Journal of Materials Chemistry A



View Article Online

PAPER

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Cite this: DOI: 10.1039/d0ta04155f

Received 18th April 2020 Accepted 20th June 2020 DOI: 10.1039/d0ta04155f rsc.li/materials-a

1. Introduction

During the past decade, the scientific community has witnessed a revival of lead halide perovskites. The primary interest of these materials is currently driven by their high photovoltaic efficiency, which by now exceeds 25% and may lead to high performance solar cells.¹⁻³ These materials are also promising for applications as light emitting diodes (LEDs) and photodetectors.⁴ Their general chemical formula is APbX₃, where X = I,

Phase transitions, screening and dielectric response of CsPbBr $_{3}$ †

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Cesium-lead-bromide (CsPbBr₃) is the simplest all inorganic halide perovskite. It serves as a reference material for understanding the exceptional solar cell properties of the organic-inorganic hybrid halide perovskites and is itself discussed as an alternative absorber material. Broadband dielectric spectroscopy has proven to yield an in depth understanding of charge screening mechanisms in the halide solar cell absorbers based on methylammonium and modifications hereof. For a deeper understanding of charge carrier screening, we have investigated CsPbBr₃ across wide temperature (120 K-450 K) and frequency ranges. Besides the two known phase transitions at 403 K and 361 K, the dielectric data show another anomaly around 220 K, which can be interpreted as another phase transition. XRD and EPR studies confirm the presence of this anomaly, but Raman scattering spectra do not show any lattice anomalies in the vicinity of 220 K. This additional anomaly is of first order character (different transition temperatures upon cooling and heating) but hardly influences the lattice dynamics. Our broadband dielectric investigations of CsPbBr₃ display the same microwave limit permittivity as for MAPbX₃ ($\varepsilon_r \approx 30$, X = Cl, Br, I, MA = CH₃NH₃⁺) but do not afford a second permittivity relaxation up to this frequency. Our prior assignment of the second contribution in the methylammonium compounds being due to the relaxation dynamics of the methylammonium ion as a dipole is herewith proven. Nevertheless, CsPbBr₃ shows large charge carrier screening up to very high frequencies which can still play a vital role in charge carrier dynamics and exciton behaviour in this material as well.

> Cl, Br, and A is a monovalent inorganic or organic cation. The Asite cation is located in a cuboctahedron cage formed by PbX_6 octahedra. The most popular compositions amongst this family of materials are the methylammonium (MA = $CH_3NH_3^+$), formamidinium (FA = $NH_2CH=NH_2^+$) and cesium (Cs⁺) lead halides.⁵

> The high photovoltaic efficiency of the halide perovskites has been attributed to the effective exciton breakup,⁶ the long lifetime of the generated charge carriers⁷ and the high carrier mobilities.⁷ All these properties are closely related to the features of the dielectric response. The large high frequency (THz) dielectric permittivity is dominated by the relaxation of the PbX₆ sub-lattice. It results in the low exciton binding energy. The dynamics of the MA cations having their proper dipole moment contributes to the large permittivity in the GHz range allowing for an effective screening of defects and the formation of hyperpolarons.⁸ There is still discussion about the necessity of having an organic molecule at the A-site to reach the high photovoltaic efficiencies.^{9,10} CsPbBr₃ photovoltaic cells show an open circuit voltage comparable to MAPbBr₃ cells.⁹ There are several reports showing that all-inorganic CsPbX₃ solar cells can

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ta04155f

exceed the efficiency of around 10%.¹¹⁻¹⁶ The most attractive feature of such solar cells is their stability compared to hybrid halides.^{11,17-19} Both MAPbBr₃ and CsPbBr₃ show similar band-edge carriers dynamics including low carrier trapping rate constants.¹⁰ On the other hand, according to transient photoluminescence and transient infrared spectroscopy studies, the lifetimes of the polarons in CsPbBr₃ are one order of magnitude shorter than in MAPbBr₃.²⁰ Also, the polaron formation time in CsPbBr₃ is more than two times longer as compared to MAPbBr₃.²¹

In general, the dielectric response of materials is strongly connected to their crystalline structure. The studies of structural aspects of phase transitions in lead halide perovskites started several decades ago.^{22–26} In hybrid MAPbX₃ (X = Cl, Br), the high temperature phase is cubic and belongs to the $Pm\bar{3}m$ space group.²⁷ MAPbCl₃ (ref. 27 and 28) and MAPbBr₃ (ref. 29 and 30) undergo transitions from the cubic to the tetragonal *P4/mmm* and *I4/mcm* phases, respectively, and afterwards from the tetragonal to the orthorhombic *Pnma* phase. In MAPbBr₃, an intermediate phase between tetragonal and orthorhombic phases was reported, which was classified as either tetragonal *P4/mmm*²⁷ or incommensurate.³¹

Inorganic CsPb X_3 (X = Cl, Br) perovskites also have the cubic $Pm\bar{3}m$ structure at high temperatures. CsPbCl₃ undergoes three consecutive phase transitions at 320 K, 315 K and 310 K.^{22,24,26} Fujii et al.25 determined the microscopic models of each phase by neutron scattering and showed that the phase transition sequence is cubic $(Pm\bar{3}m)$ -tetragonal (P4/mbm)-orthorhombic (*Cmcm*)-monoclinic $(P2_1/m)$.²⁵ In contrast, only two phase transitions have been reported for CsPbBr₃.²³ One transition takes places at 403 K from a cubic to the tetragonal (P4/mbm) phase, and the second one at 361 K - from the tetragonal to the orthorhombic (Pmbn) phase. A third phase transition has not been reported so far for CsPbBr₃, but, to our knowledge, only data above room temperature are available. All phase transitions in the cesium lead halides are of antidistortive type and occur due to the condensation of the soft mode at the Brillouin zone boundary, *i.e.* they are related to octahedral tilting.²³

There is still a controversy about the nature of the low temperature state of MAPbBr₃. Some reports claim that the lowest symmetry phase is polar,²⁷ which leads to speculations about the ferroelectricity of these compounds. However, the absence of polarization switching, the character of the dielectric anomaly, the results of pyroelectric measurements and Monte Carlo simulations indicate the antipolar nature of this state.^{8,32} The centrosymmetric space group of the cesium lead halides excludes the ferroelectricity, but may allow for antipolar ordering.

It has been argued that local thermal polar fluctuations related to disorder in the PbX₆ sub-lattice might be one of the reasons for the high photovoltaic performance.^{21,33,34} These fluctuations manifest themselves as a central peak in Raman spectra of the cubic and tetragonal phases. It was shown that the orthorhombic phase of CsPbBr₃ has less pronounced disorder than the MAPbX₃ halides.³³

Contrary to the methylammonium lead halides, the cesium analogues are less studied, especially below room temperature. Low frequency dielectric permittivity down to room temperature was measured by Hirotsu *et al.* on CsPbCl₃ crystals.²² They concluded that it does not possess any ferroelectric properties. However, there have not been thorough studies on the broadband dielectric properties of CsPbBr₃ single crystals at different temperatures. A very recent publication by K. Miyata *et al.* reports on room temperature dielectric spectra of CsPbBr₃ in the 10⁶ Hz to 10¹¹ Hz frequency range²⁰ but it lacks the microwave data. The dielectric response is not only important for solar cell applications, but it is relevant for the newly emerging field of triboelectric nanogenerators.^{35–37}

In this work, we report detailed structural, dielectric, Raman, electron paramagnetic resonance (EPR), and differential scanning calorimetry (DSC) studies of a CsPbBr₃ single crystal and powder in a broad temperature range. In particular, we display a very high dielectric constant at high frequencies and reveal a new structural phase transition at 220 K. Since CsPbCl₃ has three phase transitions,^{22,24,26} one would also expect a third transition in CsPbBr₃.

2. Sample preparation and experimental details

CsPbBr₃ single crystals were prepared by a low temperature solution-growth method described by Rakita et al.38 The precursor solution was prepared dissolving stoichiometric amounts of CsBr (Across organics 99.9%) and PbBr2 (Alfa Aesar 98+%) in DMSO (dimethyl sulfoxide, Roth 99.5%) at 323 K at ambient conditions under stirring. After cooling, acetonitrile (analytical grade) was added dropwise to the solution until a permanent solid precipitate was formed. This precipitate (Cs₄PbBr₆) is a secondary product³⁸ that is formed during the reaction and has been removed from the reaction mixture by filtration with a PTFE membrane filter with 0.2 µm size. The filtrate can be used as a precursor solution for crystal growth. The crystal growth was performed by the slow vapor saturation of acetonitrile as antisolvent. For this purpose, the filtered precursor solution was placed in a crystallization flask and covered with a filter paper and a glass Petri dish to control the antisolvent vapor diffusion. The covered crystallization flask was placed inside a bigger crystallization dish containing acetonitrile as the antisolvent. This big crystallization flask was also covered in a similar way as the smaller crystallization flask to maintain the antisolvent atmosphere in the closed system and avoid solvent loss. The crystals were obtained by heating the big crystallization flask at 313 K on a hot plate from two to three days. After 40 hours CsPbBr3 single crystals with approximate size of $1.5 \times 4 \times 1 \text{ mm}^3$ were obtained. Larger crystals with the dimensions ranging from $4 \times 6 \times 2 \text{ mm}^3$ to $6 \times 8 \times 2$ mm³ have been obtained by further growth of the small crystals repeating the following procedure several times: filtration of the "mother" precursor solution plus addition of a small amount of fresh precursor solution and then putting this mixture into the antisolvent atmosphere on the hot plate under the same conditions as described above.

The XRD studies of the grown single crystals are presented in Fig. S1 of the ESI.† The 2θ scan of the single crystal only shows

diffraction peaks from the (101), (202) and (303) planes indicating its single crystal nature. Rietveld analysis (GoF-index 2.8) of the pulverized crystal shows that the obtained data is in good agreement with the crystallographic data of PDF no. 98-009-7851, which corresponds to an orthorhombic crystal structure. No secondary phases can be seen in the XRD spectra, suggesting that the CsPbBr₃ crystals are of good quality without impurities.

Some CsPbBr₃ crystals were reduced into a fine powder and used for X-ray diffraction (XRD) characterization. *In situ* XRD study of the powders was performed using a PANalytical X'Pert MPD PRO diffractometer (Ni-filtered Cu-K α radiation, PIXcel^{1D} detector, and an exposition time corresponding to 2 s per step of 0.02° over the angular range of 10°–70°). The measurements were conducted in Anton Paar chambers HTK 16N and TTK 450 in the temperature ranges of 298–453 K and 298–100 K, respectively. Rietveld refinement of the crystal structure was performed using the FullProf package.³⁹

The powder of CsPbBr₃ doped with paramagnetic Mn^{2+} ions was synthesized according to a previously published procedure⁴⁰ by grinding the reactants in a ball mill (Retsch Ball Mill MM 400) using a grinding jar (10 ml) and a ball (ø10 mm) for 30 min at 25 Hz. The resulting perovskite powder was annealed at 523 K for 5 minutes to remove grinding-induced defects. The amounts of reagents taken into the synthesis were as follows: CsPb_{0.995}Mn_{0.005}Br₃: 212.8 mg CsBr (1 mmol), 1.1 mg MnBr₂ (0.005 mmol), 365.2 mg PbBr₂ (0.995 mmol).

Complex dielectric permittivity was measured in two different frequency bands by two different techniques. A HP4824A LCR meter was used to cover the 20 Hz to 1 MHz frequency range. The sample was placed between two metal plates, and its capacitance and loss tangent $(\tan \delta)$ were measured. The complex dielectric permittivity was calculated according to a flat capacitor model.

An Agilent 8714ET vector network analyzer was used for the experiments in the 1 MHz to 1 GHz frequency range. A coaxial line was connected to the analyzer, and the sample was placed at the end of the coaxial line. The complex reflection coefficient was measured. In order to get accurate results, a so-called "multimode capacitor" model was implemented, which takes into account higher order modes propagating in the vicinity of the sample. Thus, more accurate results can be obtained compared to a simple capacitor model at the end of the coaxial line. Details about the model can be found in the literature.^{41,42}

The temperature during the dielectric spectroscopy experiments was measured using a Keithley Integra 2700 multimeter coupled with a T-type thermocouple or 100 Ω platinum resistor.

The continuous-wave (CW) EPR measurements were performed using a Bruker ELEXSYS E580 EPR spectrometer operating at X-band microwave frequency and equipped with a standard rectangular TE102 cavity. The strength and frequency of the modulating field were 5 G and 100 kHz, respectively. A variable nitrogen temperature control system was used to vary the temperature.

Raman spectra were collected on a Bruker MultiRAM spectrometer. The wavelength of the laser beam was 785 nm (below bandgap 2.34 eV corresponding to 525 nm). The laser power was 250 mW. The experiments were carried out in a backscattering geometry. During Raman scattering measurements the temperature of the samples were changed and maintained using a Linkam FTIR600 temperature-controlled stage.

Calorimetric measurements were performed using a differential scanning calorimeter (Netzsch, DSC 204 Phoenix). The sample was placed in gas tight aluminium crucibles to avoid any environmental perturbation. Temperature was changed in the range 130 K to 480 K with a rate of 10 K min⁻¹. The measurement was performed on a single crystal of 9 mg mass in air.

3. Results and discussion

Fig. 1 presents the DSC data on a CsPbBr₃ single crystal. Several anomalies can be seen in the graph. The most evident anomaly is due to the phase transition slightly above 400 K from the cubic to the tetragonal phase. A much weaker anomaly is observed around 360 K, which indicates another phase transition to the orthorhombic phase. The temperatures of these transitions are consistent with the structural analysis data published by Hirotsu *et al.*²³ However, there is another broad anomaly at around 220 K, which has not been reported in literature. Note that one of the previous studies showed that some changes of the light absorption around room temperature is due to an apparatus artifact.

Fig. 2a shows the temperature dependence of the real part of the dielectric permittivity measured at a frequency of 100 kHz. Step like anomalies corresponding to the cubic-tetragonal (~410 K) and tetragonal-orthorhombic (~360 K) transitions can be observed on cooling. A third anomaly at around 220 K is also visible, which can be seen more clearly in the inset of Fig. 2a. This anomaly is accompanied by a thermal hysteresis in accordance with the DSC data. Fig. 2b shows the temperature dependences of the real part of the dielectric permittivity measured at different frequencies. A strong dielectric dispersion is observed, which is related to the electronic conductivity of the crystal.



Fig. 1 Temperature dependence of the heat flow of $CsPbBr_3$ single crystal. Endothermic processes are shown upwards. The arrows represent the phase transition points.



Fig. 2 (a) Temperature dependence of the real part of the dielectric permittivity of the CsPbBr₃ single crystal measured at 100 kHz on cooling. The inset shows the curves measured on both heating and cooling. (b) Temperature dependences of the real part of the dielectric permittivity measured at different frequencies.

Fig. 3 presents the frequency dependences of the complex dielectric permittivity of the CsPbBr₃ single crystal. It is evident that there is no dispersion at microwave frequencies even in the vicinity of the phase transitions. The situation differs from MAPbX₃, where the mean relaxation time diverges in the vicinity of the tetragonal–orthorhombic phase transition (refer to Anusca *et al.*⁸ and Miyata *et al.*²⁰). This suggests that the critical slowing down is absent in this material. Unfortunately, our single crystals were too small for dielectric measurements at higher frequencies. The data above 1 MHz yield a dielectric permittivity, $\varepsilon_{\infty} \sim 27$, having the same magnitude as the phonon contribution to the dielectric constant in the methylammonium lead halides.⁸ This assumption is in agreement with the recent



Fig. 3 Frequency dependences of the complex dielectric permittivity of a CsPbBr₃ single crystal at different temperatures.

paper by K. Miyata *et al.*, who reported on the absence of the dielectric dispersion in the frequency range of 10^8 Hz to 10^{11} Hz (ref. 20) at room temperature. Yaffe *et al.*³³ concluded that dynamic disorder and the central peak in all-inorganic and hybrid halides are very similar. Dielectric spectroscopy is capable of probing polar fluctuations directly. Our results show that the relaxation at microwave frequencies is absent in all-inorganic halides as opposed to the hybrid lead halides. This is an indication that the polar fluctuations are weaker in CsPbBr₃. The reason behind the difference is the absence of a rotational movement of the Cs⁺ ion at the A-site which is different from the MA⁺-ion dipole which does rotate.

Let us discuss this last fact with respect to the outstanding solar cell performance of certain members of this class of materials. A high dielectric constant that acts on the unit cell level permits to lower the exciton binding energy which is very simply given by Coulomb's law. The interaction force linearly drops with the local dielectric constant. Thus, a high value of ε_r will directly yield a dissociation level on the order of kT and circumvents the problem of too tight binding of the charge carriers within the exciton. Furthermore, polarons which are electronic states coupling to the phonon bath, will have a considerably different effective cross section when moving through the lattice. Similarly, point defects (be they electronic or ionic of nature) are screened as well yielding a very small cross section as well. As long as the additional energy of the polaron relaxation around an electron (or hole) is low enough not to generate a small polaron (meaning it generates its proper band gap state), this is advantageous for the mobility and lifetime of the charge carriers in the halide perovskites. For a further discussion hereon, please refer to ref. 8. Apparently, this is optimal for MAPbI₃ and dual or triple cation versions hereof including Cs.

To explore the low temperature anomaly at 220–230 K more thoroughly, CW EPR experiments on Mn-doped CsPbBr₃ were performed. Furthermore, single crystals were also investigated by Raman spectroscopy. These two methods probe the local environment of the lattice revealing more details about the low temperature anomaly.

Fig. 4a presents CW EPR spectra of the Mn-doped CsPbBr₃ powder taken at different temperatures. The spectra are typical for the Mn²⁺ ions having S = 5/2 electron and I = 5/2 nuclear spins.⁴⁴ The observed hyperfine splitting of the central EPR transition is 234 MHz, which is typical for the Mn–Br bond.⁴⁴ This indicates that Mn²⁺ substituted Pb²⁺ ions and forms MnBr₆ octahedra.

In addition to the hyperfine splitting of the central transition, the outer fine structure lines are also partially resolved (indicated by the arrows in Fig. 4a). We used these lines to roughly estimate the temperature dependence of the fine structure, which is presented in Fig. 4b. A clear onset of the anomalous behavior of the fine structure is observed at 200 K indicating local structural changes of the Mn^{2+} ion environment. The splitting becomes noticeably smaller upon cooling, which is a rather unusual behavior.

Fig. 5 presents temperature dependent Raman spectra of the CsPbBr₃ single crystal. Different representation of Raman

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Fig. 4 (a) Temperature dependent CW EPR spectra of $CsPbBr_3:Mn$. The arrows indicate fine structure lines, which were used to estimate the temperature dependence of the fine structure splitting presented in (b).

spectra can be found in the Fig. S4 and S5 of the ESI.† The parent cubic phase (space group $Pm\bar{3}m$) is not supposed to have Raman active modes, but they are clearly observable at 450 K (40

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K above the phase transition temperature). Such a situation is quite common for ferroelectric perovskite oxides like barium titanate.45 The persistence of Raman modes in the cubic phase indicates that some local distortions remain in the crystal lattice.46 Indeed, earlier studies of low frequency Raman spectroscopy of MAPbBr₃ and CsPbBr₃ by Yaffe et al. revealed that the central peak emerges with increasing temperature.³³ The phase transitions in these perovskites are related to the octahedral tilts (which yield an antidistortive phase transition). The gradual decrease of the intensity of the spectral bands is observed when approaching the transition temperature at 406 K. The Raman fitting procedure reveals that the phonon mode at around 130 cm⁻¹ undergoes softening (Fig. 6). This could indicate that the polar fluctuations are coupled with the octahedral tilts, which are responsible for the antidistortive phase transition (the softening in this case is away from the Brillouin zone center). Such phase transition should not be visible in Raman spectra unless it has some coupling to the local polar distortions.

The tetragonal–orthorhombic phase transition at 360 K does not show any pronounced phonon anomaly. The mode at 130 cm⁻¹, which acts as a "soft mode" around the cubictetragonal phase transition, only monotonously hardens with the decrease of temperature (Fig. 6). Higher frequency modes (at 160 cm⁻¹ and 310 cm⁻¹) monotonously soften with increasing temperature (Fig. 6). No anomaly can be observed at around 220 K. However, the accuracy of the analysis may not be sufficient to observe very small changes in the Raman spectra, as the experimental results discussed above reveal that the anomaly is rather weak. This indicates that different octahedral



Fig. 5 Raman scattering spectra of CsPbBr₃ single crystals at different temperatures.



Fig. 6 Temperature dependence of mode frequency obtained from analysis of the Raman spectra.

tilts suppress the polar fluctuations. Thus, they do not give such a contribution in the lower symmetry phases. We assume that the polar fluctuations are negligible in tetragonal and orthorhombic phase. This gives a hint that the most efficient materials for solar energy conversion should be in the cubic phase so that the polar fluctuations contribute to the solar conversion *via* contribution to the dielectric properties. Namely ease exciton splitting and polaron formation.

To clarify the nature of the low temperature anomaly at 220 K, the crystal structure behavior of CsPbBr₃ was thoroughly studied. XRD data were collected first on the as-prepared powder upon cooling, then upon heating to 453 K followed by cooling. The powder thermally treated at 453 K for 15 min was studied again upon cooling from room temperature down to 100 K. From the visual inspection of the obtained XRD patterns, it was found that the crystal structure of CsPbBr₃ is orthorhombic below 360 K, tetragonal between 360 K and 410 K and cubic above 410 K, which is in agreement with literature.^{23,47} All studied samples show the perovskite phase without impurities. No variation in the XRD patterns that could indicate a symmetry change has been detected in the vicinity of 220 K. Crystal structure refinement was successful using the space groups Pbnm (orthorhombic phase), P4/mbm (tetragonal phase), and $Pm\bar{3}m$ (cubic phase).^{23,47} Crystal structure distortions of the cubic lattice associated with decreasing temperature are induced by *in-phase* octahedral tilting about the *c*-axis that results in tetragonal symmetry and appearance of the $\sqrt{2a_{\rm p}}$ × $\sqrt{2a_{\rm p}} \times a_{\rm p}$ superstructure (where $a_{\rm p}$ is the pseudocubic perovskite unit-cell parameter). The next reduction in symmetry occurs because of an onset of anti-phase octahedral tilting along the axes a and b. This leads to the orthorhombic symmetry with the $\sqrt{2a_{\rm p}} \times \sqrt{2a_{\rm p}} \times 2a_{\rm p}$ superstructure. Using Glazer's notation,⁴⁸ the aforementioned sequence can be expressed as: $a^0a^0a^0$ $\rightarrow a^0 a^0 c^+ \rightarrow a^- a^- c^+.$

For easy comparison and analysis, the lattice parameters of the orthorhombic and the tetragonal phases obtained from Rietveld refinement were recalculated to the parameters of the primitive perovskite unit cell: $a_p = b_p \neq c_p$, $\alpha_p = \beta_p = 90^\circ \neq \gamma_p$ (*Pbnm* phase) and $a_p = b_p \neq c_p$, $\alpha_p = \beta_p = \gamma_p = 90^\circ$ (*P4/mbm*





Fig. 7 The primitive perovskite cell parameters of $CsPbBr_3$ as a function of temperature upon heating.

phase). Fig. 7 demonstrates the temperature behavior of the parameters $a_{\rm p}, c_{\rm p}$ and $\gamma_{\rm p}$.

The observed change in the $a_p(T)$ and $b_p(T)$ behaviors clearly displays the phase transitions. In the range of the tetragonal phase, the thermal expansion along the c_p -axis is negative; after the tetragonal-to-cubic transformation, $a_p = c_p$.

The phase transition between the tetragonal and cubic phases was studied upon heating and cooling by estimation of the full width at half maximum of the diffraction multiplet $(002)_{p}$, which is sensitive to the tetragonal distortion. It was found that this first-order transition⁴⁷ demonstrates a temperature hysteresis of around 7 K (Fig. S2 in the ESI†). No temperature hysteresis has been detected at the *Pbnm–P4/mbm* transition, which indicates that it is of second-order nature.

Above 360 K, the primitive perovskite unit cell angle γ_p is 90° indicating the disappearance of the *anti-phase* tilting. Below 360 K, it decreases monotonically, and between 220 and 100 K the $\gamma_p(T)$ dependence is almost linear.

It was revealed that the diffraction reflections in the XRD patterns become narrower after the thermal treatment (annealing) at 453 K. This clearly indicates a stress release or/ and annealing of defects.

The primitive perovskite unit cell volume (V_p) as a function of temperature is shown in Fig. 8. One can see that the nearlinear $V_p(T)$ dependence changes slope at the temperature of the *Pbnm–P4/mbm* and the *P4/mbm–Pm*3*m* transitions. This is in agreement with the results on the linear expansion of singlecrystal CsPbBr₃ reported by Rodová *et al.*⁴⁷ It is seen from Fig. 8 that a change of the slope similar to those that occur at the aforementioned phase transitions is also observed at around 220 K within the range of the orthorhombic *Pbnm* structure of CsPbBr₃. The peculiar temperature behavior of V_p in the vicinity of 220 K is more pronounced in the sample annealed at 453 K (see inset in Fig. 8).

The observed anomaly of the temperature dependence of the unit cell volume of the orthorhombic CsPbBr₃ can indicate a redistribution of the lead–bromine bond distances within the PbBr₆ octahedra. Non-monotonic and other unexpected thermal behaviors of the crystal lattice parameters have been observed in a monoclinic phase of $La(Mg_{1/2}Ti_{1/2})O_3$,⁴⁹ in



Fig. 8 The normalized primitive unit cell volume of CsPbBr₃ as a function of temperature. Red solid lines represent linear fits of the $V_p(T)$ dependence in the ranges of the cubic and the tetragonal phases as well as in the range of 100–220 K of the orthorhombic phase. The inset shows the temperature dependences of V_p for the same powder sample before and after annealing at 453 K for 15 min.

a hexagonal high-temperature phase of YMnO₃,⁵⁰ in a orthorhombic phase of $Sr_3Sn_2O_7$ (ref. 51) and have been attributed to isostructural transitions (transformations). It should be noticed that all the above-mentioned oxygen-octahedral compositions demonstrated anomalies of their dielectric behavior in the respective temperature ranges.

Finally, for the sake of an argument about the absence of ferroelectric order, polarization hysteresis loops were measured below room temperature. In MAPbBr₃ the low temperature state is antipolar. The obtained data for of CsPbBr₃ are presented in the ESI (Fig. S3†) clearly indicating lack of spontaneous polarization. This means that even below 220 K, the material does not go into a ferroelectric phase. This is an unambiguous experiment that concludes on the speculations of ferroic order in these materials.

Conclusions

DSC, broadband dielectric, and EPR studies revealed an anomaly in $CsPbBr_3$ at around 220 K. Detailed XRD studies confirm an isostructural phase transition at 220 K. This transition shows a thermal hysteresis and, from the structural point of view, it can be related to a redistribution of the lead-bromine bond distances within the PbBr₆ octahedra. According to the dielectric data and polarization measurements, the crystal remains paraelectric at all temperatures.

Similar to the MAPbX₃ compounds, CsPbBr₃ shows a high dielectric permittivity in the microwave frequency range. The lattice relaxation contribution to the dielectric response is of the order of $\varepsilon_r \sim 30$. There is no additional relaxation in the microwave range of frequencies, so this is the only contribution present in the all inorganic CsPbBr₃. The value is exactly the same as the high frequency value for the methylammonium compositions MAPbX₃ (the same for all three halides). The organic molecular cation MA provides yet another contribution of $\Delta \varepsilon_r = 30$. So screening is very effective in CsPbBr₃, but it is

still stronger in the organic-inorganic hybrids. This can essentially explain the differences and similarities in exciton breakup, polaron formation, charge carrier lifetime and charge carrier mean free path between the all inorganic CsPbBr₃ and hybrid MAPbX₃ compounds. A weaker screening of charge carriers in CsPbBr₃ results in their faster scattering on defects and may be a reason of the lower photovoltaic efficiency.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This project has received funding from the Research Council of Lithuania (LMTLT), agreement no. S-MIP-19-4. The research done in University of Aveiro was supported by the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/ 50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. A. K. and D. C. L. acknowledge funding through the Deutsche Forschungsgemeinschaft (Lu729/23) and through the European Union in the framework of the PeroBOOST project (EFRE-0800120; NW-1-1040h).

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