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Impact of two diammonium cations on the structure and photophysics of layered Sn-based perovskites†

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Layered metal-halide perovskites have shown great promise for applications in optoelectronic devices, where a large number of suitable organic cations give the opportunity to tune their structural and optical properties. However, especially for Sn-based perovskites, a detailed understanding of the impact of the cation on the crystalline structure is still missing. By employing two cations, 2,2'-oxybis(ethylammonium) (OBE) and 2,2'-(ethylenedioxy)bis(ethylammonium) (EDBE), we obtain a planar $\langle 100 \rangle$ and a corrugated $\langle 110 \rangle$ -oriented perovskite, respectively, where the hydrogen bonding between the EDBE cations stabilises the corrugated structure. OBESnI₄ exhibits a relatively narrow band gap and photoluminescence bands compared to EDBESnI₄. In-depth analysis shows that the markedly different optical properties of the two compounds have an extrinsic origin. Interestingly, thin films of OBESnI₄ can be obtained both in black and red colours. This effect is attributed to a second crystalline phase that can be obtained by processing the thin films at 100 °C. Our work highlights that the design of the crystal structure as obtained by ligand chemistry can be used to obtain the desired optical properties, whereas thin film engineering can result in multiple crystalline phases unique to Sn-based perovskites.

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10th Anniversary Statement written by Maria A. Loi

I was a young post-doctoral fellow when, at that time Journal Material Chemistry, published my work on the photophysics and solar cells of phthalocyanine-fulleropyrrolidine dyads and devoted the cover to the article. From that moment, I have been always considering the Journal Material Chemistry family, and especially Journal Material Chemistry C, as the perfect avenue for multidisciplinary works where new materials, deep spectroscopical investigation and even device investigations can be presented to a multifaceted community. The interdisciplinarity, breadth and plasticity in embracing the newest topics emerging from the community are the characteristics, that in my opinion, determine the continuous success of Journal Material Chemistry C. Now Journal Material Chemistry C is 10 years old but does not give any signs of ageing or rigidity. As modern science is highly accelerated, this is a merit of the team running the journal. Happy birthday to Journal Material Chemistry C, wishing it many years of youth ahead.

Introduction

Layered metal-halide perovskites are at the forefront of emerging light-emitting materials and already have proven their invaluable contributions to photovoltaic devices and light-emitting diodes.^{1–3} This class of materials offers a vast amount of different crystal structures due to its flexibility to accommodate a large number of organic cations.^{2,4} Of the large organic cations used, most reports focus on monoammonium cations

such as butylammonium and phenethylammonium. Recently, diammonium cations are gaining momentum because of the hope to obtain different functionalities, and the power conversion efficiency of solar cells is increasing using diammonium cations.⁵ These structures show exotic phenomena, enabling the design of materials that emit either narrow or broad photoluminescence (PL) bands.^{6,7}

The origin of the optical properties of layered perovskites lies in the connectivity of the inorganic framework, where we can distinguish two main types: the $\langle 100 \rangle$ - and the $\langle 110 \rangle$ -oriented perovskites.^{8,9} These structures can be envisioned as slices of the cubic perovskite structure along the $\langle 100 \rangle$ or the $\langle 110 \rangle$ crystallographic planes and are separated by organic cations. For this reason, the $\langle 100 \rangle$ -type consists of flat layers of corner-shared inorganic octahedra with metal-halide-metal

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Layered Sn-based perovskites have shown intriguing structural flexibility where the same organic cations result in two distinct crystalline structures.^{15–17} For example, Mao *et al.* found that the kinetic product of the synthesis in hydroiodic acid formed red crystals of the $\langle 110 \rangle$ type, while the thermodynamically stable black crystals crystallised in the $\langle 100 \rangle$ type.¹⁵ However, thus far, only structural isomers were found for single crystals, yet applying them in thin films could open new pathways to tune the optoelectronic properties of these materials in device applications.

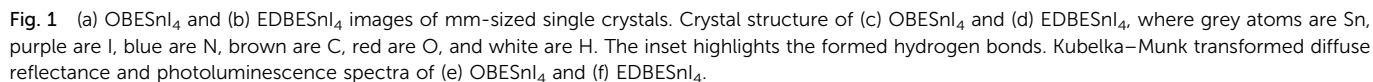
In this report, we address the need to comprehend the structure and optical properties of layered Sn-based perovskites, where we systematically investigate two diammonium organic cations that vary in length: 2,2'-oxybis(ethylammonium) (OBE) and 2,2'-(methylenedioxy)bis(ethylammonium) (EDBE). A marked contrast is obtained as OBESnI₄ forms a $\langle 100 \rangle$ -oriented perovskite with relatively narrow emission peaks compared to the broad emission obtained with the $\langle 110 \rangle$ -oriented EDBESnI₄. We show through temperature and power-dependent photoluminescence measurements that the low-energy emission in these compounds is extrinsic in nature. These compositions were successfully fabricated into thin films by a blade-coating deposition process. Furthermore, we reveal that the annealing temperature of the thin films of OBESnI₄ drastically changes the colour of the films from black to red. This change in colour originates from a new crystalline phase marking the structural and optical flexibility of layered Sn-based perovskites.

We synthesised mm-sized single crystals of OBESnI₄ and EDBESnI₄ using an Anti-Solvent Vapour Crystallisation method,

To further investigate the impact of the structure on the optical properties, we measured the Kubelka–Munk transformed diffuse reflectance $F(R)$ and PL spectra of the two compounds at room temperature (Fig. 1(e and f)). In line with the colour difference, EDBESnI₄ shows an absorption peak at 2.36 eV, a much higher value than the 1.99 eV for OBESnI₄. This large difference can be readily understood by considering the octahedral connectivity and the band edge orbitals of the compounds. Due to the antibonding character of both the valence (Sn 5s and I 5p) and conduction (Sn 5p and I 5p) band edge, the Sn–I–Sn angle has a major impact on the electronic and optical band gap.¹⁸ The close to 90° angles between octahedra in EDBESnI₄ decrease the orbital overlap, resulting in a widening of the band gap compared to OBESnI₄.¹⁶

The PL spectra of the two compounds exhibit different features. The PL of OBESnI₄ shows two peaks at 1.90 eV and 1.96 eV relatively close to the absorption edge. The relative intensity of the two peaks varies across the samples (Fig. S1(a), ESI[†]), and the high-energy peak becomes the dominant emission at high excitation fluences as the low-energy emission saturates (Fig. S1(b), ESI[†]), which suggests that the low-energy emission has an extrinsic origin, *i.e.* emission from defects. The PL of EDBESnI₄ shows a broad emission band at 1.61 eV with a Stokes shift of ≈ 700 meV, the first report on such a Sn-based system. Interestingly, the related Pb-based EDBEPbI₄ shows a much narrower emission that shows features closely resembling OBESnI₄,^{11,19} while broad emissions are more commonly observed for bromide and chloride containing systems.²⁰ To test the stability of our compounds, we measured the PL spectra by continuously illuminating the samples with our laser for 10 minutes in a nitrogen environment, as shown in Fig. S7 (ESI[†]). Only minor fluctuations in intensity are observed, indicating that our Sn-based layered structures show good stability.

To further understand the optical properties of these systems, temperature-dependent PL spectra of the single crystals were measured and are shown in Fig. 2(a). We will start the discussion with OBESnI₄, for which three interesting observations



For EDBESn₄, as shown in Fig. 2(a), two evident PL peaks are seen when the temperature is lowered. We note that others only observed a single broad emission band in related Pb-based systems down to 150 K.¹¹ The PL peaks, approximately at 1.4 eV and 1.8 eV, show a non-monotonic increase of the intensity upon decreasing the temperature (Fig. S4, ESI[†]), where the intensity of the peaks at 1.4 eV and 1.8 eV maximise at 30 K and 80 K, respectively. In addition, the PL lifetime of the peaks extends into the μ s range at cryogenic temperatures (Fig. S5, ESI[†]). These observations closely resemble the intricate interplay of low-energy PL bands we reported on layered Pb-based perovskites and suggest that the main contribution to the emission stems from defects.²⁶ This view is supported by the sublinear dependence of the PL intensity at 4.5 K, as shown in



Fig. 2(c). We note that at high fluences additional resonances are observed at approximately 2.3 eV, indicated by the arrow in Fig. 2(c).

The normalised absorbance spectra of the films are shown in Fig. 3(b). The absorbance peak of the 70 °C film at 1.98 eV matches well with the Kubelka–Munk transformed spectra

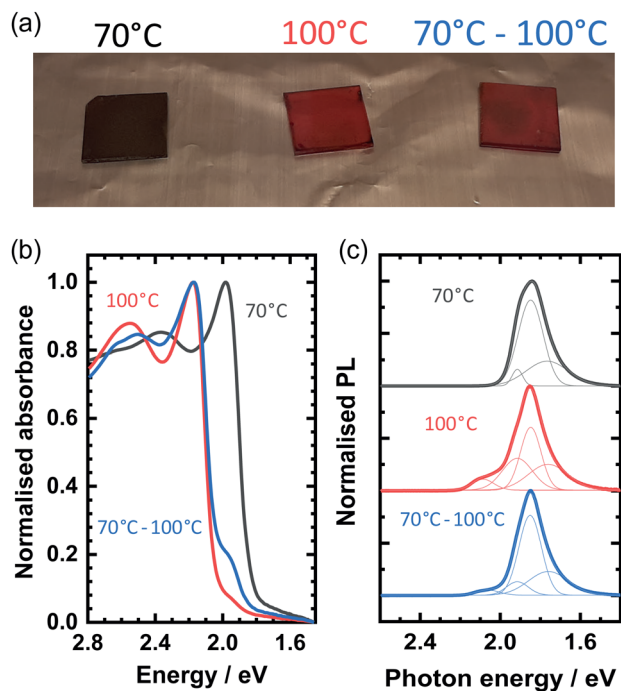


Fig. 3 (a) Optical image of OBESnI₄ thin films processed at 70 °C, 100 °C, and 70–100 °C. (b) Absorbance spectra and (c) photoluminescence spectra of the thin films.

shown previously in Fig. 1(e). The close correspondence of the absorbance and the measured powder X-ray diffraction patterns (Fig. S6, ESI[†]) to the patterns obtained from single crystals suggests that we obtained a uniform film of OBESn₄ in the *P*2₁/*c* phase. In contrast, the other two films have the dominant absorbance peak at 2.17 eV, where the peak at 1.98 eV manifests as a shoulder in the spectra. The presence of both of these peaks suggests that a mixture of two crystalline phases is present, where the unidentified second phase causes the appearance of the high-energy absorbance peak. Powder X-ray diffraction patterns confirm the presence of an additional crystalline phase as new reflections are observed in the 100 °C and the 70–100 °C film, which cannot be ascribed to the single crystal structure. Unfortunately, we are not able to identify the crystal structure of this phase with these data and hypothesise that a change in the octahedral connectivity or the occurrence of a corrugated structure could be the origin of this high-energy absorbance.^{16,30}

This view is further supported by the photoluminescence spectra as shown in Fig. 3(c). The PL spectrum of the 70 °C film can be fitted by three Gaussian peaks centred at 1.91 eV, 1.85 eV and 1.77 eV, and shows the same spectral shape as seen for the single crystal spectrum, albeit slightly red-shifted by 50 meV. The 100 °C and the 70–100 °C film show an additional emission at approximately 2.1 eV, which matches well with an emission with a small Stokes shift from the high-energy absorbance peak. The lower intensity of the 2.1 eV PL peak could be explained by photon reabsorption of the low-energy $P2_1/c$ phase as its energy overlaps with the absorbance spectrum.

To identify the spatial extent of the two different phases, we performed confocal laser scanning microscopy on the two films as shown in Fig. 4. We investigated two spectral regions: <1.91 eV belonging to the emission from the P_{21}/c phase, and >1.91 eV predominantly corresponding to the unidentified phase. Fig. 4(a) shows the PL map below 1.91 eV of the 70 °C film. The film is composed of large crystallites (>100 μm), typical for doctor-blade deposition. As expected, above 1.91 eV (Fig. 4(d)), no emission is seen from a different phase. This picture drastically changes for the 100 °C (Fig. 4(b and e)) and the 70–100 °C (Fig. 4(c and f)) films. Here, the coverage of the P_{21}/c phase is reduced in favour of the unidentified crystal phase, where a higher processing temperature of 100 °C for the doctor-blade stage further decreases the fractional coverage of the P_{21}/c phase compared to a temperature of 70 °C. The images of the two spectral regions are complementary, highlighting that the two phases crystallised separately. In addition, the needle-like crystallites of the unidentified phase suggest a significant change in the unit cell compared to the P_{21}/c phase.

The various transitions discussed above are different from earlier observations on similar systems. Thin films based on 1,4-phenylenedimethan ammonium cations showed grain-specific photoluminescence with an energy separation of 12 meV without any sign of a different crystal phase,³¹ while we report a much larger 200 meV difference concomitant with the appearance of a new crystalline phase. Structural diversity in tin-iodide perovskites has been observed before in the synthesis of powders and single crystals, where structures could be stabilised by a kinetically controlled synthesis, differing from their thermodynamically stable structures.^{16,32} More specifically, Mao *et al.* reported a Sn-based perovskite using histammonium that could be stabilised both in a thermodynamically stable black phase and kinetically trapped red phase.¹⁵ This colour change originated from a change from a $\langle 100 \rangle$ to a $\langle 110 \rangle$ perovskite, where the band gap widened by 200 meV, similar to our sample. Hence, we believe that the elevated temperature of 100 °C for our thin films is sufficient to favour a structure that is in a kinetically trapped state. Considering the similar observations for OBE compared to EDBE and histammonium, we hypothesise that the kinetically formed phase might be related to a $\langle 110 \rangle$ perovskite. This observation has broader implications for the solar cell community as the processing temperature can have a drastic impact on the properties of the film and an increasing number of reports present new organic cations.

Conclusions

In conclusion, layered tin-iodide perovskite single crystals were synthesised using two different diammonium cations (OBE and EDBE), which only differ in length by two carbon and one oxygen atom. This difference has a profound impact on the structure. The shorter ODE formed a $\langle 100 \rangle$ -oriented perovskite, while the larger EDBE formed a corrugated $\langle 110 \rangle$ -oriented perovskite

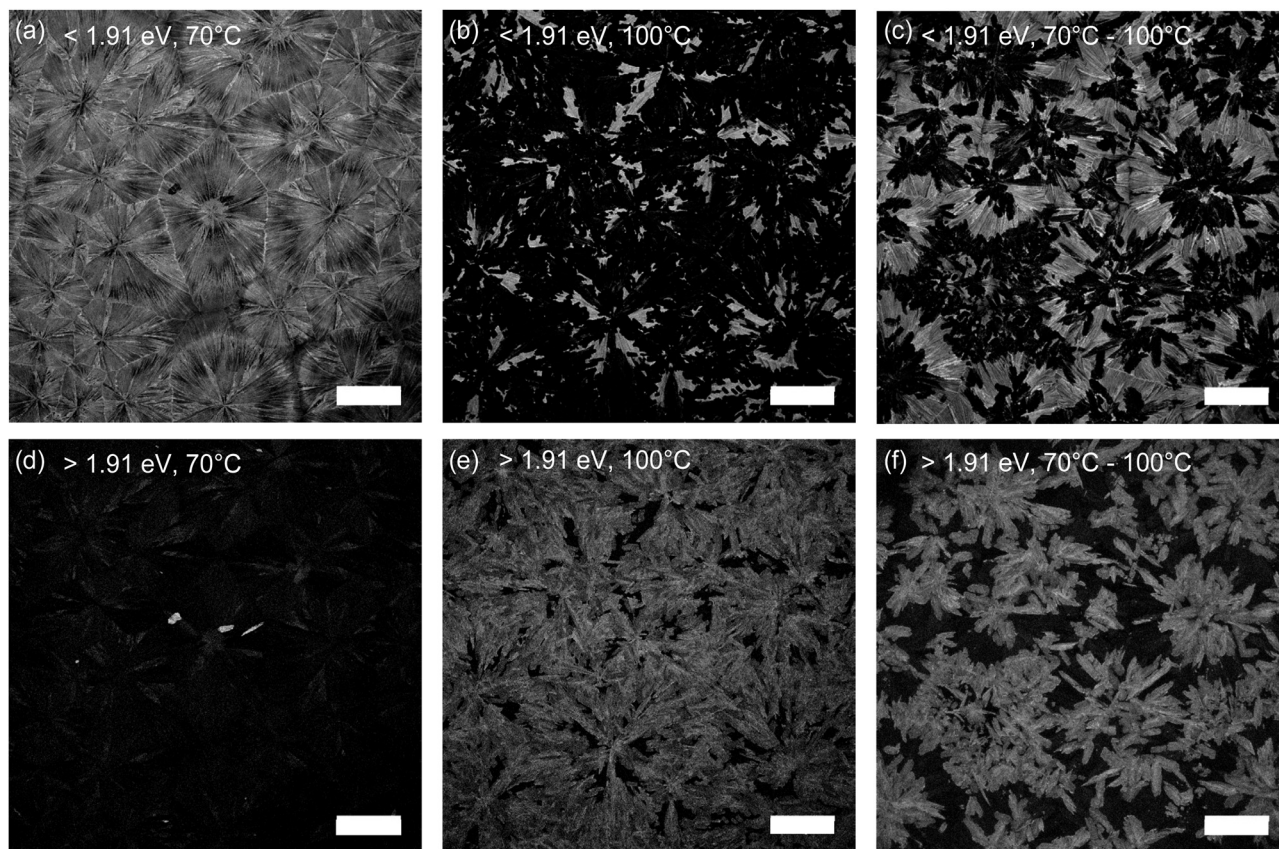


Fig. 4 Confocal photoluminescence micrographs in the range < 1.91 eV (a–c) and > 1.91 eV (d–f) for OBESnI_4 thin films processed at 70°C , 100°C , and 70 – 100°C . Scale bar is $100\ \mu\text{m}$.

as additional hydrogen bonds were formed between neighbouring organic cations. We investigated the optical properties of the new compounds, where OBESnI_4 showed two photoluminescence peaks of which the low-energy emission was thermally activated. In contrast, EDBE showed a broad emission band with multiple emissive states at low temperatures, where its fluence-dependent behaviour suggests an origin from defects. Strikingly, thin films of OBESnI_4 showed a contrasting change of colour from black to red when the processing temperature was increased from 70°C to 100°C . The red colour stems from a new unidentified crystal phase that was well-separated from the black phase. With this work, we clarify how intercation interactions can result in two different types of layered perovskites with distinct optical properties, and we highlight that the processing conditions, typically used for device fabrication, have a drastic impact on the optical and structural properties of our newly reported compound.

Author contributions

E. K. T.: conceptualisation, investigation, writing – original draft N. A.: investigation, resources L. C.: resources G. R. B.: supervision, writing – review and editing, funding acquisition M. A. L. conceptualisation, supervision, writing – review and editing, funding acquisition.

Conflicts of interest

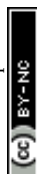
There are no conflicts to declare.

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