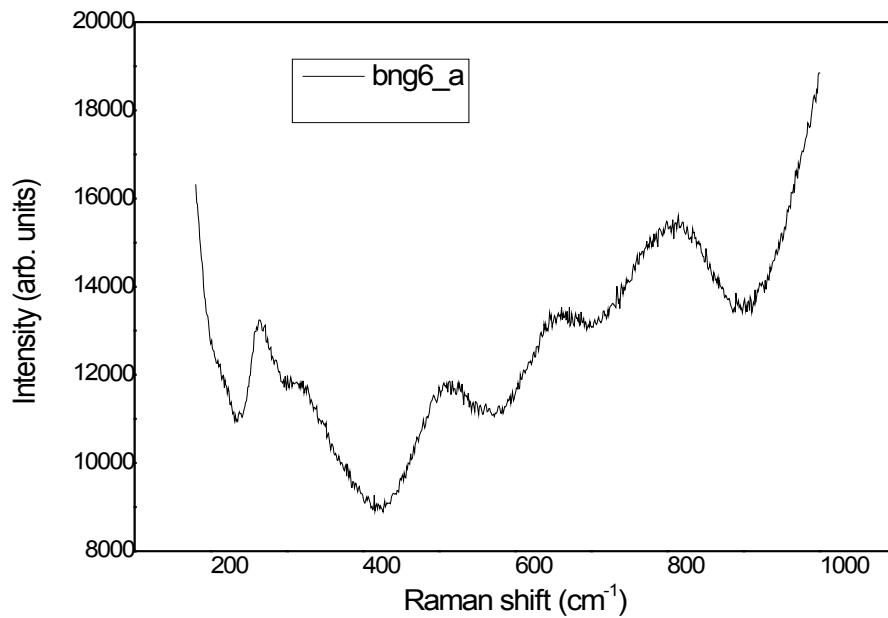
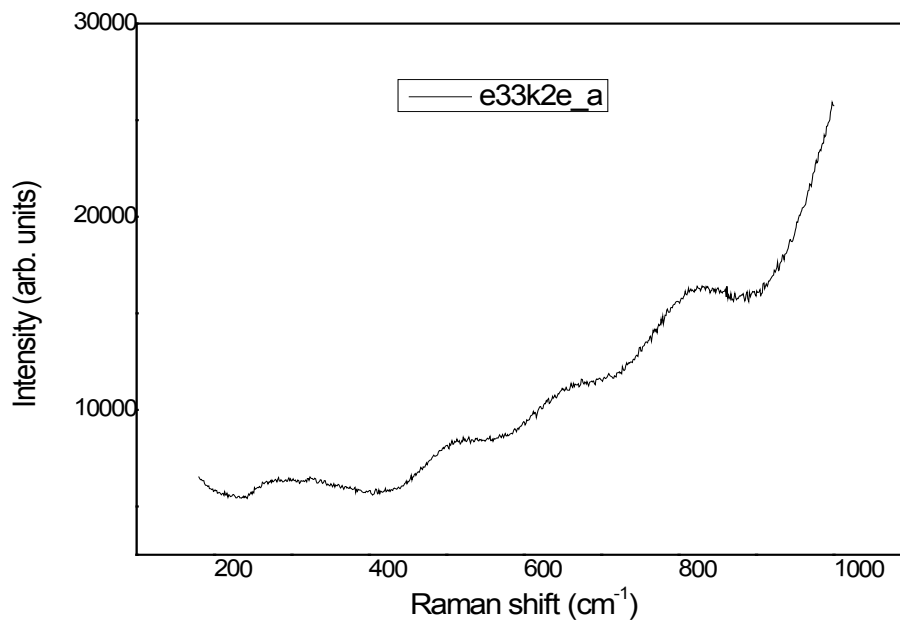


Figure 2. A micro-Raman spectrum of CdZnTe 15%Zn, undoped, after Cd-rich annealing (24 hours)

Table 1. Samples specifications

No	Specifications of the samples		
	<i>Sample</i>	<i>Annealing</i>	<i>Resistivity</i>
BNG1	CdZnTe 15%Zn, undoped	after Cd-rich annealing 24 hours, 700/610°C	n-type inhomogeneous
BNG5	CdZnTe 15%Zn, undoped	as-grown	high resistivity
BNG6	CdZnTe 15%Zn, undoped	after Cd-rich annealing 48 hours, 600/430°C	n-type, $n=1.4 \times 10^{15} \text{cm}^{-3}$, low resistivity $\rho_0=3.1 \text{ Ohm.cm}$
E33C3C	CdTe doped with In	as-grown	n-type, $n=4.2 \times 10^{15} \text{cm}^{-3}$, low resistivity $\rho_0=1.0 \text{ Ohm.cm}$
E33K2E	CdTe doped with In	after Te-rich annealing	p-type, $p=1.1 \times 10^{16} \text{cm}^{-3}$, $\rho_0=5.7 \text{ Ohm.cm}$

**Figure 3.** A micro-Raman spectrum of CdZnTe 15%Zn, undoped, after Cd-rich annealing (48 hours)**Figure 4.** A micro-Raman spectrum of CdTe doped with In, after Te-rich annealing

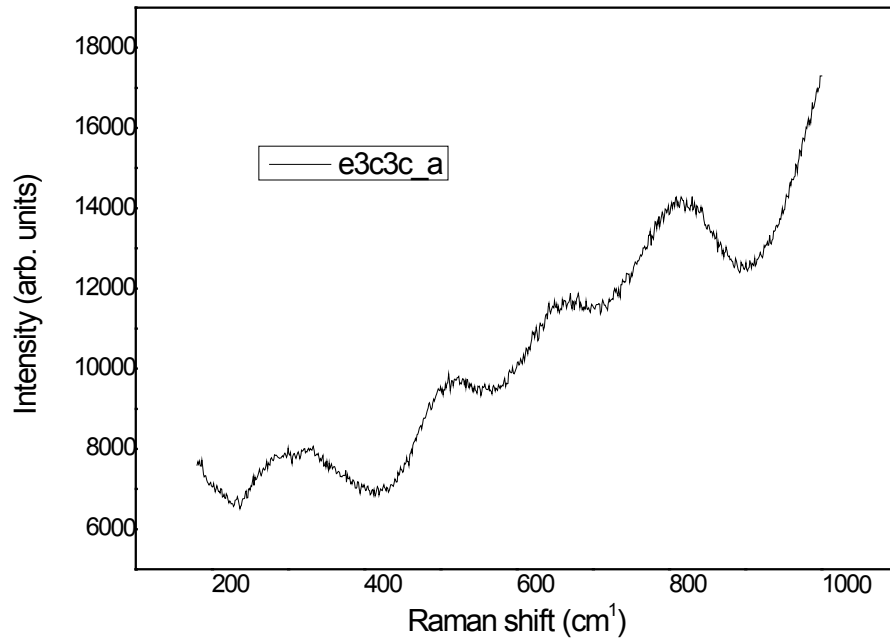


Figure 5. A micro-Raman spectrum of CdTe doped with In, as-grown

3. Results and Discussion

First, we studied in details the samples of CdZnTe 15% Zn, in the range of 150-550 cm^{-1} . Their typical Raman peaks were confirmed, according to the literature [9,10]. A possible origin for a Raman peak identified could be a secondary phonon with A1 symmetry and E symmetry of Te inclusions. A minor difference of the vibrational frequencies related to the annealing temperature towards lower frequencies, as shown in the Figs 6-8 was observed.

Additionally, we can observe from the Figs. 1, 2 and 3 that the peak intensity and the area under the (LO) phonon peaks increases and the FWHM values decreases with annealing temperature, which is due to the improvement of crystallinity of the films.

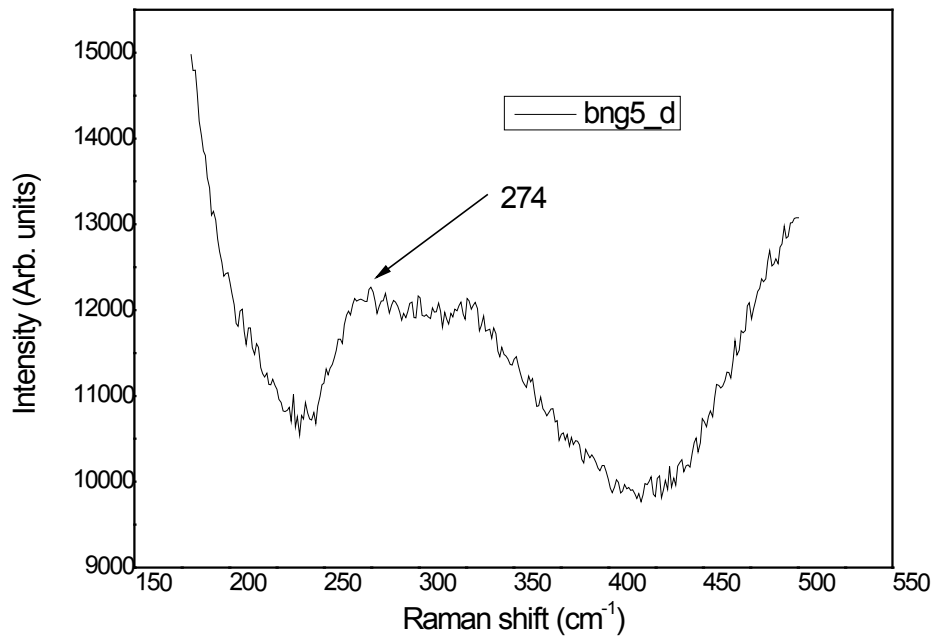


Figure 6. A micro-Raman spectrum of CdZnTe 15%Zn, undoped, as-grown, in the range 150-550 cm^{-1}

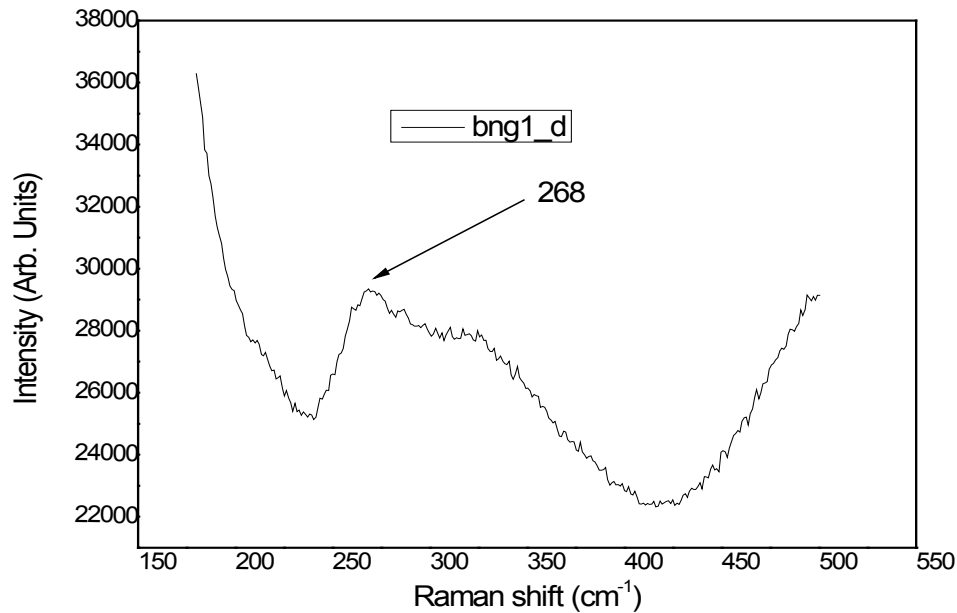


Figure 7. A micro-Raman spectrum of CdZnTe 15%Zn, undoped, after Cd-rich annealing (24 hours), in the range 150-550 cm^{-1}

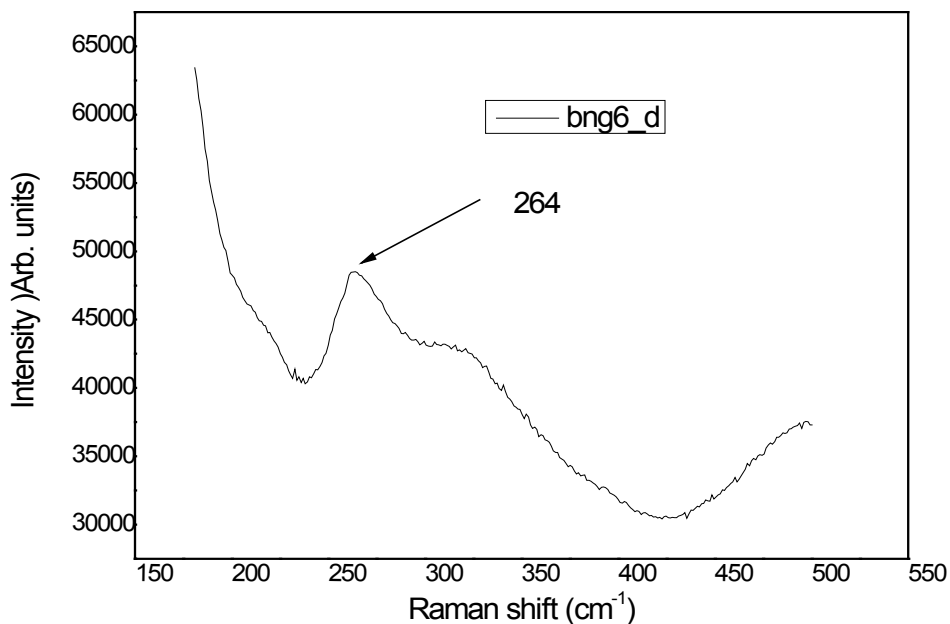


Figure 8. A micro-Raman spectrum of CdZnTe 15%Zn, undoped, after Cd-rich annealing (48 hours), in the range 150-550 cm^{-1}

In the Figures 9-10 the Raman spectra for the In doped CdTe in the range of 180-2000 cm^{-1} are presented. After the Te-rich annealing, changes in the peaks of the CdTeIn samples were observed. Under these conditions defecting scattering by one longitudinal optical (LO) phonon as well as Fröhlich-induced two-LO phonon scattering is observed. We present the results of (LO) phonon frequency as function of the temperature. In both cases scattering is found to be strongly affected by In doped and related to the annealing temperature.

As shown in the Figures 9 and 10, the peaks of triangle Te inclusions in Te-rich annealing wafers are shifting to high energy after Te-rich annealing, and this is in good agreement with the literature. [11] This shows the compressive stress exists around Te inclusions.

The Raman measurements in our wafers revealed that in those with Te-rich annealing, the Te aggregates, at least part of them, formed particles with a crystalline structure. The crystals are most likely to deposit in the form of inclusions around the grain boundaries and dislocations. Grain boundary movement and dislocations slipping could produce a stress field resulting in the formation of a compressive stress around the Te inclusions.

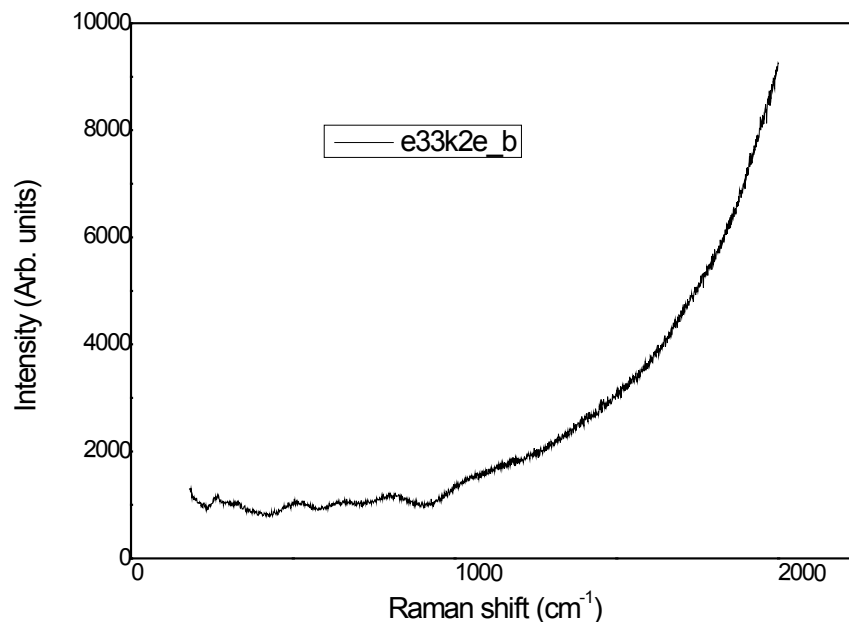


Figure 9. A micro-Raman spectrum of CdTe doped with In, after Te-rich annealing, in the range 180-2000 cm^{-1}

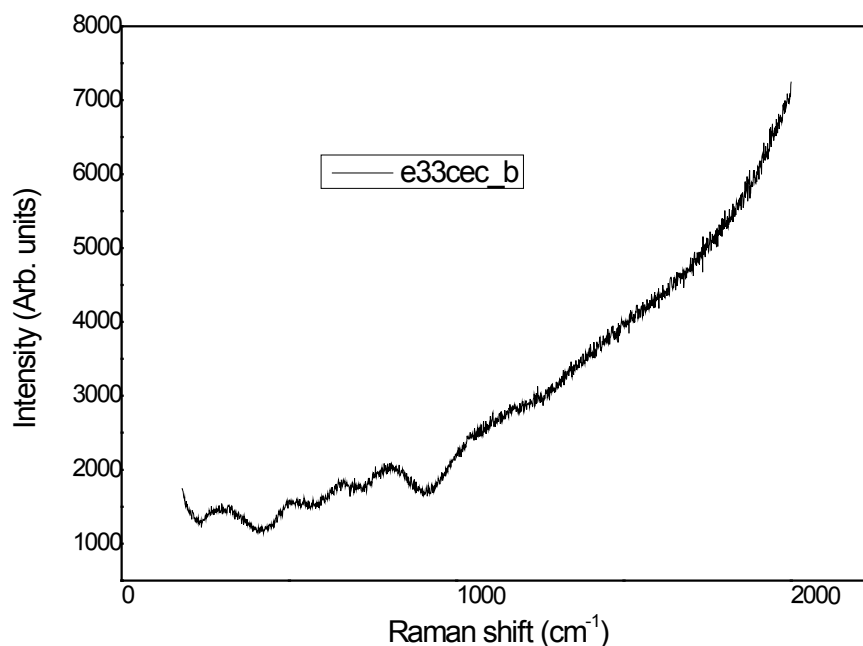


Figure 10. A micro-Raman spectrum of CdTe doped with In, as-grown, in the range 180-2000 cm^{-1}

4. Concluding Remarks

It is well known that the resistivity of CdTeIn strongly depends on the In doping concentration and growth and post-annealing conditions. In this research work we studied In-doped CdTe and CdZnTe after annealing at various temperatures using Raman spectroscopy. We present the results of (LO) phonon frequency as function of the temperature.

Additional changes are observed in the spectral range above 200 cm^{-1} , where the clean CdTe surface shows the 2LO multiphonon structure at 314 cm^{-1} in accordance with

bibliography [9-10]. The increase in the peak intensity and the decrease in FWHM of the Raman peak for the annealed films indicate the improvement in the crystallinity of the films during thermal annealing.

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REFERENCES

- [1] R. Hilton, "Chalcogenide for Infrared Optics" Mc Graw Hill, 2010, pp. 52–55.
- [2] T. Ganetsos, E. Belas and B. Kotsos, "Electrical properties and Raman study of In-doped effects of CdTe" *Procedia Engineering*, vol. 25, 2011, pp.354–357.
- [3] E. Belas, Grill R., Toth A.L., Moravec P., Horodyský P., Franc J., Höschl P., Wolf H., Wichert Th, "Electrical and optical properties of In-doped CdTe after Cd-rich annealing" *IEEE Transactions on Nuclear Science*, vol. 52, 2005, pp. 1932–1936.
- [4] M. Perraki, Andrey V. Korsakov, David C. Smith, and Evripidis Mposkos, "Raman spectroscopic and microscopic criteria for the distinction of microdiamonds in ultrahigh-pressure metamorphic rocks from diamonds in sample preparation materials", *American Mineralogist*, vol. 94, 2009 pp.546-556.
- [5] S. H. Wei and S. B. Zhang, "Theoretical Study of Doping Limits of CdTe" *National Renewable Energy Laboratory*, 2001, pp.1-4.
- [6] A. A. Al-Duri et al, "Optical Properties of Al- and Sb-Doped CdTe Thin Films," *Advances in Condensed Matter Physics*, vol. 2010, 2010, pp.1-5
- [7] E. Belas, M. Bugár, R. Grill, J. Franc, P. Moravec, P. Hlídek, P. Höschl, "(podíl=70%) Reduction of Inclusions in (CdZn)Te and CdTe:In single crystals by post-growth annealing", *J. Electron. Mater.*, vol. 37, 2008, pp. 1212-1218.
- [8] J. Franc, Grill R., Belas E., Hlídek P., Kubat J., Höschl P., "Characterization of Transport and Charge Collection in high resistivity CdTe photoelectric measurement" *IEEE Trans. Nucl. Sci.*, vol. 52, 2005, pp. 1937-1940.
- [9] M. G. Sridharan, M. Mekaladevi, Sa.K. Narayandass, D. Mangalaraj, H.Chul Lee, "Raman scattering studies on polycrystalline $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ thin films" *Journal of Optoelectronics and Advanced Materials* Vol. 7, No. 3, June 2005, p. 1479 - 1482.
- [10] C. M. Ruiz, O. Vigil, E. Saucedo, G. Contreras-Puente and V. Bermúdez, "Bi doped CdTe: increasing potentialities of CdTe based solar cells", *J. Phys.: Condens. Matter*, vol. 18, 2006, pp.7163.
- [11] Jiahua Min, Xiaoyan Liang, Jun Chen, Dong Wang, Hui Li, Jijun Zhang, "Investigation of Te inclusions in CdZnTe crystalline material using Raman spectroscopy and IR techniques", *Vacuum*, vol. 86, 2012, pp.1003-1006.