Spectroscopic Ellipsometry Study of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ Hybrid Perovskite Single Crystals

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Organic-inorganic hybrid perovskites have the generic formula ABX_3 , where X denotes a halide anion and A and B stand for an organic and a metal cation, respectively. These hybrid compounds are semiconductors with highly interesting and tunable properties. They are the subject of intense research for several applications, mainly in solar cells but also as light-emitting diodes and lasers. Tunability of the optical properties may be accomplished by site-substituted solid solutions in A, B, or X sites. In particular, some mixed-cation systems show increased stability for these applications. In this work, we report on the variation of the optical constants in mixed A-site cation methylammonium/formamidinium (MA/FA) lead iodide perovskites $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ evaluated by spectroscopic ellipsometry in single crystal samples. The two main polymorphs of FAPbI_3 are measured. The study is complemented by photoluminescence measurements to gain a better insight into observed spectroscopic features related to the electronic interband transitions of the crystals and their structural integrity. The main result is a continuous variation of the pseudo-cubic perovskite band structure of the solid solutions between the two end compounds MAPbI_3 and $\alpha\text{-FAPbI}_3$.

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I. INTRODUCTION

Hybrid perovskites ABX_3 , where X denotes a halide anion and A and B stand for an organic and a metal cation, respectively, are semiconductors that show promise for several optoelectronic applications. The most widespread research is in the field of photovoltaics motivated by the quick improvements in efficiency^{1,2} with a record efficiency at present³ above 25%. Materials of this class also display excellent properties suitable for other applications such as light emitters or detectors.⁴⁻⁷ For all these applications, knowledge of the optical properties is both of fundamental and practical interest. Spectroscopic ellipsometry (SE) provides a detailed experimental knowledge of electronic transitions which can be related to specific aspects of band structure calculations. In addition, values of the optical constants determined by SE enable the design and optimization of light harvesting and out-coupling in solar cells and other devices.⁸ One of the main drawbacks of hybrid perovskites are structural changes due to degradation or crystalline phase instabilities.^{9,10} Although for applications thin films are employed, studies on single crystals allow for an improved understanding of many properties, among them the optical constants, due to the better quality of samples for structural and optical studies.¹¹

Here, we focus on the optical spectra of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ solid solution single crystals by SE. The improved stability of some of these mixed organic-cation crystals compared to the workhorse compound methylammonium lead iodide (MAPbI_3) makes them interesting. The detailed structural phase behavior of the solid solutions and the near-band-gap absorption have been well determined.^{12,13} In contrast, the optical spectra at higher energies have not been studied and, in particular, that of the end compound formamidinium lead iodide (FAPbI_3) is not well established. One possible cause for this is the difficulty to stabilize its perovskite *black* phase at room temperature, α - FAPbI_3 , versus the hexagonal *yellow* phase δ - FAPbI_3 .^{12,14,15} Three previous investigations by SE of thin films of FAPbI_3 have reported on the optical constants of the α phase¹⁶⁻¹⁸ showing differing results both in terms of observed higher electronic transitions and absolute values of the optical constants. In contrast, only one of these SE investigations¹⁷ reports on the measurement on a thin film of the stable δ phase, probably because of its wide band gap and limited practical interest for applications.

In this work, we study the variation of the optical constants in single crystal samples of mixed A-site cation $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ perovskites as measured and evaluated by SE. We analyze the observed electronic transitions as a function of organic-cation composition x , obtained by fitting the

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numerically built second derivatives of the dielectric function. We discuss the results in combination with photoluminescence measurements. In particular, we examine the spectra of the two pure organic cation end compounds in comparison with previous reports.^{16–19}

II. EXPERIMENTAL DETAILS

A. Sample preparation

The samples used in this study were single crystals with dimensions large enough for ellipsometry measurements, at least in millimeter range, grown by inverse solubility crystallization in γ -butyrolactone.²⁰ Ref. 12 contains full details of the precursor synthesis and the reaction compositions. The resultant crystal sizes tended to decrease in solid solutions with large FA contents and some compositions ($x = 0.8, 0.9$) could not be measured. Special effort was made for $x = 1$ to obtain good quality large FAPbI_3 crystals, since the corresponding optical functions of this pure end compound are not well known.

B. SE measurements and fitting

Ellipsometric spectra were measured at several angles of incidence with a Sopralab GES5E rotating polarizer ellipsometer using the microspot option. We attempted to detect optical anisotropy in some non-cubic crystals (e.g., MAPbI_3 and the MA-rich alloys are tetragonal at room temperature) by measuring the SE data at different orientations of the single crystals, including different in-plane azimuths and different faces. The detected differences were rather small and of the order of differences also seen even at different points of a same large crystal. These variations could be likely originated in irregular surface conditions, in any case, we could not reliably establish any optical anisotropy within our experimental error. Therefore, all the samples were considered as optically isotropic in the analysis regardless of their crystal symmetry. The *true* dielectric functions of the bulk crystals were deduced by considering a roughness overlayer calculated by a standard effective medium approximation of 50% material and 50% voids.²¹ More details about the effect of the roughness and a comparison with the typical surface morphology of the crystals is given as Supplementary Information (SI). The dielectric functions were obtained by regression analysis without imposing any analytical model, the only structural unknown parameter was the surface roughness layer thickness. The numerical inversion result was smoothed by cubic splines.²² The

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SE data and regression analysis results are included in the SI as well. The electronic transition parameters were analyzed by numerically building second derivatives of the dielectric function and fitting the observed features by critical point lineshapes.^{9,23}

C. Photoluminescence measurements

The PL spectra were excited with the 633 nm line of a He-Ne laser at very low incident light power density below 15 W/cm^2 to avoid any photodegradation or thermal damage of the samples by the laser. Spectra as function of temperature from 10 to 365 K were measured using a gas-flow cryostat from CryoVac that fits under the microscope using a $20\times$ long working distance objective with $\text{NA} = 0.35$ and dispersed with a high-resolution LabRam HR800 grating spectrometer equipped with a charge-coupled device detector. PL spectra were corrected for the spectral response of the spectrometer by normalizing each spectrum using the detector and the 600 grooves/mm grating characteristics.

III. OPTICAL SPECTRA OF $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$

In this section we discuss the measured values of optical constants in the solid solution series and their variation with the organic-cation composition x . The advantage of measuring single crystals is that the bulk structure is well determined whereas thin films are polycrystalline and prone to contain some porosity which affects the value of the optical constants, as is known from the case of MAPbI_3 ⁹ and other hybrid perovskites.²⁴ Even in bulk single crystals there is uncertainty in the absolute values due to the correction of surface imperfections, i. e., roughness or overlayers of the as-grown crystal facets. In any case, by now the values for MAPbI_3 are rather well established¹⁹ whereas, in contrast, those for FAPbI_3 are more uncertain.

Furthermore, formamidinium lead iodide has two main polymorphs^{12,14,15} with very different optical properties: The photoactive *black* α - FAPbI_3 phase and the non-perovskite hexagonal *yellow* phase δ - FAPbI_3 . The black phase is metastable at room temperature and depending on the sample environment it transforms slower or faster to the yellow phase.²⁵ We measured SE spectra of both phases using the same crystal. The transformation from yellow to black could be quickly induced by heating the crystal on a hotplate to about 80°C for several minutes. After removing it from the hotplate, SE measurements were immediately performed. In fact, no spectral changes

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could be detected for several hours in the clean room environment at 23°C ambient temperature and 28% relative humidity in agreement with previous observations of large thermal hysteresis of the cubic-to-hexagonal phase transition.²⁵ Figure 1 shows the obtained dielectric functions of the pure end compositions. The roughness correction was chosen to render the minimum possible values of the imaginary part ϵ_2 at low energies, in the transparency region of the materials. The thickness of the rough layers needed for the analysis were 9 nm for the yellow phase and 12 nm for the black phase. These relatively large roughnesses are in the range of those previously found for MAPbI_3 and which produced valid results, also plotted for comparison. The slight roughness parameter increase from the initial crystal to the phase-transformed one correlates with a real worsening of the as-grown surfaces when the crystals undergo a phase transformation.

Comparing with previous determinations of α - FAPbI_3 optical functions in thin films, our results are most similar in value (somewhat higher) and spectral dependence to those reported by Ndione et al.¹⁶ The values reported by Kato et al.¹⁷ and Subedi et al.¹⁸ were not very different but their spectra contained more transitions. In particular, Kato et al.¹⁷ assigned the transitions based on a density functional theory (DFT) calculation. These authors also reported the δ - FAPbI_3 optical functions, in their case, each phase was a different film deposited in different conditions. In this regard, the largest difference with our data is the refractive index that they determine for both films: they obtain about the same value for the α and the δ phase, whereas we obtain a much lower value for the δ phase, as is evident from Fig. 1. This lower value of the real part ϵ_1 is more consistent in view of the much higher band gap of δ - FAPbI_3 , clearly seen as a pronounced excitonic peak at about 3.2 eV.

Except for the δ - FAPbI_3 , all other measured single crystals were perovskite phases. The dielectric functions of the solid solutions determined from the measurements are presented in Fig. 2. No large differences in the optical spectra are observed as the composition varies; the most obvious change is the bandgap redshift from low to high FA content, also visible in measurements of photoluminescence shown in Fig. 3 together with the absorption coefficient near the band gap extracted from SE measurements. The highest absorption coefficients just above the band gap are those of the pure end perovskite crystals. However, the observed absolute value fluctuations can be influenced by variations in crystalline quality and surface perfection that are difficult to control. Nevertheless, different crystals of the same composition usually lead to very close results. However, two different spectra for the mixed crystal with FA content $x = 0.7$ are displayed in Fig. 2 that correspond to two crystals from different growth batches. In this case, the difference is intriguing

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and thus, we investigated more closely this composition to cross check the resulting spectra. Another motivation was that one clear extra peak is apparent near 3 eV in the uppermost spectrum. Note that this composition approximately delimits the region of perovskite phase stability¹⁰ and above this value the FA containing perovskite could transform into the hexagonal phase so that a slight change in stoichiometry could cause the observed difference. We anticipate that we ruled out this possibility as it will be further discussed below.

IV. ELECTRONIC TRANSITIONS IN $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$

In principle, all numerically obtained dielectric functions reported in this work can be parameterized using different analytic models. For MAPbI_3 different parameterizations have been published. The spectra can be reproduced with the smallest parameter number by using critical point (CP) lineshapes⁹ although some authors prefer a sum of Tauc-Lorentz (TL) oscillators²⁶ to enforce a vanishing value of the absorption coefficient below the band gap. The drawback of this approach, is that not all TL oscillators present in the model correspond to electronic transitions, in contrast to the CP oscillators. From the point of view of suppressing the non-physical absorption below the band gap, the CP model can be improved as shown by Leng et. al.²⁷ However, to investigate the band gap only, the TL model provides a physical representation giving the optical band gap as well as the peak transition energy.²⁸ In this work, we apply the TL model to the bandgap region to retrieve the optical band gap energy value. In addition, to determine the energies of all observed electronic transitions we used the CP model to analyze the spectra by numerical derivatives.

Derivatives allow a more accurate determination of the CP parameters because the background is eliminated and at the same time CP structures become more pronounced. In this work, we have built numerical 2nd derivatives using the smoothing polynomials method^{23,29} to smooth out the experimental noise as much as possible without significant distortion of the spectral features. Therefore, the sharp gap transitions were analyzed separately from the rest of broader upper transitions. From previous study of MAPbI_3 crystals⁹ it was found that zero-dimensional CPs represented well all transitions. Therefore, we chose 0D CPs for the regression analysis of the experimental numerical derivatives of all samples. The second derivative of the 0D theoretical lineshape is given by:

$$\frac{d^2\epsilon(\omega)}{d\omega^2} = 2Ae^{i\varphi}(\hbar\omega - E_g + i\Gamma)^{-3}, \quad (1)$$

where A is the amplitude, φ the phase, E_g the transition energy, and Γ the linewidth. Zero-

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dimensional transitions given by Eq. (1) are characteristic of excitons or localized excitations but also take place in case of dispersionless electron-hole states, for example when the effective masses of both electron and hole are large at the transition k-point and its vicinity, as was calculated for MAPbI_3 .¹⁹

Figure 4 displays relevant 2nd derivative spectra together with the fit results to illustrate both the similarities and the differences among the investigated samples. In general, the spectra of perovskite phases (in the figure MAPbI_3 , $\alpha\text{-FAPbI}_3$ and the pristine $x = 0.7$ crystal) are indeed rather alike. The main critical point energies obtained from the fits are indicated and labeled using the assignments obtained from electronic structure calculations.¹⁹ Four main CPs were identified from the calculations at the four main symmetry points of the pseudo-cubic Brillouin zone: The fundamental gap, CP1, at the R point, and the upper gaps CP2 at the M point, CP3 at the X point and CP4 at the Γ point. The dependence with composition of these CPs is plotted in Fig. 5. Our experimental results indicate that the optical spectra of all $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ including $\alpha\text{-FAPbI}_3$ are very similar although slightly shifted, suggesting that the electronic band structures are basically coincident with some small corrections that progressively evolve to give the continuous redshift as x increases. The fitted linewidths do not depend on composition, there are some variations but no definite trend. The lowest energy CP1, the fundamental bandgap, is the sharpest and is around 50 meV broad independently of the sample composition. The total energy shift, represented in Fig. 5(a), is about 90 meV. Note that the fitted errors for the energies are much smaller than the linewidth, in the range of 3 meV. Different values are plotted for each composition; the highest value is always given by the value CP1 (fit of the 2nd derivative), and the lowest one the optical gap energy (E_g) fitted from the TL lineshape. The difference between these two values is about 20 meV. The PL peak shows an additional Stokes shift of about 10 meV.

The upper transitions plotted in Fig. 5(b) also show a progressive redshift that is between 50 and 90 meV in all cases. For these transitions the fitted linewidths are much broader and even if there are differences among samples they are also roughly independent of composition. It is worth to mention that the highest energy part of the UV spectrum is the most affected by the performed roughness correction, cf. Sect. III, and with it, the CP energies of rougher samples (here, $x = 0.6, 0.7$ and mainly CP4) have an added uncertainty. We also point out that this fact has no effect on the fitted linewidths. Linewidth variations may be indicative of crystalline quality. In general, sharper transitions are taken to mean better quality. For these samples this assertion is true referred to the band gap, CP1. In contrast, we must be aware that this is not necessarily

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true for the higher energy transitions, in particular extended defects in the crystals may also lead to sharper higher energy transitions. For good quality crystals the width for CP2 is about 250 meV and the error in the fitted energies is typically 10 meV. For CP3 the width is about 400 meV and the error in fitted energies about 20 meV. There is a shoulder to CP3 resolved in the 2nd derivative with similar width but larger error in its energy determination, about 40 meV. Finally, CP4 is the broadest, about 500 meV but rather well determined, energy fitting errors are about 30 meV. Since the widths of all these electronic transitions do not show definite trends with solid solution composition, we conclude that the electronic structure is mostly given by the inorganic cage structure and the influence of the organic cation is relatively small in the system FA/MA, at least in terms of the electronic structures and their transition energies. In addition, our observations are consistent with a rather continuous change of the band structure and do not support differences in the bandstructures of the end compounds obtained from some calculations.¹⁷

V. SIGNATURES OF DEFECTS IN $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$

From Fig. 4 we can easily compare the two different spectra measured for the mixed crystals with FA content $x = 0.7$. One of them differs from a typical perovskite sample and we label it accordingly as defect ($\text{d-FA}_{0.7}\text{MA}_{0.3}\text{PbI}_3$). In fact, the intensity of the bandgap transition in the derivative is clearly smaller than those of the other perovskites. As already mentioned, the width of all perovskite bandgaps fitted in this work is around 50 meV independently of the sample composition. In the atypical $x = 0.7$ sample it is both weaker (smaller amplitude) and broader (70 meV), probably indicating worse crystal quality of the perovskite in this sample. It is relevant to comment on this because, in contrast, the upper transitions appear stronger and sharper than the ones observed in the perovskites, as is typical of structures with weakly interacting $[\text{PbI}_6]^{4-}$ octahedra, such as PbI_2 , hydrated MAPbI_3 , and $\delta\text{-FAPbI}_3$. Note that the energies of the peaks are rather similar in both samples except for the feature near 2.9 eV. Some extra peaks were found in previous reports of the dielectric function of $\alpha\text{-FAPbI}_3$ ^{17,18} In particular, a transition reported at 3.04 eV¹⁷ is quite analogous to this extra peak and it does not appear in our $\alpha\text{-FAPbI}_3$ crystal. This led us to the conclusion that those $\alpha\text{-FAPbI}_3$ films must have had defects similar to our $\text{d-FA}_{0.7}\text{MA}_{0.3}\text{PbI}_3$ crystal. It is difficult to identify which kind of defect could give rise to such strong features in the upper electronic transition spectrum. In principle, it could correspond to some other component phase or phases. For comparison, the derivative of $\delta\text{-FAPbI}_3$ is also

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plotted in Fig. 4. In this case all transitions are strong and sharp but do not coincide with those observed in our atypical $x = 0.7$ crystal or the reported $\alpha\text{-FAPbI}_3$ ^{17,18}, therefore we should discard as explanation that some δ phase is present in these samples. Actually, it seems clear that the 2nd derivative spectrum of $\text{d-FA}_{0.7}\text{MA}_{0.3}\text{PbI}_3$ is not composed by a perovskite part with additional superimposed peaks from another phase. Instead, the anomalous upper spectrum seems likely to arise from some kind of structural variation that leads to weaker interactions of the $[\text{PbI}_6]^{4-}$ octahedra. We should also mention that the pristine $x = 0.7$ crystal was quite stable and these peaks did not appear even after several months, in agreement with the fact that the different structure of the anomalous crystal was formed during growth and was not a degradation product. This stresses the importance of the growth conditions to obtain perfect perovskite samples, either single crystal or films. The main difference in the crystallization processes of both $x = 0.7$ crystals which we are aware of, was a higher temperature heating of the solutions in the case of the $\text{d-FA}_{0.7}\text{MA}_{0.3}\text{PbI}_3$ crystal that probably degraded the FA and even more the less stable MA ions in the precursor solution and their incorporation into the structure was affected.

In order to obtain further insight of the defect structure, we have measured PL as a function of temperature. Selected spectra of the $\text{d-FA}_{0.7}\text{MA}_{0.3}\text{PbI}_3$ crystal are shown in Fig. 6. The different colors denote two sets of measurements performed at two different spots on the sample, separated by several tens of microns (spot diameter ca. $4\ \mu\text{m}$). At room temperature, a single broad PL peak is observed. However, for one of the series and as temperature is lowered, the sharpening of the linewidth allows to observe two PL lines with variable intensity, whereas for the other series only one peak remains (see Fig. 6). The ratio of intensities of the peaks is very influenced by the exact point on the sample and by changing the temperature we could not avoid small displacements of the measurement points. Hence, the relative intensities cannot be interpreted. However, the energy positions of these lines are well determined regardless of the measured point and seem to indicate two different compositions. Note that for a pristine crystal of this composition only one line is seen at each temperature.¹³ These results clearly show that the crystal is inhomogeneous. On the one side, different spectra can be observed at different points. On the other side, two PL peaks at well determined energies are observed regardless of the point. The difference in energy between the peaks is about 30 – 40 meV, which can mean a composition change of $x \sim 0.3 - 0.4$. We actually ascribe these two peaks to two compositions, that is, this sample contains segregated FA-rich and MA-rich regions although the average broader bandgap observed by SE corresponds to the nominal $x = 0.7$ FA content. Note that, for the splitting to be resolved,

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low temperature measurements are needed and probably a better spatial resolution than that given by the microspot (spot diameter ca. $100\ \mu\text{m}$) in SE. The exact compositions of the segregated phases cannot be reliably determined because of the strain induced by defects in these regions and the strain-dependence of the PL energy positions.¹¹ The non-monotonous dependence of the band gap energy with temperature is influenced by different contributions, in particular for intermediate x the change from blue to red shift observed in Fig. 6 seems to be due to evolution of tilting of the PbI_6 octahedra in the crystal structure and the changing contribution of the thermal expansion term.³⁰ This point is still under evaluation and the complete phase diagram with composition and temperature for these alloys will be published elsewhere.¹³

Considering both the PL and the ellipsometry results together, the picture that emerges is that this sample consists of FA/MA segregated perovskite domains that determine the near-band-gap PL and absorption. These domains are spatially separated. However, the presence of these segregated phases does not explain the observation of some sharp higher energy electronic transitions. To understand them, we speculate that between the segregated domains there must be surrounding regions in which internal structural deformations can suppress the interactions of the normal perovskite structure. Such suppression is probably caused by high concentration of vacancies. Local structural changes can be created both by organic-cation (predominantly MA) or iodide vacancies,^{31–33} usually present in lower concentrations. This is a possible and most plausible explanation to reconcile all observations in this case, in particular the sharp electronic transitions observed in SE at higher energies.

VI. CONCLUSIONS

The dielectric functions of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ single crystals have been studied in the whole concentration range x . As-grown crystal facets were measured without further preparation and the measurements were corrected for surface roughness or overlayer effects to determine the true values. Although some compositions crystallize in anisotropic symmetries, no optical anisotropy could be determined and all samples have been considered isotropic. Based on these premises, the results for the best crystals were reported. The two end compositions $x = 0$ and $x = 1$ gave rather similar results in terms of values of optical constants for the perovskite structure with values of absorption coefficient just above the band gap slightly larger for MAPbI_3 ($\alpha \sim 1.8 \times 10^4$ (1/cm)) than for FAPbI_3 ($\alpha \sim 1.4 \times 10^4$ (1/cm)).

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The influence of the organic cation is not only visible as a red shift of the band gap energy from $x = 0$ to $x = 1$ but also of all upper transitions. In fact, our observations are consistent with a rather progressive *nearly rigid* shift of the entire band structure.

Also, the complete upper spectrum and specially the second derivative is very sensitive to the presence of structural deformations or other phases. The region of the band gap shows mainly the normal perovskite regions which are characterized by relatively broad higher energy electronic transitions. Sharper higher energy peaks are more characteristic of crystal structures with weaker interactions in the lead-iodide framework. We believe that the ones we have observed here provide signatures of such suppressed interactions due to internal structural deformations originated in boundary phases between segregated regions which contain numerous vacancies.

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FIGURE CAPTIONS

FIG. 1. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric functions at room temperature determined for the two pure organic cation compositions. Both perovskite crystals (MAPbI_3 and $\alpha\text{-FAPbI}_3$) display very similar spectra, in contrast to that of the hexagonal phase $\delta\text{-FAPbI}_3$.

FIG. 2. Dielectric functions at room temperature determined for the measured solid solution $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ perovskites with compositions between $x = 0.1$ to $x = 0.7$. The vertical scales are indicated for the lowest graphs and the rest are displaced for clarity. The two spectra displayed for the highest FA content $x = 0.7$ correspond to two crystals from different growth batches. The label d stands for *defect* as explained in the text.

FIG. 3. Near-band-gap absorption and photoluminescence spectra at room temperature showing the concomitant redshift as FA content increases. The maximum intensities of the PL curves were arbitrarily rescaled to show the shifts more clearly. The curves that correspond to the two pure organic cation end compounds are plotted with thicker lines.

FIG. 4. Second derivative spectra for some relevant samples. One of the solid solution samples is distinguished by the label "d" meaning defect. The vertical scale is indicated for the lowest graph ($\delta\text{-FAPbI}_3$) and the rest are displaced for clarity but keeping the same proportions with the indicated scale factors. Vertical lines are drawn at the main fitted critical point (CP) energies for $\alpha\text{-FAPbI}_3$ and their shifts with respect to MAPbI_3 are indicated by arrows. These main critical points were assigned in MAPbI_3 to transitions from the upper valence band to the lower conduction band at different symmetry points of the pseudo-cubic Brillouin zone¹⁹ noted by labels.

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FIG. 5. Electronic interband transitions as function of composition. (a) Fundamental band gap energies found from different analyses. Circles display results from fitting the 2nd derivative spectra with 0D CPs. The dielectric function spectra fitted with a TL oscillator give the optical band gap (E_g , down-triangles) and the transition energies (E_0 , up-triangles). For comparison, PL peak positions are displayed by squares. The lines are linear fits to the data points. (b) Upper electronic transitions observed in 2nd derivative spectra and fitted with 0D CPs. The assignments to k-points of the Brillouin zone correspond to the mainly identified contributions in band structure calculations.¹⁹ The label CP3-s denotes the shoulder of the CP3 transition. The fitting errors are in all cases smaller than the size of the symbols. The lines are linear fits to the data points.

FIG. 6. Photoluminescence spectra as function of temperature for the d- $\text{FA}_{0.7}\text{MA}_{0.3}\text{PbI}_3$ crystal. The two sets of curves are measured by focusing the laser at two different spots on the sample.

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