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Red mercuric iodide crystals obtained by isothermal solution evaporation: Characterization for mammographic X-ray imaging detectors

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ABSTRACT

Millimeter-sized mercury iodide crystals were obtained by the isothermal evaporation technique using dimethylformamide (DMF), diethyl-ether/DMF mixture and THF. Different concentrations (18 mM and 400 mM) and solution temperature (25–80 °C) were used to obtain varied evaporation rates (0.1×10^{-4}–5000×10^{-4} ml/h). Different crystal sizes and shapes were obtained by changing solvents, mixture and initial solution volume. According to X-ray diffraction the samples are monocrystalline. The top surface was investigated by SEM. Optical band-gaps above 2 eV were obtained from photoacoustic spectroscopy. Photoluminescence spectra indicated band-to-band electronic transitions, and the presence of sub-band gap states. Excitons, structural defects and the presence of impurities are discussed and correlated to the electrical measurements. Crystals obtained using pure DMF as solvent showed better general properties, including under the exposure to mammographic X-ray energy range that led to sensibility of about 25 μC/Rcm^2.

1. Introduction

Mercuric iodide (HgI_2) is one of the most promising materials for the detection of ionizing radiation and direct electric conversion. Other wide band-gap semiconductor candidates are thallium bromide (TlBr), lead iodide (PbI_2) and others [1–14]. HgI_2 properties are large optical band-gap (2.13 eV), high atomic number ($Z_{Hg}=80$, $Z_I=53$, $Z_{eff}=67.12$) and high mass density (6.4 g cm^{-3}) [2,3,7–17].

HgI_2 crystals and films have been fabricated by different techniques, like solvent evaporation [3,7,18–20], spray pyrolysis [16], physical vapor deposition [2,3,17], and others. However many investigations must still be performed aimed at the optimization of the material for a final use as X-ray commercial sensors.

Isothermal solution evaporation, or solvent evaporation with constant solution temperature, has been investigated for several years with organic solvents as ethanol, acetone, dimethyl sulfoxide (DMSO), diethyl ether and others [3,7,18–20]. But crystals have not been obtained with dimethylformamide (C_3H_7ON—DMF) and tetrahydrofuran (C_4H_8O—THF).

This research aims the fabrication of HgI_2 crystals by isothermal solution evaporation using three different configurations with DMF, diethyl-ether/DMF mixture and THF. Crystals were characterized morphologically by scanning electron microscope (SEM) and structurally by X-ray diffraction (XRD). Optical characterization was performed by photoacoustic spectroscopy (PA), photoluminescence (PL). Electrical characterizations in the dark and under X-ray illumination in the mammographic energy range were also performed.

2. Materials and methods

HgI_2 powder (VETEC, 99%) was dissolved in DMF, DMF-ether and THF. The chemical structures of these solvents are shown in Fig. 1. DMF and THF are polar ((a) and (c), respectively) and diethyl ether is apolar (b) [21].

Different solutions were prepared: (i) 400 mM HgI_2 in 8 ml of DMF (named solution I, used for the fabrication of HD crystals); (ii) 75 mM HgI_2 in 58 ml of a DMF-ether mixture previously prepared using 8 ml of DMF and 50 ml ether (named solution II, used for the fabrication of HDE crystals); and (iii) 18 mM HgI_2 in 60 ml of THF (named solution III, used for the fabrication of HT crystals). The different solutions and concentrations were chosen due to the different solubility of HgI_2 in those solvents. The conditions are summarized in Table 1, and compared to other samples from the literature [7].

Solution I was placed in a furnace at 80 °C, what led to an evaporation rate around 6.2×10^{-4} ml/h. Solution II was submitted to solvent evaporation at room temperature (about 25 °C) with average evaporation rate of 9.2×10^{-6} ml/h. Finally, solution

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III was put in a glass beaker which was then covered with PVC-film for the reduction of the evaporation rate at room temperature (5.0×10^{-1} ml/h).

X-ray diffraction was performed with Cu-K_{α} radiation ($\lambda = 1.5405$ Å) for 2θ from 10° to 60° with steps of 0.02 degrees. The stoichiometry was investigated by energy dispersive spectroscopy (EDS). Surface morphologies of the crystals were performed by SEM. Optical band-gaps were obtained by different techniques: Optical Transmission (OT), Photoacoustic (PA) and Photoluminesce (PL). PA measurement were obtained with continuous laser excitation (from 1.5 to 4.5 eV and normalized with a fine coal dust) with 1 kW Xe lamp on 20 Hz. The samples responses were detected by BK microphone and processed by a lock-in amplifier (PAR 5210). Alternatively, a continuous Ar-ion laser (2.72 eV) was used as excitation source. PL spectra were obtained from 1.6 to 3.1 eV with laser excitation of 3.8 eV, at 15 K.

Aquadaq® was used to fabricate electrical contacts to the samples. Electric current in DC mode was measured in the dark and under X-ray illumination on mammographic energy range. X-ray mammography unit (General Electric Senographe 500 T model) had a molybdenum anode (k_{α} and k_{β} of 17.5 eV and 19.6 eV, respectively) and inherent filtration. The electrical resistivity and current gain were obtained for an exposure of 430 mR for X-ray tube with peak voltage of 30 kVp. The photoconductivity studies, under mammographic X-ray exposure, were performed by measuring current density as a function of electric field (64–258 V/cm), exposure (79–1264 mR) and X-ray tube energy (22 –30 kVp).

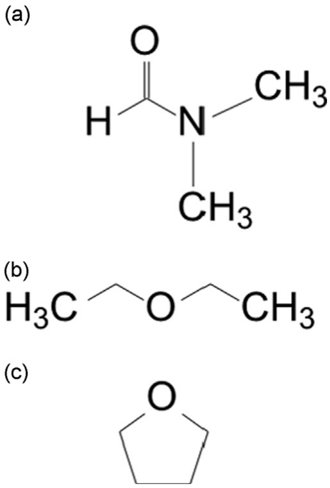

Fig. 1. Chemical structural formula of solvents used in this report: (a) dimethylformamide (DFM), (b) ethyl ether and (c) tetrahydrofuran (THF).

3. Results and discussion

Taking into account the evaporation rates and solvent polarity, varied crystal sizes resulted from the different crystallization processes and that could have important consequences in samples qualities with respect to structural, optical and electrical properties.

Millimeter-sized crystals were obtained in different shapes. HD and HDE were rectangular and HT could not be properly defined. HD sample dimensions were 3.00 ± 0.05 mm × 3.10 ± 0.05 mm × 0.80 ± 0.05 mm. This crystal has a volume around seven times bigger than HDE, whose dimensions were 1.70 ± 0.05 mm × 1.30 ± 0.05 mm × 0.50 ± 0.05 mm. The maximum dimension of HT samples ranged to about 5 mm. All crystals were larger than those previously reported for the same growth method, but using different solvents such as ethanol, acetone and others [7]. Nevertheless, the irregular shape of HT samples prevented any kind of electrical measurements, and thus the main comparison in this work is focused on samples HD and HDE. HT sample is mentioned when necessary.

The morphologies of the surface of the samples were investigated by SEM, and the pictures are presented in Fig. 2. Fig. 2(a) corresponds to sample HD: crystallites are observed on its surface. Fig. 2(b) shows a smoother surface and smaller amount of crystallites for the case of HDE sample. That result was the same observed for HT samples (not shown here). The larger concentration of Solution I might induce nucleation and growth of the observed micrometer-sized crystallites. The larger temperature might also play a role as reported in a previous publication [7] where crystals were obtained with ethanol at 40 °C. In this sense, evaporation rate itself does not seem to be a determining parameter for the final morphology of the surface of the samples.

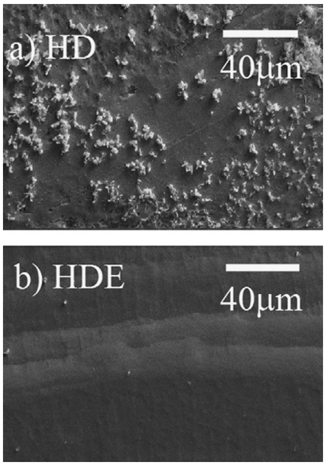

Fig. 2. SEM micrographs of the surface of the crystals: (a) HD (DMF only) and (b) HDE (DMF + ether) samples. HT samples have similar results as presented in (b).

Table 1
Summarized conditions of HgI_2 crystals' growth and properties of this paper compared with literature [7].

Sample	T (°C)	M (mM)	Solvent	V (ml)	ER (10^{-4} ml/h)	E_g (eV)	ρ (G Ω cm)	Ref.
HD	80	400	DMF	8	6.2	2.20	0.10	This paper
HDE	25	75	DMF –ether	58*	0.1	2.15	0.01	This paper
HT	25	18	THF	60	5000	n.a.**	n.a.**	This paper
Dark-crystal	25	33	ethanol	50	780	2.26	0.20	[7]
Light-Crystal	25	33	ethanol	50	600	1.74	0.25	[7]
Oven-crystal	40	33	ethanol	50	1260	n.a.**	n.a.**	[7]

T – Evaporation temperature, M – Molar Concentration, V – Solvent Volume, ER – Evaporation rate, E_g – Band-gap Energy, ρ – Resistivity.

* (50 – ether/8 – DMF),

** n.a. – not available.