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X RAY SWITCHING STUDIES OF BISMUTH (III) OXIDE AND ITS COMPOSITES

GAURAV SURYAN[1a] AND KULVINDER SINGH[b]

[a]Research Scholars, Singhania University, Pacheri Bari, Rajasthan, India

[b]Associate Professor, DeenDayalUpadhyaya College, University of Delhi, India

ABSTRACT

Due to variety of applications, detectors for high energy sensors are extremely important in our day to day life. In present study pallets of pure bismuth oxide (99.9%) were prepared using KBR press.Composites of bismuth oxide ware also prepared using polymers Poly-Methacrylate (PMMA)& Poly- Styrene (PS) as matrix materials. Bismuth oxideceramic pallet and its composites were subjected to X-ray switching studies under different electric fields. All are found to have stable X-ray sensing and low on – off time switching. Though Bi_2O_3 in itself is a good high energy sensor, its composites with PMMA and PS show good results. Out of the two polymer composites, PMMA composite shows better results as compared to poly- styrene composite. This behavior may be because of absence of benzene group in PMMA. It is found that PMMA composite shows better results as compared to poly- styrene composite

KEYWORDS – X-Ray Sensor, Polymer composite, 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. Many solid state detectors like alpha-selenium, cadmium zinc telluride mercuric-iodide, lead-iodide, cadmium-iodide etc. are found to be good detectors(Spekowius G, Wendler T.(Eds),2006). Some of the latest detector material are listed in table-1 and its environmental hazards are listed according to MSDS data from sciencelab.com.

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 at room temperature and it has good photosensitivity,so bismuth oxide is a better semiconductor material for fabricating the direct solid state detector (Suryan G., Singh K., 2015). In order to enhance its mechanical properties composites are best option (McEvoMA.y, CorrelN.,2015). Polymers provide additional strength and flexiblility in shape of such detectors. In our present study we have fabricated the polymer composites of bismuth oxide with two polymers used as matrix materials- Poly-Methyl-Methacrylate (PMMA), and Poly-Styrene (PS). Further they are subjected to X- ray switching studies.

S.NO.	SENSOR	HEALTH HAZARDS (0-4)
1	Cadmium Telluride	2
2	Cadmium Zinc Telluride	3
3	Silicon	2
4	Germanium	3
5	Mercrric Iodide	2
6	Gallium Arsenide	3
8	Alpha - Selanium	2
7	Bismuth(III) Oxide	1

[1]Corresponding Author

Table1: Material Safety Data Sheet (MSDS) rating of several solid state detector materials along with bismuth oxide in respect of health hazards caused by them (sciencelab.com)

MATERIALS AND METHODS

Bismuth oxide (99.9%, Alfa Aesar) was used as base material for making bismuth oxide pallets. Pale yellow crystalline powder of bismuth oxide was 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.

For preparation of composite material following two polymers were used as matrix materials, viz.

1. Poly-Methyl-Methacrylate (PMMA)
2. Poly-Styrene (PS)

Initially pure $Bi_2O_3$is grinded using agate mortar and pestle to a fine powder. No additive was used during this process. Due care was taken to keep the powder dry. PMMA granules were dissolved in chloroform (99% Fisher Scientific India) and mixed with powder of Bi_2O_3. Uniform mixture was then kept to settle down for 48 hours in vibration free atmosphere. No further hot pressing was done to prevent any mechanical damaging to the sheets. After this fine sheets of PMMA- Bi_2O_3 composite were obtained.

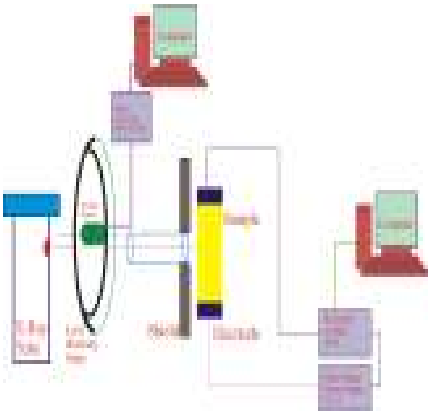
Poly–Styrene is easily soluble in acetone. Styrene granules were dissolved in sufficient amount of acetone.Slurry formed wasvigorously mixed with fine powder of Bi_2O_3. Material wasthen left to settle down for 24-48 hr. After this fine sheets of PS- Bi_2O_3 composite were obtained. Polymer composites ware then cut into small plates of (1cm X 0.5 cm) size for X-ray switching experiments.

All samples weresubjected to XRD for the determination of their crystallite size.

Electrodes on the samples were made by silver paste. Fine coating of silver paste was left for air drying for 1-2 hr. Samples 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 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 1).

Figure 1: 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 ~$8X10^3$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 $\frac{d\ I}{d\ x} \propto\ I$ …… (1)

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

$$I_L = I_0(1-r)\exp^{-\beta t} \quad \text{…….. (2)}$$

Thus the intensity absorbed by the material is

$$I_a = I_0(1-r)(1-\exp^{-\beta t}) \quad \text{……..…… (3)}$$

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 nearly1) light energy absorbed by the material per unit time is given as:

$$E_a = I_0 A(1-r)(1-\exp^{-\beta t}) \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Total number of photons absorbed per unit time is

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

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

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

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

$$I_P = \frac{\xi \lambda e I_0 A(1-r)(1-\exp^{-\beta t})}{hc} \quad \ldots\ldots(7)$$

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)

RESULTS AND DISSCUSSION

As theory reveals that the total number of actual charge generation per unit time(equation 6) is

$$N_{acc} = \frac{E_a \lambda}{hc} \xi$$

Number of actual charge collection is directly proportional to the electric field applied in bismuth oxide composite also, an experimental data obtained also shows the similar trend in maximum (when X-rays are on) to minimum current (when X-rays are off) ratio (I_{Max}/I_{min}) ,i.e. decreases for both polymer composites as well as pure Bi_2O_3 pallets on increasing the applied electrical field

It is found that all composites has stable X-ray sensing and also has low switching time. Pure bismuth oxide and polymer-composites (PMMA-Bi_2O_3, PS-Bi_2O_3) Of Bismuth Oxide were found to have low electrical conductivity at room temperature (~300K). Their switching curves shows following Observation

1. With PMMA polymer dark current reduced to minimum as compared to pure Bi_2O_3 ceramic and its other composite , which is good for better detector.[Fig. 2]

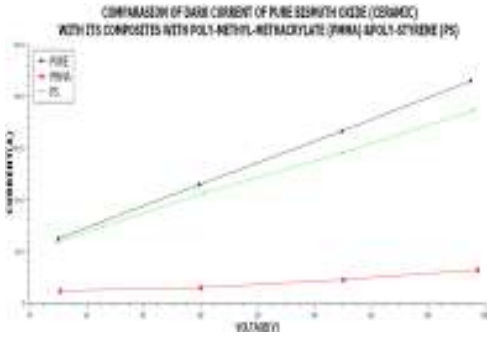


Figure 2: comparison of dark current for pure bismuth oxide with its composites

2. Although current in presence of X-Rays for PMMA is lass at low potential but it increases faster with increase in electric field.[Fig.3]

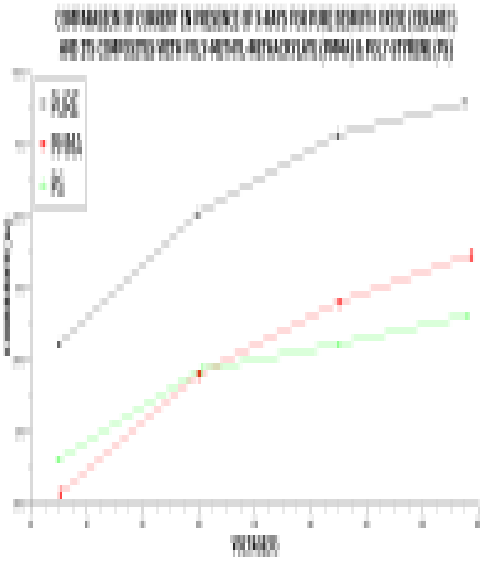


Figure3: comparison of current in presence of X-rays for pure bismuth oxide and its composites

3. The ratio of current in presence of X-Rays to dark current (I_{max}/I_{min})is maximum for PMMA composite[Fig. 4]

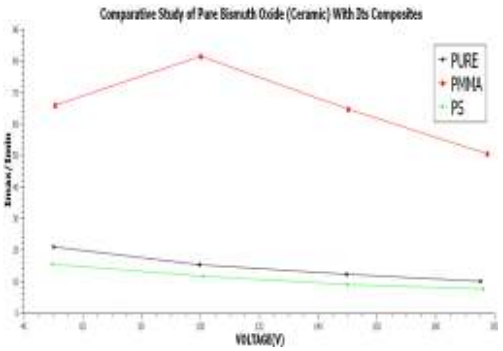


Figure 4: variation of I_{max}/I_{min} versus electric potentail for pure bismuth oxide and its composites

In pure bismuth oxide there are grain boundaries which are trapped in between the crystallites. When electric field is applied, some of the charge carriers are trapped in these grain boundaries. During switch on time, some delay in increase of current is observed, as charges are tapped in these grain boundaries. Similarly during switch off time, these trapped charges were released and again delay in decrease of current to attain its dark current is observed due to release of these trapped charges.

For composites with polymer as a base material, trapping of charges in grain boundary is very limited [Fig. 5].

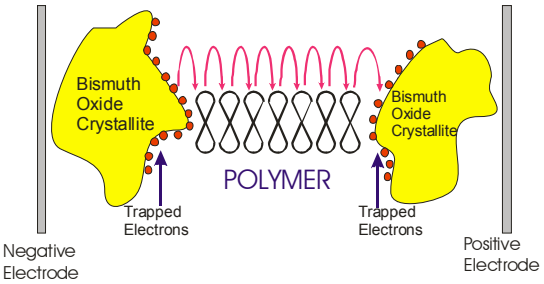


Figure 5: Schematic diagram showing the phonon assisted hopping mechanism of charge transmission through the PMMA-Bi_2O_3 composite sheets

The figure shows that the bismuth oxide crystallite is separated by polymers and Conductivity of such hybrid structures can be given by combining Mott Variable Range Hopping equation (For PMMA) and basic Arrhenius Equation for semiconducting materials (Bi_2O_3).

$$\sigma = \sigma_m Exp[-\frac{To}{T}]^{1/4} + \sigma_a Exp[-E_g/2K_bT]$$

Here σ_m is mott conductivity coefficient and T_0 constant, σ_a is Arrhenius conductivity coefficient, T is absolute temperature, Eg is band gap and K_b is Boltzmann constant. Electrical conductivity of PMMA is negligible (10^{-14}-10^{-15} $\Omega^{-1}cm^{-1}$) in comparison to the conductivity of bismuth-oxide ($1.46x10^{-12}$ $\Omega^{-1}cm^{-1}$). Hence first term in the above equation is relatively very small as compared to the second term. Thus, polymer composites behave like semiconductors in our case. This feature is promising feature for composites to act as X-ray sensors.

$$\sigma_{effective} = \sigma_a Exp[-E_g/2K_bT]$$

This feature is also in accordance with the experimental observations. Electrical conduction in these composites is facilitated by the hopping process. This process helps in releasing the trapped charges in the grain boundaries of bismuth oxide crystallites. These charges using π -bond electrons move through the polymer molecules to the nearby bismuth oxide crystallite.

Further these electrons drift under electric field through the bismuth oxide crystallites. Hence polymer acts as a helping separator with effective electrical conduction. This decreases the on and off time for X-ray switching.

Out of the two polymers investigated in the present study, it is found that PMMA offers better transport of the charged electrons in comparison to polystyrene. This is primarily due to

- Absence of benzene group in PMMA. In PS, due to presence of benzene group hooping process is hindered.
- More resistance of PMMA to the high energy radiation as compared to PS.(G. Geuskens, C. David ,1975: G. Geuskens, C. David, 1979)

CONCLUSION

`The studies reveal that PMMA-Bi_2O_3shows better X-ray sensitivity as compare to pure bismuth Oxide ceramics and its composite with poly-styrene , hence PMMA-Bi_2O_3 can be a better polymer composite.

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