

BISMUTHOXIDE AS A GREEN ALTERNATIVE OF MERCURIC IODIDE FOR SOLID STATE X-RAY DETECTOR MATERIAL

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ABSTRACT

Crystals of mercuric iodide were grown using slow evaporation technique at room temperature (25°C-35°C) and pallets of bismuth oxide were also prepared using KBR press. HgI₂ single crystal and Bi₂O₃ ceramic pallet were subjected to X-ray switching studies under different electric fields. Both these were found to have stable X-ray sensing and low switching time. Results show that Bi₂O₃ can be a good competitor of HgI₂ in respect to X-Ray sensing. On the other hand HgI₂ based X-Ray sensitivity deteriorates with time while Bi₂O₃ is highly stable and does not deteriorate with time. Secondly HgI₂ is very poisonous and hazardous to health while Bi₂O₃ is nonhazardous.

KEYWORDS: X-Ray Sensor, Switching, High Energy Green Material, X-Ray Imaging.

In modern society, digital X-rays imaging technologies are growing with very fast pace because of their utility in many fields like medicines, astronomy, security, scientific researches etc. X-rays are used for both, diagnosis and treatment in the field of medicine. Now a days, physicians are using technologies like CT or CAT (Computerized axial tomography) on regular basis [Conference 9783, 2016]. High-powered X-Ray machines are also used in industrial radiography cameras to examine hard to reach or hard to see places. One of the most familiar X-ray machines is the baggage scanner for security checking found at airport terminals and other places [Ignatyev et al.,2011]. Apart from medicine and other industrial uses, these technologies are very useful tool for research work for studying the inner structure of materials. X-rays telescopes are also used to study different aspect of the universe [Lodewijk et al.,2001]. All in one we can say that digital X-Ray imaging is one of the important tools in modern era. But there are some problems associated with modern X-ray detectors. X-rays are not safe to human body because radiation exposure can cause cell mutations that may lead to cancer. Hence there is a need of least X-rays dose to the patient [Pauley et al.,2016;Van'o et al.,2007] and it can be done only if our X-rays detectors are very sensitive to high energy radiation and it must also be environmental friendly. Out of many well-known solid state detectors mercuric-iodide, is found to be one of the good solid state detector [Lodewijk et al.,2001]. But according to MSDS data (sciencelab.com) the HgI₂ is very hazardous material to our environment. On the other hand bismuth oxide can be its good alternative as it has good photosensitivity as well as least hazardous to environment. [Table 1].The data from table-1 clearly shows that bismuth oxide is least harmful to nature so it can also be regarded as green material. As Bismuth oxide is highly stable

material [Simone et al.,2015] at room temperature and it has good photosensitivity, bismuth oxide based materials are the building blocks for modern ferroelectrics [Cross et al.,1971], multi-ferroics [Wang et al.,2003], gas sensors [Sears, 1989], light photo crystals [Gurunathan, 2003] and fuel cells [Azad et al.,1994]. Therefore it can be expected that bismuth oxide can be a better semiconductor material for fabricating the direct solid state detector.

Table 1: Material Safety Data Sheet (MSDS) rating of mercuric iodide and bismuth oxide in relation to health hazards caused by them (sciencelab.com)

S.NO.	SENSOR	HEALTH HAZARDS (0-4)
1	MERCRRIC IODIDE	3
2	BISMUTH (III) OXIDE	1

MATERIALS AND METHODS

Formation of Bismuth-oxide Pallet

Bismuth oxide (99.999%, Alfa Aesar) was used as base material for making bismuth oxide pallets, pale yellow crystalline powder of bismuth oxide was fine grinded using agate mortar and pestle to a fine powder. Small amount poly-vinyl alcohol was used as a binder during this process. Due care was taken to keep the powder pure. Uniform powder was compressed into pallets using KBr press under pressure of 7 ton per square inch for a minute. Pallets were dried in air. No oxygen annealing was done. No further hot pressing was done to prevent any mechanical damaging to the pallets.

Formation of Mercuric-oxide Crystal

Single crystals of mercuric iodide are grown using slow evaporation technique at room temperature (25 °C -35 °C). For growth of pure mercuric iodide crystals, high purity (99.9%) material (Luba, India) in powder form is taken and dissolved in absolute ethanol (Merk India). Mixture is stirred well using magnetic stirrer. Mixture is then allowed to settle down. Undissolved material is separated from the solution by filtering it through watt-man filter paper. Since solubility of the compound is poor, the solution is further centrifuged to remove any small crystallite from the solution, before keeping it in a chamber (Figure 1). For growth of crystals in dark, pettri-dish was covered with black paper foil and stainless steel metallic cover top. Crystals start growing within two to three weeks to the size of few mm. Electrodes were made using silver paste on both pallet of Bi₂O₃ and single crystal of HgI₂. Fine coating of silver paste was left for air drying for 1-2 hr. Both were then subjected to visible microscopic studies to find-out any possibility of cracks etc. Only those samples were put to studies which are free from any crack of silver electrode or otherwise. X-ray source with copper target is used. X-ray generator is operated at 30KV (nickel filtered) with 10mA plate current. For X-ray beam chopping, switching rotor device was used. For blocking X-rays 4mm semicircular lead disc was used. Rotation is controlled by a stepper motor using microprocessor P89C51RD2. Photocurrent was recorded by Keithley 6485 pico-meter (Figure 2).

Figure 1: Experimental setup for solution growth

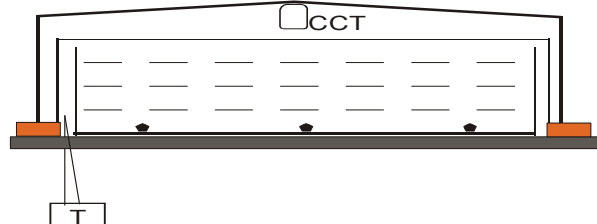
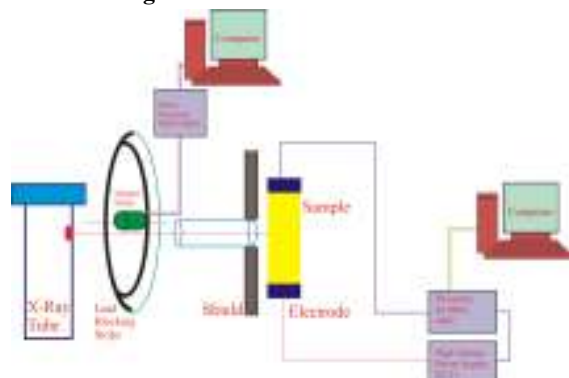


Figure 2: Lay out device set-up used to study switching characteristics of sensor material



To understand the photo charge carrier generation, let X-rays of wavelength λ and of intensity I_0 is allowed to fall normally on the sample of thickness 't'. We used X-ray of wavelength 0.154nm. Photons of these X-rays have energy $\sim 8 \times 10^3$ eV. This energy is sufficient to produce charge carrier. Let 'r' is reflectance co-efficient of material. It means that only $I_0(1-r)$ intensity of X-ray enters into the material. Intensity of X-rays decreases as they pass through the material. Decrease in intensity is directly proportional to the intensity itself, according to the relation $\frac{dI}{dx} \propto -I$ (1)

Here x is the depth of the sample and β is absorption coefficient. Hence the intensity of X-rays leaving the material is

$$I_L = I_0(1-r) \exp^{-\beta t} \dots\dots\dots (2)$$

Thus the intensity absorbed by the material is $I_a = I_0(1-r)(1 - \exp^{-\beta t})$ (3)

If area exposed is 'A' and it is assumed that it remains almost same throughout (as refractive index of most of the materials for X-ray is nearly 1) light energy absorbed by the material per unit time is given as:

$$E_a = I_a A (1-r)(1 - \exp^{-\beta t}) \dots\dots\dots (4)$$

Total number of photons absorbed per unit time is

$$N_a = \frac{E_a \lambda}{hc} \dots\dots\dots (5)$$

When an X-ray photon is absorbed by the material two major phenomenon occur i.e.

1. Multiple production of electron-hole pairs as energy is high
2. Recombination of electron-hole pairs due to defects and impurities present in the material

Let the total number of charge generation, by all the three processes together is ' ξ ' per photon. Hence the total number of actual charge generation per unit time is

$$N_{acc} = \frac{E_a \lambda}{hc} \xi \dots\dots\dots (6)$$

Here ξ is called quantum efficiency. The photo current generated is

$$I_p = \frac{\xi \lambda e I_a A (1-r)(1 - \exp^{-\beta t})}{hc} \dots\dots\dots (7)$$

This clearly indicates that photo current so generated is dependent on: Quantum efficiency of material (ξ), Area exposed (A), Reflectance co-efficient (r), Intensity-wave length product ($I_0\lambda$). For fixed intensity larger wavelength means more photons and thickness of sample (t). (Figure 3(a) & 3(b)).

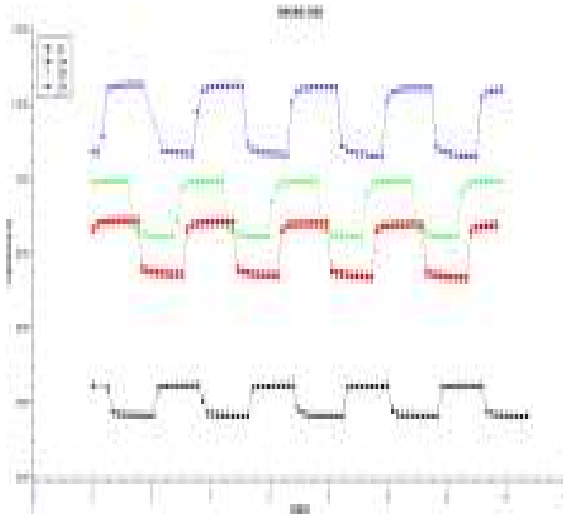


Figure 3(a): Current Vs Time Graphs of Mercuric Oxide for Different Voltages [50V, 100V, 125V & 150V]

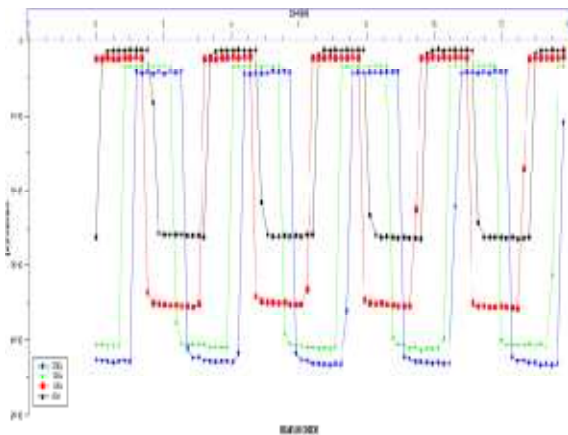


Figure 3(b): Current Vs Time Graphs of Bismuth Oxide For Different Voltages [50V, 100V, 150V, 200V]

OBSERVATION AND RESULT'S DISSCUSSION

As theory reveals that number of actual charge generation is directly proportional to the electric field applied (Eq.- 6), however experimental data obtained shows that maximum (when X-rays are on) to minimum current (when X-rays are off) ratio (I_{Max}/I_{min}), decreases both for HgI_2 as well as Bi_2O_3 pallets on increasing the applied electrical field. (Figure.4(a) & 4(b)). It is found

that both has stable X-ray sensing and has low switching time also.

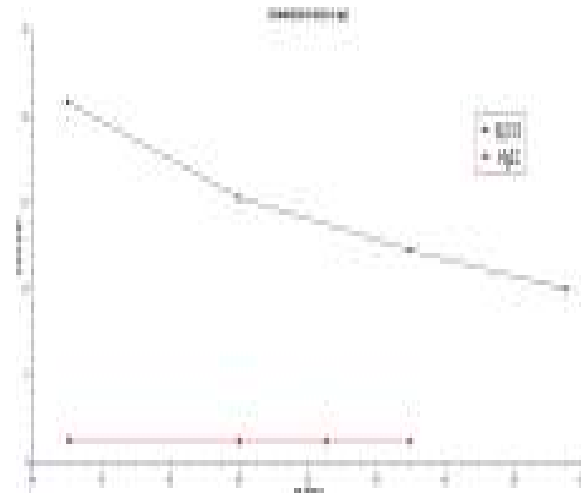


Figure 4(a): Comparative Study of I_{max}/I_{min} For Bi_2O_3 & HgI_2

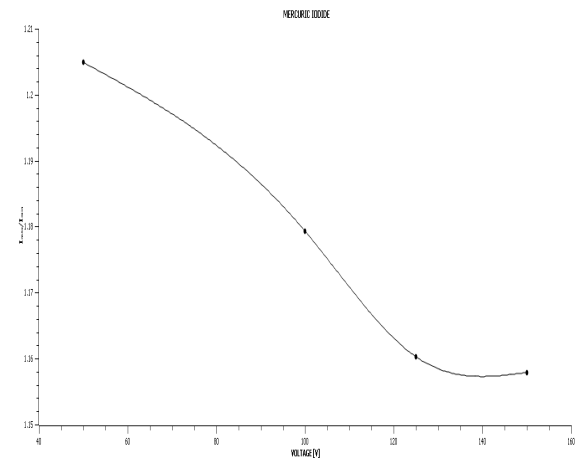


Figure 4(b): Graph showing the variation of I_{max}/I_{min} for HgI_2

Single crystal of mercuric iodide and the pallet of bismuth oxide were found to have low electrical conductivity at room temperature ($\sim 300K$). Their switching curves were obtained at varying electric fields through the sample without changing their physical parameters. (Figure 2) In HgI_2 , dark current increases with increase in external field while Bi_2O_3 does not show large variation on changing the field for dark current as shown by HgI_2 .

Mercuric iodide has layered structure with I-Hg-I...I-Hg-I layers along c-axis. Iodine ions of adjacent layers are bound by weak van-der-waals force. When electric field in a-b plane is increased, conduction is expected to increase due to enhancement in the charge carrier. This is responsible for increase of

dark current with increase in electric field in mercuric iodide. However in bismuth oxide, number of charge carriers is little influenced by external electric field due to absence of weak van-der waal bonds. There are grain boundaries in ceramic form of bismuth oxide, which trap some charge carries but are less influenced by external field. This is primarily due to non-layered structure of bismuth oxide. Further due to stronger bonds, sliding is relatively difficult in bismuth oxide. This is an important characteristic for X-ray detector, due direct influence on I_{\max}/I_{\min} ratio.

Further in switching curve of mercuric iodide, it is clearly visible that current increases and decreases gradually during off and on time of X-rays, in comparison to bismuth oxide ceramic. This may be due to large crystal defects in single crystals of mercuric iodide. Moreover due to growth of these crystals (ionic movement) and high reactivity of the material its time degradation is large as compared to bismuth oxide. [Singh et al, 2011]

CONCLUSION

Hence the studies reveal that Bi_2O_3 is a green material and good alternative for HgI_2 .

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