Perovskites for Spectrometric X-ray Imaging (PerXI)

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ABSTRACTs
Spectral sensitivity would provide chemical contrast to medical X-ray flat panel imagers, delivering new clinically relevant information to improve the diagnosis and treatments of patients. Today, no detection material fulfils the requirements of large area spectral imaging, but the perovskites semiconductor studying in the PerXi project might meet this need. First, we set up a reproducible method to produce high quality crystals. Then, we developed two processes to integrate these single crystals on a readout circuit. We succeeded in demonstrating gamma ray photon counting with these pixelated devices. Finally, we propose a strategy to scale this technological development to higher TRL.

Keywords: hybrid perovskite; spectrometric gamma-ray imaging;

1. INTRODUCTION

Medical X-ray imaging improvements contribute to better diagnosis and treatments of many medical conditions. The next breakthrough in radiography will be X-ray spectral imaging with high spatial resolution, which will make it possible to distinguish much better between the different types of biological tissues of patients' organs than current imaging techniques. Such highly precise medical imaging based on chemical contrasts will deliver new clinically relevant information to improve the diagnosis, treatments and therapeutic follow-up of patients. This new revolution (X-ray spectroscopy and high spatial resolution) will only be possible by using direct conversion of X-rays through a photoconductive layer that converts directly X-rays into electrical signals, which is much more favourable in photo-detection efficiency and spatial resolution than the current indirect photo-detection involving a phosphor. Thus, in this implementation spectral imaging will lead to much more accurate analyses than the finest current ones and will be combined with significant reduction in the X-ray doses administered to patients for the same image quality.

Measuring the energy of every single X-ray photon impinging the detector requires the use of a semiconductor as energy resolved photoconductive layer. Numerous semiconductors have been developed for X-ray detection. However, there is no identified large area semiconductor capable of measuring the energy of individual X-ray photons in the medical energy range (30-90keV) and at clinical flux. Recently, hybrid organic-inorganic perovskites have been shown to be very promising candidates for direct conversion X-ray detectors. Several teams have shown the possibility to use thick freestanding single-crystals perovskite for discrete X-ray detectors in integration mode and in gamma-ray counting mode. None of these approaches allows reaching a pixelated spectrometric radiographic imager with small pixel pitch. The PerXi project breakthrough was to prove the feasibility of a hard radiation spectrometric imager composed of 16 pixels with a pitch of 220 µm or 600µm.

In the PerXi project, the growth of single crystals in solution has been studied leading to a protocol that decreases their structural defects (dislocations, strains, inclusions) that could be further detrimental to their electronic performances [1]. Relevant charge transports properties of $CH_3NH_3PbBr_3$ single-crystals have been investigated (electron and hole mobilities, carriers lifetime, electrical field profile) [2]. Such parameters must be known to anticipate the behavior under spectrometry. In a first mode of realization, the crystals were grown in solution directly on the readout circuit surface. On an alternative mode of realization (self-standing single crystal), an array of electrodes was evaporated on the crystal surface and the crystals were hybridized on a readout circuit. To our knowledge, this is the first demonstration of perovskite crystal hybridization with such low resolution. For the first time, thanks to this advanced integration, it has been possible

to demonstrate photon counting with the $CH_3NH_3PbBr_3$ perovskite composition.

2. STATE OF THE ART

Among the semiconductors considered for large area X-ray radiography, only amorphous selenium has proven to be well suited for mammography (~20 keV). Nevertheless, its low atomic number does not allow its use at higher energy (50-70 keV) for general radiography. Thus, active research has been carried out on different materials (e.g. HgI_2, Cd(Zn)Te, PbI_2, PbO) to identify suitable polycrystalline thick layers. It must be noted that the use of heavy metals such as Cd, Hg, or Pb is not prohibitive to the realization of X-ray detectors as they are effectively confined in perfectly sealed detection devices. Even so, none of these materials fulfil all spectral imaging's requirements, mainly because of poor charge carrier transport properties. On the other hand, monocrystalline semiconductors with high transport properties, such as CdTe, are not compatible with the large area of medical radiography. Thus, so far, there is no identified semiconductor suitable for large area X-ray photon counting for medical imaging (50keV).

Lead perovskites are an old class of semiconductors that have seen renewed interests during the recent years through their hybrid organic-inorganic family. The latter has a unique combination of intrinsic properties: high density and high Z elements (X-ray absorption enhancement), large bandgap (> 1.5 eV, dark current reduction), high charge carrier mobility-lifetime product (good charge collection) and solution-processability (cost reduction and large area compatibility). One important feature is the possibility to reach thick layer (> 500µm) to absorb incident X-rays (> 90%), while maintaining high crystallinity to efficiently extract the photo-generated charge carriers. Photodetectors based on hybrid perovskites $CH_3NH_3PbX_3$ (X = Br, I, Cl) single crystals grown in solution have been tested for X-ray radiography in integration mode by CEA and others academic teams (Univ. of Nebraska, ETH Zürich).

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The PerXI project focuses on spectral X-ray imaging which is expected to be a major revolution for the next generation of X-ray imagers: a significant reduction of X-ray doses delivered to patients coupled with much more accurate discrimination between the different biological tissues that constitute organs. Thus, we would move from black and white to color X-ray radiography, as it were. The technical breakthroughs of the project were related to various steps required to build a flat panel for radiography.

The crystal growth in solution has first been studied. A protocol was established to decrease the structural defects (dislocations, strains, inclusions) that could be detrimental to the electronic performances. Relevant charge transports properties of $CH_3NH_3PbBr_3$ ($MAPbBr_3$) single-crystals have been investigated (electron and hole mobilities, lifetime and electrical field profile). Such parameters must be known to understand the sample photocurrent under irradiation. Once a reproducible process for producing high quality crystals was defined (lowest reported dislocation density for this material), the next step was, for the first time, the integration of this crystal onto a pixelated readout circuit. In a first approach, the crystals were grown from solution directly onto the readout circuit surface. This solution growth mode is very well suited to scaling of large area detector. An alternative route consisted to evaporated an array of electrodes on the crystal surface (self-standing single crystal) then the crystals were hybridized on the readout circuit.

This second process should lead to higher spectrometric performances through better surfaces and interfaces control. Finally, the photon counting with the $CH_3NH_3PbBr_3$ composition has been demonstrated for the first time thanks to high crystal quality and optimization of their integration.

Tab. 1. PerXi progress beyond the state of the art.

State of the art	PerXi breakthrough
Single electrode	Array of 4×4 pixels
Large area electrode	200µm and 600µm pitch electrodes
Wire bonded electrode	Direct growth on a PCB (approach 1)
Wire bonded electrode	Bump bonding on a PCB (approach 2)
Remote from the readout circuit	Integrated on a PCB
Current integration	Gamma photon counting

4. PROJECT RESULTS

PerXi project addresses the different steps required to develop X-ray spectrometric imagers. First, the crystal growths and characterization. Second, the integration of semiconductor crystal layers onto readout circuits, including surface preparation and electrode engineering. Last, the measurement under gamma-ray irradiation.

The first step was to develop a solution-process with a robust and reproducible protocol of seeded crystal growth combined with appropriate temperature profile selected from continuous growth monitoring. Details could be found in reference [1]. A clear improvement in crystal quality was reached with higher transparency, minimized internal strains (Fig 1.), and a low dislocation density in the range of 10^4–10^5 cm^{-2}.
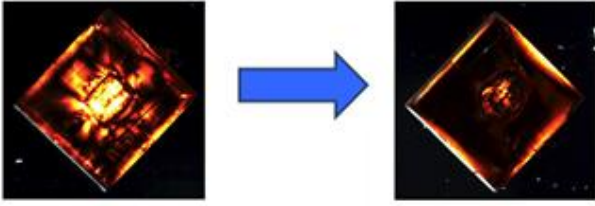
Fig. 1. Polarized light microscopy images. Left: stressed crystal. Right: single crystal without stress. Seeds are visible on crystal centres

The second step was to measure accurately the electro-optics performances of these crystals in order to interpret the spectrometric experiments results. Laser time of flight measurements and X-ray focused experiments along the edge of the samples were carried out. We report homogenous holes transit throughout the thickness of the samples (hole mobility: 13 cm²V^{-1}s^{-1}, hole lifetime: 20µs) as well as poor electrons transit (electron mobility: 18 cm²V^{-1}s^{-1}, electron lifetime 1µs). The charge carrier mobility will contribute to define the maximum X-ray flux that the device can handle whereas the mobility-lifetime product will contribute to define the device energy resolution. We also report on the continuity of the electric field throughout the whole thickness of the MAPbBr$_3$ samples which is necessary to ensure a high detection efficiency [2].

In parallel, specific printed circuit boards (PCB) have been designed with pixelated arrays of 4×4 electrodes with 220µm and 600µm pitch plus a guard ring. The role of these PCB was to emulate a backplane and to interconnect the semiconductor electrodes with an external readout circuit. The 220µm pitch was close to the flat panel actual pixel pitch (150-200µm). The 600µm pitch should enable a higher energy resolution through a better trade-off between small pixel effect and moderate charge sharing among adjacent pixels.

Two types of integration of the crystals onto the PCB were implemented as shown in Fig 2. In a first mode of realization, the crystals were grown in solution directly on the PCB surface (Fig 2. a). This mode avoids the complex operation of hybridization and is thus easily scalable to larger areas. However, the control of the interface between the crystal and the electrode on the PCB is lower. On an alternative approach, a self-standing single crystal was used (Fig 2. b). An array of electrodes (Cr/Au) was evaporated on the crystal surface and the crystals were hybridized on the PCB using silver bumps (Fig 2. c). This route should lead to higher spectrometric performances through better surfaces and interfaces control but may be more difficult to scale over large areas. For both modes, the top electrode (C60/BCP/Cr/Au) were evaporated. Thus, the realization of an array of electrode on a perovskite single crystal as well as the bump bonding of the device on a PCB was realized for the first time (Fig 2. d). The dark current in the order of a few nA per pixel at 50V was consistent with a resistivity of 10^8 Ω.cm.

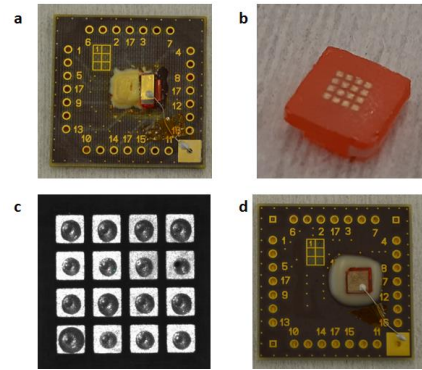**Fig. 2. a**, crystal grown directly on the PCB surface. **b**, array of electrode on a single crystal. **c**, silver bumps on the PCB electrodes. **d**, single crystal bump bonded on a PCB.

Finally, the devices were tested under gamma-ray irradiation using 16 low-noise preamplifiers and a tunable shaper. Gamma-ray irradiation has lower count rate and more better defined energies than X-ray, and is a prerequisite for the more demanding X-ray spectrometry. The signal was recorded using an oscilloscope and the pulse amplitude was histogrammed as shown in Fig 3. Three sources were used to assess the device energy discrimination: americium 241 (59.5 keV), cobalt 57 (122 keV) and barium 133 (81 and 356 keV). The gamma photon counting was demonstrated for the first time through the CH$_3$NH$_3$PbBr$_3$ composition.

However, even if the energy discrimination has been proved, the photopeak are not visibles. The next step will be to reduce the noise through the study of the noise spectrum and an optimal filtering.
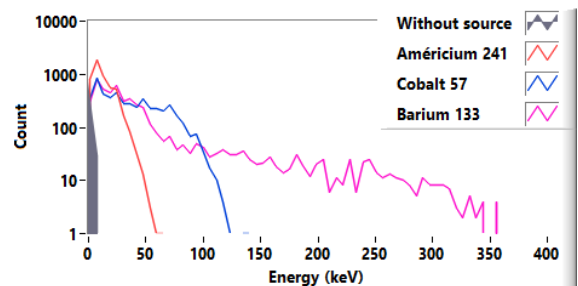

Fig. 3. Gamma spectrum acquired on one pixel of a hybridized device (bias 50V, 10µs shaping).

5.   FUTURE PROJECT VISION

5.1. Technology Scaling

The final goal of this project is to build spectral sensitive flat panel detectors for X-ray radiography, which simply doesn't exist today. ATTRACT phase 1 enabled to prove the feasibility of high energy photon counting using hybrid perovskite semiconductor on a small prototype. The technical results are very promising and allowed identifying some the key point to be solved: electric noise

need to be reduced, charge carrier mobility has to be increased while the process for the integration on a backplane has to be scaled to larger area. All these points should be overcome by a combination of improvements through materials, processes, devices and electronics.

For ATTRACT phase 2, we propose a two approaches strategy to be successful in making spectral sensitive flat panel detectors. By analogy to the development of dual energy CT, we propose to split the project into two tracks that should lead to two distinct generations of energy sensitive medical flat panels. In the first route, we propose to develop a stacked dual-layer detector system in integration mode. The second approach will be the development of a photon counting flat panel detector. This riskier track is more demanding but should lead to higher performances through better energy separation. These two approaches should be led in parallel and will feed on each other because they share several technological steps in material development and integration. The first approach could expect to reach a TRL 5-6 at the end of the phase 2 while the second could reach a TRL 4-5. Thanks to direct detection, both tracks will provide energy information along with higher spatial resolution than current flat panels.

The following items will be developed:
- Fine device specifications (experience in Trixell and Siemens).
- Dedicated flat panel and counting flat panel (experience in CEA Leti and Trixell and TNO).
- Large area semiconductor layers (experience in Liten, Institut Néel and Siemens).
- Reduce noise (necessary in integration and counting mode) through material composition tuning and electrode and interface engineering (experience in CEA Liten and Institut Néel).

The technological improvements for spectrometric performances will also benefit to others challenging but less demanding applications such as low noise medical radiography in integration mode with high spatial resolution thanks to direct detection. A concrete application would be cardiovascular imaging. Moreover, phase contrast imaging system could benefit of a large area flat panel with higher spatial resolution than currently commercial flat panel.

5.2. Project Synergies and Outreach

The PerXi project consortium is composed by an academic partner, an RTO, and an industrial partner who is the world leader in X-ray large area flat panel digital detectors designed for a wide range of medical applications in radiology. A complementary consortium would be composed by additional industrials (potential investors), RTO and academic partners in the field of radiation imagers. The ATTRACT ESSENCE project could be highly complementary to our developments,

and European industrial partners such as Siemens, Philips or Trixell would be well suited to support these developments with precise applicative specifications.

Partners of the PerXI project are involved in another H2020 project called PEROXIS (RIA: 2020-2023) with the aim of developing process approaches to integrate thick perovskite layer into active matrix backplane for medical radiography (X-ray integration mode). The PEROXIS project do not deal with spectrometric issues, nevertheless some technological aspects related to the process and integration of thick perovskite crystal layers should be solved, and could act as the foundations for an ambitious ATTRACT phase 2.

From a purely technical points, the next step would require competences in materials, chemistry and physics as well as readout circuits (TFT or CMOS backplane). Also, it could be a plus to work with partners that could take advantage of the high spatial resolution enabled by direct detection, in order to develop new systems, like phase contrast imaging.

Public dissemination of the results will be made as for the phase 1 project, including conference, peer reviewed publications [1, 2], report, video and PhD dissertation.

5.3. Technology application and demonstration cases

The development of large area X-ray spectrometric imagers is fully in line with the major health societal challenge. Multi-energy radiography will provide new clinically relevant information, improving patient diagnosis with a cost-effective and highly accessible radiography exams compared to current Computed Tomography exams. The high-precision medical imaging based on chemical contrasts will improve the detection atherosclerotic plaques and the identification of kidney stones. Associated with injected contrast product (iodine), it will enhance the visualization of blood vessels imaged in the chest even behind the coasts or the spine (by bone removal) improving the diagnostic of pulmonary diseases. In a longer term, new high-resolution functional images could be produced with the use of markers linked to molecules with specific affinity for pathological organs. Also, direct detection could be a key technology for phase contrast imaging systems

Increasing the quality of care, particularly for diagnostic radiology is a goal for imaging teams in Hospitals, notably reducing the X-ray exposure while improving the quality of images thanks to a better X-ray detector. Recent experience of Covid-19 showed the importance of obtaining excellent image quality bedside chest radiography, performed directly in the emergency ward, for selection of severe cases who should be hospitalized.

Also, this project will contribute to safeguard jobs in Europe and create growth, as the European manufacturers who will produce these sensors (Trixell,

France) and systems (Siemens, Germany, Philips, the Netherlands) will have a strong comparative advantage over Americans and Asians companies.

Finally, X-ray photon spectrometric imagers could be involved in large research infrastructure communities of Europe such as synchrotrons or in X-ray/gamma-ray astronomy. Thus, a presentation of the perovskite capabilities has been made this year at ESRF and an evaluation of the outcome detector of the PerXi phase 2 project should be made with the ESRF detector group.

5.4. Technology commercialization

Trixell (France), the world leader in X-ray large area flat panel digital detectors designed, who is already part of the PerXi consortium, will make the commercialisation of the technology. Trixell shareholders, namely Thales, Siemens, and Philips, will build medical systems around this new generation of flat panels and sell it to hospitals around the world.

5.5. Envisioned risks

First, the semiconductor material itself could not reach the required performance (charge carrier mobility, resistivity). We are currently working on the fine-tuning of the fine-tuning of the perovskite composition to reach the required level. Secondly, the device could not reach the required performance (stability, dark current). This point could be mitigated through electrode engineering (electron and hole blocking layers, work function tuning). Even with this mitigation strategy, it could happen that the photon counting at high rate is not good enough. That is why we propose a two tracks project, including a first approach based on dual layer X-ray imager in integration mode, and a second approach based on spectrometric imager in counting mode. This two-steps methodology would enables to orient medical imaging toward spectrometric mode while controlling the risks related to technology developments and increasing the performances gradually.

5.6. Liaison with Student Teams and Socio-Economic Study

During the ATTRACT phase 1 project, we trained two students for noise measurement and electric field measurement. We also employ two PhD students for crystal elaboration and electro-optical characterization. In ATTRACT phase 2, we will continue this students training. More specifically, we will nominate an experienced researcher to facilitate MSc. level explanation materials of our X-ray imager technology.

Also, we will contribute to the socio-economic study of the ATTRACT initiative through interview and technology impact references.

6. ACKNOWLEDGEMENT

7. REFERENCES

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