Current status of perovskite in X-ray detection for medical imaging technology

Bhavana Butey1, Swatika Butey2, Bhakti Patankar3, V D Raut4, Mugdha Dambhare5, S V Moharil6

1,3,4,5G H Raison College of Engineering, Nagpur
2Intern, MBBS, Indira Gandhi Government Medical College Nagpur
4Retd. Professor, Department of Physics, PGTD, Nagpur
E-mail: butey.bhavana@raisoni.net

Abstract. The X-ray imaging is a powerful tool used in medical diagnostics, non-destructive material inspection, security checks, nuclear plants and research field. Perovskites is considered as a promising candidate for X-ray detection owning to its remarkably improved sensitivity, low-cost synthesis, detection limit, response time and better special resolution. In this review paper the challenges and future scope of the reported work in the lead based and lead free single and polycrystalline perovskites is studied. Most of the reported results are based on single pixel detection. Hence, it is proposed that an interdisciplinary collaborative work will only facilitate its practical implementation in state-of-the-art X-ray imaging technology.

1. Introduction

In the COVID-19 pandemic there was a surge in the computed tomography (CT) imaging all across the globe as it is considered to provide the best diagnosis of the disease. The CT imaging uses high radiation dose of X-rays. Even a single chest CT scanning has a dose which is approximately equal to two years accumulation of dose from natural background [1]. In medical imaging, X-rays transmitted by the irradiated body parts are detected by X-ray detector and an image is formed. Hence, to reduce radiation dose in X-ray imaging and for better quality of the image produced, a highly sensitive detector is required.

The modern digital X-ray detectors due to its advantages viz. ease of image processing, storing and sharing the data has almost replaced the analogue film-based detectors. The biggest advantage of digital X-ray detector is the accurate diagnostic interpretation as this technique allows easy image resize to see potential issues without affecting the quality of the image. Thus, from the same image more information can be obtained which avoids patient’s further exposure to X-rays. Commercial X-ray detectors either use direct or indirect conversion method. For example, in digital X-rays detector, flat panel detectors are used which converts X-ray into charge either directly or indirectly which is then processed and transformed into a digital image. In direct conversion X-rays are converted into charge by using X-ray sensitive photoconductor (eg, amorphous Selenium) [2-4] whereas in indirect conversion a scintillator (eg. Thallium-doped cesium iodide) converts X-rays to visible light first and then a photodetector converts it to charge [5-6]. The direct detectors are preferred as it can achieve higher resolution, have simple structure and are less expensive with ease of manufacturing. Thus, there has been massive research ongoing to synthesize an efficient and cost-effective direct X-ray detector [7-8].
Low atomic number crystalline semiconductors viz. Silicon, Germanium, Gallium Arsenide are seldom used as detector due to their poor attenuation coefficient. Commercialization of amorphous Selenium (a-Se) detector is only for mammography due to its requirement of low energies of X-rays viz. less than 40 keV. Hence, a new class of semiconductors is required for high performance and cost-effective X-ray detectors for minimal dosage for medical imaging. The qualities looked for in the detector material are high X-ray attenuation coefficient, low ionization energy, minimum dark current, good charge carrier transport, stability processing and scalability. The unique properties of perovskite crystals along with the low-cost synthesis make them suitable for X-ray detection. Perovskite crystals structure, performance parameters, crystallization techniques, advantages and limitation of reported perovskites as a detector material and challenges and future scope are discussed in the following sections.

2. Perovskite crystal structure

Perovskite are those materials have a stoichiometry of AMX₃. It is a three-dimensional network where A is usually a small organic or an inorganic cation like methylammonium (MA) or formamidinium (FA). The ion at site A is surrounded by four adjacent MX₆ corner sharing ions forming an octahedra as shown in figure 1.

\[
t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)},
\]

where \( r_A, r_B, r_X \) are the ionic radii of the A, B and X ions. For halide perovskites the tolerance factor is in the range of 0.7 to 1. Thus, to get the required structure during the synthesis the tolerance factor must be satisfied. The distortion is mainly due to tilting of BX₆ octahedra on account of non-ideal size effects and other factors including strain on the B-X bond.
It is reported that with increasing temperature, crystal structure of perovskite transforms from orthorhombic (T, 160 K) to tetragonal (162.2K<T<327.4K) to cubic (T> 327.4K) [9-10]. However, it must remain as a 3D structure because with temperature if it disintegrates into a 2D structures then it is not good for transport of the charge carrier compromising efficiency of the device.

Band gap of the perovskite material can be altered by changing cation at position A or by changing M or anion X. By making these changes, the crystal structure changes as the tolerance factor, t is changed. By creating a changed crystal geometry one can manipulate the band gap of the perovskite crystal. Thus, with orientational disorder the electronic properties is also different for a perovskite crystal structure having orthorhombic or tetragonal or cubic structure.

3. Performance parameters for detectors
In X-ray detector absorption of X-rays i.e., attenuation, electron-hole pair generation and charge carrier transport are responsible for its performance. Let’s first understand them before discussing the operational parameters which decides the performance of a detector.

In medical imaging, energy of X-ray photons is usually less than 120 eV. The attenuation of X-rays is mainly due to absorption of photons by electrons. For the material under consideration, its attenuation ratio ε for X-rays is given by

$$\varepsilon = 1 - e^{-\alpha L},$$

where L is the thickness of the material and α is the attenuation coefficient. It has been found that the attenuation coefficient depends on the photon energy as for higher energies > 36 keV, inner shell electrons ejection process starts, thus affecting the attenuation ratio. The photon absorption rate (φ) by the material which gives number of photons absorbed per second is estimated by

$$\varphi = \varepsilon D m_\text{s} = E_{\text{ph}},$$

where $E_{\text{ph}}$ is the energy of X-ray photons, the dose rate is D and the mass of the absorbing material is $m_\text{s}$.

In medical imaging the absorbed X-ray photons creates multiple electron and hole pairs (β) by ionizing low binding energy electrons on its way through the absorber which is given by the equation

$$\beta = E_{\text{ph}}/ W_{\pm}$$

where, ionization energy which is produces an electron-hole pair is $W_{\pm}$ and depends on band gap ($E_g$) for crystalline semiconductors [11-12].

The electron hole pairs generated due to the photoelectric absorption; drift due to electric field within the absorber. On account of recombination and crystal defects the actual number of charge carriers collected at electrodes are very less. The carrier collection efficiency (CCE) mostly depends on the applied electric field (E), mobility (μ) and life time (τ) of the charge carriers. Thus, materials with high mobility and lifetime product are preferred as detector. The photocurrent, $I_P$ generated by excluding losses which determines the efficiency of detector is approximated by the equation

$$I_P = \varphi \beta e$$

3.1. Dark Current
Dark current is the flow of charge carriers in the detector under no X-ray exposure. Large values of dark current limits the detection sensitivity as it will mask the signal, generate large noise and will increase the lower limit of detection (LOD). The maximum accepted value of dark current for a detector used in diagnostic medical imaging is 0.1 nA/cm². The novel perovskite absorber used as a detector has a drawback of generating high dark current owing to large concentration of intrinsic charge carries, ionic
conductivity and low values of interfacial barriers [13]. Thus, for reducing the dark current to acceptable values, manipulation of its intrinsic properties and interfacial barrier through material engineering is required.

3.2. Sensitivity

The sensitivity of the direct X-ray detector depends on all parameters discussed earlier viz. electron-hole generation, attenuation and carrier collector efficiency [14-15]. It is given by

$$S = \frac{I_R}{D \times A},$$

where $I_R$ is the difference between the output current with and without X-ray exposure, $A$ is the active area of absorber and $D$ is the dose rate. For perovskite detectors the reported sensitivity values are manifold higher as compared to the theoretical values on account of large photoconductive gain ($I_R/I_P > 1$) [16]. However, high values of dark current needs to be tackled.

3.3. Lowest Limit of Detection (LoD)

The LoD represents the minimum dose rate required for obtaining good resolution images. As per standard definition, the LoD is the minimum dose rate for which the signal-to-noise ratio (SNR) of 3 is produced. SNR is the ratio of $J_s$ and $J_n$, where $J_s$ and $J_n$ are the signal and noise current densities respectively as given by equations

$$J_s = J_p - J_d$$

$$J_n = \frac{1}{\sqrt{N}} \sum J_i^2 - J_p^2,$$

where, $J_p$ and $J_d$ are the photo and dark current densities respectively. Minimal values of dark current, high sensitivity and low values of noise signal are required to achieve the desired low value of LoD.

3.4. Response Speed

To reduce X-ray exposure time the response speed of the detector must be very high. Thus, the response time of the detector should be less. The response speed of the detector depends mainly on the transport and collection of the charge carries. In thick perovskite detectors the carrier transit lengths are relatively on a higher side increasing the response time. Ionic conductivity and large values of life time of charge carriers trapped due to defects [17-18] are also responsible for larger response time. However, it has been reported that the significant response speed can be attained in thin perovskite but at the expense of the photocurrent hampering the sensitivity of the detector. Thus, it’s a tradeoff between the absorption and the thickness of absorber to achieve optimum values of the response speed [19].

4. Crystallization techniques

For any device, stability is very important. The stability of device depends on the material morphology. Morphology means a defect or trap free material. Ideally synthesized material should have minimum defects or traps as they act like a potential energy minimum which leads to the electron hole recombination. Thus, material must have good morphology which is governed by the synthesis technique used. Hence, engineering of the material to the desired specification is required for success of the device. Single perovskite crystals are found to have much lesser defects.

The general mechanism of the crystallizations process can be summarized as, first there is a super saturation which leads to the nucleation which further leads to the crystal growth and then to crystal structure formation which is an equilibrated structure. If there is no super saturation, then it will be a non-equilibrium, however finally over the time period it will also reach to an equilibrium system. To grow perovskite single crystal, methods used are categorized by the growth environment that includes
solid, liquid and vapor growth. If the perovskite crystals are grown in a solid state then it is a solid growth else if we grow them in a liquid state then it is a liquid growth or vapor growth if it is grown in a vapor phase.

Perovskite crystals have been prepared with the specifically the liquid growth method as per the reported data. The common methods used to produce perovskite single crystal are the slow cooling, anti-solvent precipitation and Inverse temperature Crystallization (TTC) method.

4.1. Slow cooling method
In a slow cooling method, the crystals can be grown by gradually reducing the solubility of the target sample in the precursor solution. In line with this basic principle, we can produce single crystal of perovskite material by cooling the precursor. For example, in the solvent of CH3PbI3, lead iodide is a precursor material. If it is cooled gradually then the solubility starts decreasing. At low temperature they will start forming the crystals. Thus, slow cooling also led to the crystal formation. [20]

4.2. Anti-solvent precipitation method
In this method anti-solvent is used. Anti-solvent is a solvent where the perovskites precursor does not dissolve. In the anti-solvent as the target sample does not dissolve precipitation will occur since the solubility of the desired product will be drastically reduced. So first the solution the precursor is dissolved in a good organic solvent. Then slowly anti-solvent is added to this material so the solubility of the precursor will be decreased and it will precipitate at the bottom where crystals are formed. [20]

4.3. Inverse temperature Crystallization (TTC) method
The increasing of the temperature of the precursor solution (N, N-dimethylformamide (DMF)/γ butyrolactone (GBL)/dimethyl sulfoxide (DMSO)-based solutions) results in abnormal solubility of the perovskites in these solvents resulting in quick formation of large perovskites crystals. As precursor concentration is much higher than the allowed solubility, precipitation of perovskite crystals at bottom starts quickly with the heating of the solution. [20]

High quality perovskite single crystals can be grown from solution using above synthesis methods with the required physical and chemical properties suitable for radiation detection.

5. Perovskites as a detector material for X-rays
The parameters discussed above mainly, mobility and life time product (μτ) must be large for large carrier collection efficiency, trap density to be less for less noise and for reduced non-radiative recombination, optimum thickness for high attenuation, less ion migration, all of them together decide the eligibility of the perovskite material for X-ray detection. These properties are predominantly governed by the chemical composition and structure of the perovskite crystal. Hence, scientist across the globe are actively engaged in engineering the appropriate detector material for X-ray imaging. The current status of the reported lead based and lead free single and polycrystalline perovskites are discussed below along with the future challenges and the scope for improvement of detector performance.

5.1. Lead based single crystalline perovskites
For X-ray detector, this class of perovskites is suitable due to the presence of heavy element lead and halide which results in high X-ray attenuation coefficient. Wei et al. [21] in 2016 reported a single crystal MAPbBr3 used for X-ray detector. These crystals were synthesized by using anti-solvent method. The vertical photodiode structure of the detector consisted Au/MAPbBr3/C60/BCP (Bathocuproine)/Au. For a continuous X-ray irradiation of energy 50 keV, the detection efficiency close to zero bias was reported at 16.4%. The LoD and sensitivity obtained by them was 0.5 μGy/s and 80 μC/(Gy·cm²). In
continuation of their work, they came up with a monolithic integrated MAPbBr₃ single crystal on a Si substrate as X-ray detector [22]. The reported LoD and sensitivity for 8 keV X-ray irradiation as < 0.1 μGyair/s and 2.1x10⁴ μC/(Gyair cm²). Thus, sensitivity increased 64-fold and the LoD decreased by rationally engineering the synthesis and device interfaces. Wei et al. further used the dopant compensation strategy to reduce dark current in MAPbBr₃ to reduce intrinsic charge carrier concentration. The detector using alloyed MAPbBr₂.₉₄Cl₀.₀₆ showed remarkable values of LoD and sensitivity viz. 7.6 ηGyair/s and 8.4 x10⁴ μC/(Gyair cm²) [23]. This finding is for a very low dose rate which needs further affirmation as it is reported that with increase in dosage the sensitivity drops significantly [16,24-25]. Another non-stoichiometric approach adopted by manipulating crystal orientation of MAPbBr₃ obtained remarkable sensitivity of 3928 μC/(Gyair cm²) [26].

Another halide perovskite, MAPbI₃ is a promising detector material on account of its higher atomic number and smaller band gap for good attenuation and for generation of more electron-hole pairs. Ye et al. obtained single cubic crystal by using seed dissolution and regrowth process reaching sensitivity of the order of 968.9 μC/(Gyair cm²) but with a large dark current [27]. In order to reduce dark current, resistance is increased by integrating large sized cation (DMA-dimethylammonium and GA-guanidinium) in MAPbI₃. The LoD and the sensitivity obtained by GAMAPbI₃ detector is reported as 16.9 ηGyair/s and 2.3 x10⁴ μC/(Gyair cm²) which is approximated same as that of MAPbBr₃ [28].

One more all-inorganic halide perovskites have created its mark due to higher stability and large attenuation coefficient. Single crystal CsPbBr₃ were synthesized by a modified ITC method by Zhang et al. The CsPbBr₃ detector showed sensitivity of 1256 μC/(Gyair cm²) with minimal dark current. Another effort to attain higher sensitivity by doping CsPbBr₃ by rubidium as reported by Wang et al. resulted in the RbCsPbBr₃ detector sensitivity of 8097 μC/(Gyair cm²) [29].

5.2. Lead free single crystalline perovskites
Toxicity of the lead element for all organic and inorganic perovskites undermines the extraordinary success attained by the lead halide single crystal perovskites. To tackle the environment issues, poisonous lead was replaced by heaviest stable element Bismuth which has excellent attenuation coefficient and has the other properties required for a detector material for X-ray imaging. Thus, Cs₂AgBiBr₆, a lead-free single crystal perovskite-based detector offers sensitivity and LoD of 24 μC/(Gyair cm²) and 59.7 ηGyair/s respectively [16]. The intrinsic ordering of cations Ag and Bi in Cs₂AgBiBr₆ is brought about by deliberate introduction of phenylethylamine (PEABr) leads to increased sensitivity of 288.8 μC/(Gyair cm²). It is well known that perovskites of low dimension show subdued ion migration with less defects and large resistivity [30-32] resulting in dropping of dark current. A 2D single crystal structure BA₂CsAgBiBr₄ where BA is butylammonium for X-ray detection was reported by Xu et al., has a quasi-cubic geometry offers a sensitivity of 4.2 μC/(Gyair cm²) and negligible dark current [33]. Similarly layered single crystal 2D structures like (NH₄)₂Bi₂I₉ with structural anisotropy were presented as a detector material which exhibited facet dependent performance. This detector offered sensitivity and LoD of 8000 μC/(Gyair cm²) and 210 ηGyair/s for parallel and 803 μC/(Gyair cm²) and 55 ηGyair/s for perpendicular direction respectively. This detector showed exceptional stability as the detector performance did not deteriorate even after 2 months of ageing in air [34].

One- and zero-dimensional bismuth based single crystal perovskite-based detector are also reported for X-tackle the ray detection. A single crystalline (H₂MDAP) BiI₅ where H₂MDAP is N-methyl-1, 3-diaminopropanium based detector showed poor sensitivity of 1 μC/(Gyair cm²) due to relatively higher trap densities. Slightly improvement in the sensitivity of 72.5 μC/(Gyair cm²) is seen in another 1 D (DMEDA) BiI₅ detector where DMEDA refers to N, N’-dimethylthanediamine. The increase in sensitivity is due to application of high electric field. [35-36]. Zero-dimensional bismuth-based detector material MA₃Bi₂I₉ is catching attention due to extraordinary performance as X-ray detector. The
reported values of sensitivity and LoD are $1 \times 10^4 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ and $0.62 \, \text{ηGyair}/\text{s}$ which surpasses all the achieved results reported till date of all perovskite detectors. The low value of LoD of MA$_3$Bi$_2$I$_6$ makes it viable for real time X-ray detection [37].

Thus, from above information it is evident that lead based perovskites have relatively higher sensitivity in comparison to Bismuth based perovskites. However, 0 D bismuth based perovskite detector exhibited extraordinarily high sensitivity and extremely low LoD. The other significant characteristic properties of 0 D perovskite are less ion migration resulting into minimal dark current and stability of detector in terms of continuous exposure of X-rays [18, 38].

5.3. Lead based polycrystalline perovskites

Polycrystalline thick perovskite crystals of MAPbI$_3$ developed by isostatic-pressing method were reported by Shrestha et al. with significant sensitivity of $1 \times 10^4 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ but with large value of dark current [39]. To tackle high dark current, efforts to arrest ion migration and better charge collection efficiency resulted in new perovskite material synthesis. Kim et al. reported $830 \, \text{μm}$ thick MAPbI$_3$ polycrystalline detector exhibiting high order sensitivity of $1.1 \times 10^4 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ making it practically viable but with poor spatial resolution making it unsuitable as detector material [4]. Cs-MA-FA, a $450 \, \text{ηm}$ thick mixed cation perovskite was reported with sensitivities of $3.7 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ under no bias condition which rose to $39.5 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ under $0.4 \, \text{V}$ reverse bias [40]. A $3.7 \, \text{μm}$ thick flexible X-ray detector Cs$_{0.1}\text{FA}_{0.75}\text{MA}_{0.15}\text{PbBr}_{0.5}\text{I}_{2.5}$ was reported with sensitivities of $33.5 \, \text{μC}/(\text{Gyaircm}^2)$ but again with detrimentally large values of dark current [41].

By using dissolution and recrystallization process, a $18 \, \text{μm}$ thick CsPbBr$_3$ polycrystalline film was grown presenting sensitivity and LoD of $1700 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ and $53 \, 0.62 \, \text{ηGyair}/\text{s}$ respectively [42]. Higher sensitivity of the order of $11840 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ was reported for CsPbBr$_3$ large area and thick crystals fabricated by using ultrasonic assisted mist deposition method. Thus, novel synthesis techniques were used to get the desired detector performance [43]. Quasi-monocrystalline $240 \, \text{μm}$ thick CsPbBr$_3$ was obtained by hot pressing CsPbBr$_3$ powders using slow cooling rate. It exhibited sensitivity and LoD of $55684 \, \text{μC}/(\text{Gy}\text{air}\text{cm}^2)$ and $4150 \, \text{ηGyair}/\text{s}$ for $5 \, \text{V/mm}$ applied electric field [44]. This detector material showed drastic changes in sensitivity and LoD values with lowering of applied electric field making it inappropriate as a detector material for medical imaging.

5.4. Lead free polycrystalline perovskites

Less work is reported for this class of perovskites. Cs$_2$AgBiBr$_6$-PVA (polyvinyl alcohol) is a perovskite polymer composite having good morphology exhibited sensitivity of $40 \, \text{μC}/(\text{Gyaircm}^2)$ at high applied voltage of $400 \, \text{V}$ [45]. Polycrystalline Cs$_2$AgBiBr$_6$ obtained from its single crystal by using modified isostatic-pressing method detector sensitivity and LoD of $10 \, \text{μC}/(\text{Gyaircm}^2)$ for applied field of $20\,\text{V/mm}$ and $95.3 \, \text{ηGyair}/\text{s}$ [46]. The poor crystal quality has resulted in lower sensitivity which is much smaller as compared to valued achieved in its single crystal form [16]. Another polycrystalline detector material reported was Cs$_2$TeI$_6$ of $25 \, \text{μm}$ thickness having appreciable attenuation coefficient and good morphology exhibiting detector sensitivity of $19.2 \, \text{μC}/(\text{Gyaircm}^2)$ at $40 \, \text{V/mm}$ applied electric field [47-48].

6. Advantages and disadvantages of reported perovskites as a detector material

Owing to absence of grain boundaries, fewer defects and longer charge carrier lifetime, single crystal perovskites exhibit remarkable detection performance. From the reported data it is apparent that lead perovskites have higher sensitivity as compared to lead free counterpart due to low μτ values. However, due to high bulk resistivity resulting in low dark current achieving low LoD makes lead free perovskites suitable as detector material even with moderate sensitivity considering environmental concerns.
regarding lead toxicity. Zero-dimensional bismuth-based perovskites even removes this limitation of low sensitivity as the remarkable sensitivities and LoD values are achieved along with good operational stability over long runs of X-ray exposures [38]. The main limitations associated with single crystal perovskites is the growth of bigger crystals, slicing them to the required thickness for integration with electronic backplane for commercial usage and interfacial charge blocking material deposition technique for both sides of a single crystal for enabling high electric field application.

Biggest advantage of polycrystalline over single crystal perovskites is deposition over large area resulting into direct integration with backplanes of electronic readouts for realizing real time X-ray imaging. Another major advantage is that the charge transport layers can be assembled at both the sides of a polycrystalline perovskites allowing application of high electric field resulting into good CCE for thick crystals and promoting pixel arrays dimensions which are commercially viable as cross talks between neighboring pixels is completely eliminated. The disadvantage with polycrystalline perovskites is high values of dark current due to leakage of charge carriers through interfacial energy barriers at high electric fields [49]. Another disadvantage with polycrystalline perovskites is difficulty in maintaining uniformity in sub millimeter thick films as else it leads to varied pixel to pixel sensitivity. Synthesis of perovskite films under harsh conditions like high temperature and pressure hinders its integration with electronic readouts. Very few polycrystalline lead-free perovskites results are reported to figure out any concrete opinion about its viability as a commercial detector material for X-ray imaging.

7. Challenges and future scope
From the exhaustive study of all the results reported for novel perovskite as a detector material it is inevitable that it holds a bright future due to its excellent properties. However, before their commercialization, more efforts are needed to take up challenges to improve its detection performance for X-ray imaging.

The unacceptable values of large dark current in comparison to the requirement of 0.1 nA/cm² is an open challenge for ensuring low radiation dose for medical imaging. It is proposed through all the reported literature on this aspect that, the manipulation of intrinsic properties is required through efficient engineered synthesis rout to suppress charge carrier concentration, defects and traps to mitigate ion migration and high intrinsic resistance of the synthesized perovskite. Interfacial engineering is required to reduce interfacial lattice strain produced due to lattice mismatch where interfacial recombination occurs and through device interface engineering, carrier injection from electrodes is reduced to ultimately achieve reduction in the dark current without affecting the sensitivity. Thus, further exploration of more efficient growth techniques for large area and high-quality crystals and understanding of deep mechanism of self-doping and defect states is now required.

Scalability is a major issue as till date a patterned array of only 30cm² single crystalline perovskite crystal is prepared by merging epitaxially grown small crystals [50] whereas for a real time imaging million of pixel detector are required. For polycrystalline pervoskites, maintaining homogeneity throughout the sub-millimeter thick film is a biggest challenge. Till date single pixel detector measurements are reported so up-scaling, integration with electronic readout panel and then other features like special resolution, imaging lag needs to be investigated in future [51].

In comparison to the conventional X-ray detector, stability is a measure concern as majority of the reported perovskite materials degrade after their exposure to heat or moisture, strong electric fields as well as with longer duration of X-ray irradiation. It remains to be seen how these factors affect environment stability of these perovskite detectors as they will be encapsulated by the X-ray absorbing material.

Although lead free perovskite detectors are reported but their performance is limited which needs to be improved as it holds the future of nontoxic detection of X-rays.
8. References

[1] Lin, E C Radiation risk from medical imaging 2010 Mayo Clin. Proc. 85 1142–1146
[2] Rowlands J A Material change for X-ray detectors 2017 Nature 550 47-48
[3] Chen Q, Wu J, Ou X, et al. All-inorganic perovskite nanocrystal scintillators 2018 Nature 561 88-93
[4] Kim Y C, Kim K H, Son DY, et al. Printible organometallic perovskite enables large-area, low-dose X-ray imaging 2017 Nature 550 87-91
[5] Zhou F, Li Z, Lan W, Wang Q, Ding L and Jin Z. Halide Perovskite, a potential scintillator for X-ray detection 2020 Small Methods 4 2000506
[6] Cao F, Yu D, Ma W, et al. Shining emitter in a stub: host Design of halide Perovskite Scintillators for X-ray imaging from commercial concept 2020 ACS Nano 14 5183-5193
[7] Zhuge F, Luo P and Zhai T. Lead-free perovskites for X-ray detecting 2017 Sci Bull. 62 1491-1493
[8] Åslund M, Fredenberg E, Telman M and Danielsson M. Detectors for the future of X-ray imaging 2010 Radiat Prot Dosimetry 139 327-333
[9] Bai Y, Xiao S, Hu C, et al. Dimensional engineering of a graded 3D–2D halide perovskite interface enables ultrahigh $V_{oc}$ enhanced stability in the p–n photovoltaics 2017 Adv Energy Mater. 7 1701038
[32] Zhang T, Hu C and Yang S Ion migration: a “Double-Edged Sword” for halide-PeroSivite-based electronic devices 2020 Small Methods 4 1900552

[33] Xu Z, Liu X, Li Y, et al. Exploring Lead-free hybrid double perovskite crystals of (Ba)2CsAgBiBr7 with large mobility- lifetime product toward X-ray detection 2019 Angew Chem Int Ed. 58 15757-15761

[34] Zhuang R, Wang X, Ma W, et al. Highly sensitive X-ray detector made of layered perovskite-like (NH4)2Bi4I15 Single crystal with anisotropic response 2019 Nat Photonics 13 602-608

[35] Tao K, Li Y, Ji C, et al. A lead-free hybrid iodide with quantitative response to X-ray radiation. 2019 Chem Mater 31 5927–5932

[36] Yao L, Niu G, Yin L, et al. Bismuth halide perovskites derivatives for direct X-ray detection. 2020 J Mater Chem C 8 1239-1243

[37] Zheng X, Zhao W, Wang P, et al. Ultrasensitive and stable X-ray detection using zero-dimensional lead-free perovskites 2020 J Energy Chem 49 299-306

[38] Te S, Zhao W, Xin D, et al. Robust fabrication of hybrid Lead-free perovskite pellets for subpixel X-ray detectors with low detection limit 2020 Adv Mater. 32 2001981

[39] Shrestha S, Fischer R, Matt G J, et al. High-performance direct conversion X-ray detectors based on sintered hybrid lead triiodide perovskite wafers 2017 Nat Photonics 11 436-440

[40] Basiricò L, Senanayak SP, Ciavatti A, Abdi-Jalabi M, Fraboni B and Sirringhaus H Detection of X-rays by solution-processed cesium-containing mixed triple cation perovskite thin films 2019 Adv Funct Mater 29 1902346

[41] Mescher H, Schackmar F, Eggers H, et al. Flexible inkjet-printed triple cation perovskite X-ray detectors 2020 ACS Appl Mater Interfaces 12 15774-15784

[42] Gou Z, Huanglong S, Ke W, et al. Self-powered X-ray detector based on all-inorganic perovskite thick film with high sensitivity under low dose rate 2019 Phys Status Solidi RRL 13 1900094

[43] Haruta Y, Ikenoue T, Miyake M and Hirato T. Fabrication of CsPbBr3 thick films by using a mist deposition method for highly sensitive X-ray detection 2020 JPhysCood Adv. 5 395 401

[44] Haruta Y, Ikenoue T, Miyake M and Hirato T. Fabrication of (101)-oriented CsPbBr3 thick films with high carrier mobility using a mist deposition method. 2019 Appl Phys Express 12 085505

[45] Li H, Shan X, Neu J N, et al. Lead-free halide double perovskite-polymer composites for flexible X-ray imaging 2018 J Mater Chem C 6 11961-11967

[46] Yang B, Pan W, Wu H, et al. Heteroepitaxial passivation of CaAgBiBr6 wafers with suppressed ionic migration for X-ray imaging 2019 Nat Commun 10 1989

[47] Xu Y, Jiao B, Song TB, et al. Zero-dimensional Cs2TeI6 perovskite: solution-processed thick films with high X-ray sensitivity 2019 ACS Photonics 6 196-203

[48] Guo J, Xu Y, Yang W, et al. Morphology of X-ray detector Cs2TeI6 perovskite thick films grown by electrospray method 2019 J Mater Chem C 7 8712-8719

[49] Luo D, Zou T, Yang W, et al. Low-dimensional contact layers for enhanced perovskite photodiodes 2020 Adv Funct Mater 30 2001692

[50] Lei Y, Chen Y, Zhang R, et al. A fabrication process for flexible single-crystal perovskite devices 2020 Nature 583 790-795

[51] Xiuwen Xu X, Qian W et al. Halide perovskites: A dark horse for direct X-ray imaging 2020 EcoMat 2 12064