

Electrical Conduction in Pmma-Mx₂ Composite Materials Under X-Rays Illumination



Chemistry

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ABSTRACT

Poly-methyl methacrylate (PMMA) and metal di-halide (MX₂) composites are emerging as new promising materials for X-ray sensing. With continuously increasing demand for digital X-ray processing, need for highly stable detector materials is increasing. New composite materials are fabricated using inorganic compounds like cadmium iodide and lead iodide. These materials are blended with Poly-methyl methacrylate (PMMA) and casted using organic solvents. Sheets of these materials were investigated for their electrical conductivity both with and without X-rays. These materials are found to have high energy radiation detection properties. Further switching studies were conducted on these materials. Results were analysed in light of photo-generation and photoconduction theories.

INTRODUCTION

In recent years there is continuously increasing digitalization in medical diagnostics field. Use of X-ray computed tomography (CT) or computerized axial tomography scan (CAT scan) and digital X-ray imaging are now routine activities [1-4]. These techniques require the digital data which can be processed by a computer. Normally this data is obtained by use of X-ray detector. In earlier versions of such machines, cesium iodide crystals were used as scintillation detectors. Later in 1980s use of high pressure Xenon gas ion chambers were used [5]. In modern machines, scintillation materials like rare earth oxide ceramics are in use. These materials absorb X-rays and re-emit the absorbed energy in the form of light. Light signals are then converted into electrical signals by photodiode and processed. However there is a possibility of direct conversion of X-ray signals into electrical signals with help of solid state X-ray detectors. These are basically semiconductor materials like silicon or germanium doped with lithium. X-rays passing through these materials are absorbed and are converted to electron-hole pairs to create electrical signals. For proper sensitivity, operations of such detectors require liquid nitrogen temperature. This helps in minimizing thermally generated electron hole pairs. In 1990s many solid state detector materials were explored like alpha-selenium, poly cadmium zinc telluride, mercuric iodide [6], lead iodide etc. Basis for a good solid state detector material is dependent on the following major properties:-

- Material should have high band gap. This helps in minimizing thermally generated noise.
- Constituent atoms should have high atomic number. This is for maximum absorption of X-ray energy.
- Mobility-life time product of the material should be high. This helps in better charge collection.
- Operating electric field should be low. It helps in keeping electronics involved simple.
- Operating temperature likely to be room temperature for ease in operation.
- Response time should be small for faster data processing.
- Fabrication of detector should be simple with flexibility of design, shape and size.
- Highly stable or have low degradation.

Solid state detector material known so far, has some of the above properties but lacks in some other properties. One of the important issues is flexibility in design. X-Rays are high energy radiations. When they interact with these materials they are partially reflected and partially refracted through the material. Limited portion is absorbed by the material. If detector is properly shaped, it is possible to maximize the absorption of X-rays.

Single crystalline material gives limited flexibility in designing the shape of detector. Keeping this in mind, it was planned to develop composite detectors. To have better spectrum of physical and chemical properties it was planned to blend an inorganic materials (cadmium iodide,

lead iodide) with organic polymer (poly-methyl methacrylate). Inorganic materials are selected having elements (Table 1) with high value of mass number. With heavy elements chances for better interaction with X-rays increases. This helps in good absorption of X-rays.

Table 1 Elements with mass number

S.No.	Chemical Element	Mass Number (u)
1	Cadmium	112.4
2	Iodine	126.9
3	Lead	207.2

Further it is very important to have materials with high value of electronic band gap [10-11]. This is especially helpful in reducing the dark current due to thermal agitation at room temperature

Table 2. Electronic band gaps of various materials

S.No.	Compound	Electronic band Gap (eV)
1	Cadmium iodide	3.3-3.1
2	Lead iodide	2.63

Poly-methyl methacrylate (PMMA) is well known polymer. It is selected due to its following properties [12-14]

- Low linear mold shrinkage (0.003-0.0065 cm/cm)
- Good mechanical properties {Hardness (63-97 Rockwell,M) and Tensile strength (47-79 MPa)}
- Most resistant to direct sunshine exposure.
- Low water absorption (0.3-2%) makes it very suitable for electrical device making.
- Very low electrical conductivity (10^{-14} - $10^{-15}\Omega^{-1}\cdot\text{cm}^{-1}$)
- High dielectric strength (17.7-60kV/mm)

Experimental and Results

Cadmium iodide and lead iodide (99.99% pure from Alfa Aesar) are used as starting materials. These compounds are first zone refined under argon atmosphere. Materials were taken in cleaned quartz boats and are given 20 zone passes using electrical heating at a slow speed of 1mm per hour. Purified mate-

rials from the initial portion of the boat were used for further processing. These materials were grinded in pastel mortar to fine powder. PMMA granules were dissolved in chloroform and mixed with fine powder separately. Uniform mixture is then kept to settle down for 48 hours in vibration free atmosphere. No further hot pressing is done to prevent any mechanical damaging to the sheets. After this fine sheets of composites were obtained. They were cut in square sizes of 1cmX1cm for further study. Sheets, without air bubble are used for the study. Sheets were polished for smooth surfaces and coated with silver paste. Coated sheets were kept for drying for nearly two hours. Coated sheets were then subject to electrical studies for determination of their band gap.

Electrically these sheets have very high resistance ($3-4 \times 10^{11} \Omega$) at room temperature. Two probe methods are used to study their electrical conductivity. Composite sheets with silver paste on both sides were gripped by two spring loaded electrodes. This assembly is kept in a PID controlled oven. Regulated power supply is used to provide voltage and current is measured by pico-ammeter (Kethley 6485). All measurements for band gap determination are done at low voltage (18V). Temperature is kept below 60 °C, as glass softening temperature of PMMA is 100 °C. These sheets show semiconducting behavior.

Conductivity of such hybrid structures can be given by combining Mott Variable Range Hopping equation (For PMMA) and basic Arrhenius Equation for semiconducting materials.

$$\sigma = \sigma_m \exp\left(-\frac{T_0}{T}\right)^{1/4} + \sigma_a \exp\left(-\frac{E_g}{2kT}\right)$$

Here σ_m is Mott conductivity coefficient and T_0 constant, σ_a is Arrhenius conductivity coefficient, T is absolute temperature, E_g is band gap and k is Boltzmann constant. These structures can be visualized as three dimensional-network of electrical resistors. There are two categories of resistors:

High resistors of PMMA separator and Relatively low resistors of MX_2 micro-granules embedded in PMMA matrix.

Electrical conductivity of PMMA is negligible (10^{-14} - $10^{-15} \Omega^{-1} \cdot \text{cm}^{-1}$) in comparison to the conductivity of inorganic materials (10^{12} - $10^{10} \Omega^{-1} \cdot \text{cm}^{-1}$). In this network of very high resistors having inter-linking of relatively low value of resistors, current finds the path through low value resistors preferably.

Hence the term $\exp\left(-\frac{T_0}{T}\right)^{1/4}$ is negligibly small as compared to the term $\exp\left(-\frac{E_g}{2kT}\right)$. This means that conductivity variation with temperature will show Arrhenius behavior. Same is observed experimentally.

It is found that number of charge carriers passing through the sheets increases with rise in temperature. This can be understood as the polymeric chains of PMMA and cadmium iodide/lead iodide crystallites act as traps of charge carriers. With rise

in temperature, phonon excitation increases. Phonon assisted hopping process helps in releasing the trapped charges. These charges using π -bond electrons move through the polymer molecules to the nearby cadmium iodide/lead iodide crystallite.

Sheets were exposed to X-rays (Cu target 30KV, 10 mA plate current) parallel to electrode plates. X-ray intensity to which sheets were exposed is of the order of 10^{-2}W/cm^2 . It was found that photo current increases by a factor of 200-1000 in comparison to the dark current.

Under the X-rays illumination photocurrent generated (I_p) is directly proportional to five main parameters

Radiation term eI_x (e =Electronic Charge And I_x =Radiation intensity),

Performance factor of material μ (μ =efficiency of conversion of radiations into charge carriers, τ =carrier life time i.e. average life time of carrier before recombination and μ =charge mobility),

Electric field applied (E),

Dimensional parameters like area to volume ratio of crystallite and

Temperature of material.

Material used as a sensor should have very low response time. To evaluate response time switching studies were conducted on these films. Switching study reveals following important findings:

Rise time and fall time is nearly 2 second for 10 second pulse on these films.

Photocurrent does not stabilize very fast. It shows some zig-zag variation with time as seen experimentally. This variation is expected as charge trapping occurs on the surfaces of cadmium iodide/lead iodide crystallite. At higher temperature stability is higher. This is due to quick release of trapped charges under thermal agitation. Such materials still require improvements before they can be used as X-ray Imaging Detectors [15, 16]. Similar results were obtained in all the sheets.

CONCLUSIONS

PMMA-cadmium iodide/ lead iodide are a good X-ray sensors as photocurrent amplification is quite high. Although these sensors are not good for fast data switching as rise time and fall time is high. However at temperature close to 40-50°C stability of photocurrent is high. Such sheets are however transparent to low energy gamma rays.

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