Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Temperature dependent phase transitions and their relation to isosbestic point formation. Case study of C(NH$_2$)$_3$PbI$_3$

M. Bukleski *, S. Dimitrovska-Lazova, S. Aleksovska

"Ss Cyril and Methodius" University, Faculty of Natural Sciences and Mathematics, Institute of Chemistry, Arhimedova 5, 1000 Skopje, Macedonia

HIGHLIGHTS

- Characterization of phase transitions (PT) in C(NH$_2$)$_3$PbI$_3$ by vibrational spectroscopy.
- Discovery of an unambiguity in the low temperature IR spectra, ascribed as a PT.
- Defining isostructural phase transition by temperature-induced isosbestic points.
- Redefinition of the phases according to the recommendations given by IUCr.

GRAPHICAL ABSTRACT
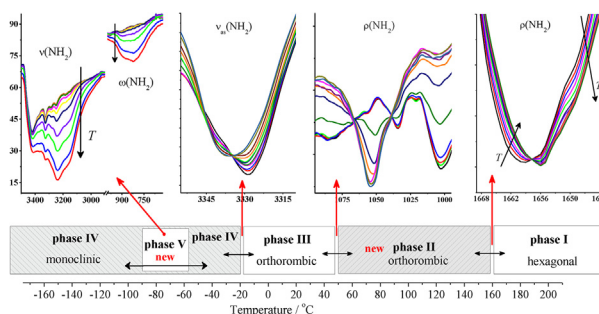
ARTICLE INFO

ABSTRACT

Besides the vast research regarding the hybrid organic-inorganic perovskite (HOIP) materials used in the solar cell production, their properties are still not fully uncovered. In this paper, detailed investigation on the phase transitions in guanidinium lead iodide (GAPbI$_3$) using vibrational spectroscopy techniques (IR and Raman) are presented. In addition to the well-known three phases of GAPbI$_3$ (denoted as I, II and III) another one existing in the temperature range from 48 °C to 160 °C is characterized. The thorough inspection of the vibrational spectra revealed some interesting changes occurring in the low temperature region (from −90 to −62 °C) that suggest presence of a new phase. Finally, a redefinition of the phase nomenclature according to the recommendations given by the IUCr is proposed.

1. Introduction

Since the synthesis of guanidinium lead iodide (C(NH$_2$)$_3$PbI$_3$, GAPbI$_3$) and its' incorporation in methylammonium and formamidinium lead iodides [1–4], great interest for its' potential use has arisen. The importance of this compound has been found in the possibility to improve the properties of the mentioned organic-inorganic perovskites as light harvesting materials. Although GAPbI$_3$ structure is well established and researched [5,6], even at low temperatures [7], it seems that this compound successfully hides its' unique properties connected to the temperature dependent phase transitions (PTs). The reason for this lies in the fact that the changes happen in a narrow and unexpected temperature intervals. Conventional methods such as XRD, TG/DTA and DSC have failed to identify these changes so far [5–9]. On the other hand, the vibrational spectroscopy techniques, ones again proved their advantage for detecting even the smallest changes and managed to give a valuable insight of some important structural characteristics.

The power of the vibrational spectroscopy methods in uncovering the phase transitions comes from the fact that PTs are almost always accompanied by a change in the geometry and symmetry. These changes can be successfully detected by these methods

---

* Corresponding author.
    E-mail address: mihabukleski@pmf.ukim.mk (M. Bukleski).

[10–12]. The isostructural phase transitions (IPT) are difficult to detect since they are not accompanied by a change in the space group of the substance. On the other hand, the energy changes during these IPTs are low and it is hard to detect them by the means of TGA or DSC methods commonly used to reveal the presence of phase transitions (PT). Minor structural changes in the IPT, such as flipping of the functional groups in the crystal structures or insignificant position rearrangement of the wobbly (loose) atoms or atomic groups go unnoticed by the commonly used techniques. These rearrangements can be detected by solid state NMR spectroscopy [13] or in this case, vibrational spectroscopy techniques.

A detailed study of the isostructural phase transition in GAPbI$_3$ based on the vibrational spectroscopy, especially IR transmission techniques will be given in this paper. In addition, the other phase transitions will be considered. The investigation is based on the temperature induced isosbestic points formation in the regions of $-17 \rightarrow -16$ °C, $+47 \rightarrow +48$ °C and $+159$ °C $\rightarrow +160$ °C in the IR spectra. In the low temperature region, -90 to -72 °C, another anomaly has been detected, that has not been reported previously. The obtained results are supported by the findings based on the Raman spectra.

2. Experimental

The IR absorption spectra were recorded on a Perkin-Elmer System 2000 FTIR Spectrometer using Liquid Nitrogen Cell (LNC). For the absorption measurements, KBr pellet technique was used. The absorption spectra were recorded with resolution of 2 cm^{-1}, using 32 scans (both for the background and the sample spectra) in the temperature range starting from -175 °C up to $+200$ °C and again down to room temperature on the same pellet. The CO$_2$/H$_2$O software compensation was used in order to reduce the bands intensity originating from the atmospheric moisture and the CO$_2$. All IR spectra were recorded with five degrease interval of the temperature change between two spectra. Additionally, one degree temperature difference was set in order to record the temperature in the vicinity of the phase transition.

Raman spectra of the corresponding samples were recorded on a MicroRaman 300 from Horriba Jobin-Yvon. The spectra were recorded employing the red He-Ne 633 nm laser line. Long-distance × 50 lens (Olympus) was used as an objective in both cases. The maximum power on the sample was 6.43 mW. A D0.3 filter was used to lower the intensity. The integration time employed was 80 s, 180 s or 240 s, using two or four cycles for the Raman shift from 10 cm^{-1} to 4000 cm^{-1}.

All chemicals used for the synthesis were with purity grade "for synthesis" and were used as received. The concentrated hydroiodic acid (57%, w/w) was purchased by Carlo Erba Reagents with 1.5 % H$_3$PO$_2$ as stabilizer, the lead(II) carbonate (99,0 %, w/w) was purchased by Merck Millipore while the guanidinium carbonate (99,0 %, w/w) was purchased by Sigma-Aldrich Company.

The synthesis of C(NH$_2$)$_3$PbI$_3$ was described in our previous papers [14]. The compound was obtained using PbI$_2$ and C(NH$_2$)$_3$I as precursors. They were dissolved in acetonitrile and evaporated under reduced pressure at 40 °C. After the filtration, needle-like shaped crystals were obtained.

3. Results and discussion

3.1. Changes in the low temperature region

The measurements were performed by cooling the sample to LNT and keeping at this temperature long enough to reach equilibrium. Afterwards, by conducting several runs of heating and cooling it was established that the phase transitions below room temperature are reached almost instantly. The changes always occur at precisely the same temperatures, independent on the number of runs or the direction of the temperature alteration (heating or cooling). This suggests a first-order phase transition [15].

The first change that took place when the temperature was gradually increased, starting from LNT, was observed at -90 °C. At this temperature the intensity of the bands in the region of stretching NH$_2$ vibrations (3450–3000 cm^{-1}) started to increase up to -72 °C, when maximal transmittance was achieved. At the same time a band at 821 cm^{-1} started to appear, while the band at 893 cm^{-1} gained intensity (Fig. 1a). The maximal intensity of the bands was achieved at -72 °C both for the bands originating from the stretching NH$_2$ vibrations as well as for the newly formed band at 821 cm^{-1}. Afterwards, when the temperature was increased further on, the bands started to diminish and return to their starting intensities characteristic for temperatures below -90 °C. Above -62 °C the spectra started entirely to resemble on the ones below -90 °C with no additional band at 821 cm^{-1} (Fig. 1b).

According to the previous assignation [16] of the bands of GA$^+$, the band appearing at 821 cm^{-1} can be assigned to the wagging CN$_3$ vibrations. They are expected to be inactive both in the IR and Raman spectra. In the studied compound, this is the case for all other temperatures except the interval from -90 to -62 °C. Based on the appearance of the wagging CN$_3$ vibrations it can be assumed that the entire C(NH$_2$)$_2$ group rotates and flips to an equivalent position making a 180° rotation. As reported by the Grottel et al. [13], in the low temperature region of GAPbI$_3$, flipping and rotations may be detected by solid state NMR. The described behavior is interesting and unusual since it happens in the temperature region where the energy of the system is low and the bands are well defined. These findings based on the results from the IR spectra point to a PT. Also, the available results from the temperature dependent solid state NMR measurements [13], show a disruption in the linearity of the proton second moment as a function of temperature. This change has not been discussed by the authors but also suggests a presence of PT, especially if a comparison to the region of II → I phase transition is made. Information available from investigations of GAPbI$_3$ [5,6,13] suggest that only one phase is present below -18 °C even though detailed study of GAPbI$_3$ for the low temperature range is performed. A confirmation that these low temperature rearrangements are mainly associated with the guanidinum cation can be found in the solid state NMR spectra [17], as well as in the IR spectra [16–20]. A study of a structurally similar compound FAPbBr$_3$ [21], supports these findings. Namely, the most significant change associated with the PT in FAPbBr$_3$ for the low temperature region is at -91 °C, temperature that corresponds to the determined PT in GAPbI$_3$. Mozur et al. relate this PT to a molecular motion of the FA$^+$ while the PbBr$_6$ octahedra stay undisturbed. They do not record changes in the XRD, while the molecular motion of FA$^+$ is registered by quasielastic neutron scattering spectra.

3.2. Phase transition $-18 \rightarrow -17$ °C (III → II)

This phase transition has already been detected and the structural data for both phases, denoted as III and II are available [5,6,14]. The IR spectroscopy can offer a solid evidence of the existence of a phase transition in the specified temperature region. Recently, a way to determine a phase transition based on a temperature induced isosbestic point [14,22] has been published. That approach will be used throughout this paper for the characterization of the PTs.

From the spectra recorded in the temperature region from -30 to -5 °C (Fig. 2), an appearance of a temperature dependent
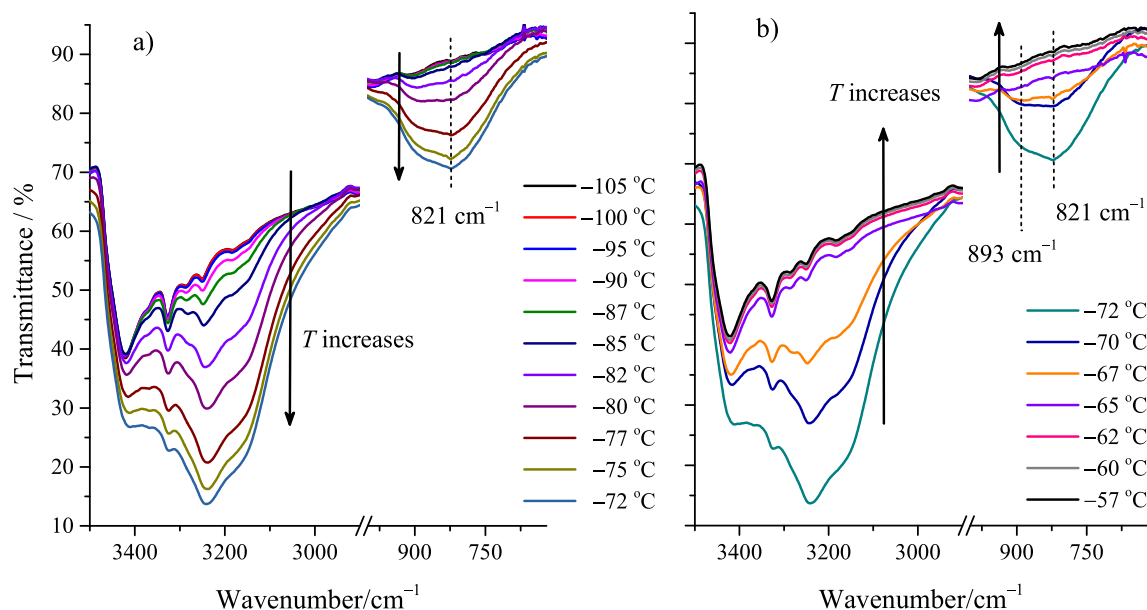
Fig. 1. IR spectra recorded in the low temperature region indicating: a) increase of the transmittance in the stretching region of NH$_2$ groups (3450–3000 cm^{-1}) and the appearance of the bands in the bending NH$_2$ region (950–700 cm^{-1}) for temperature interval −90 to −72 °C; b) return to the starting transmittance intensity and vanishing of the bands in the bending NH$_2$ region for temperature interval −72 to −62 °C.
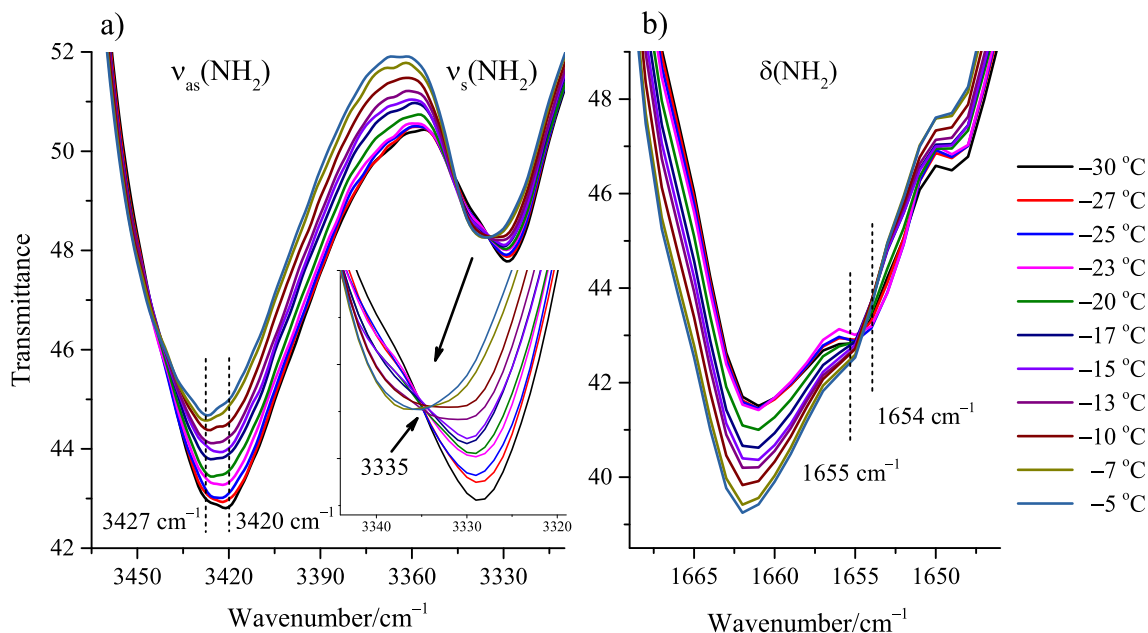
Fig. 2. Appearance of an isosbestic points in the region of symmetric stretching and bending vibrations of the NH$_2$ groups indicating a PT.

isosbestic points can be detected. The first one is associated with two bands, both originating from the symmetric stretching vibrations of the NH$_2$ groups - ν_s(NH$_2$). The band at 3328 cm^{-1} vanishes as the band at 3336 cm^{-1} appears (Fig. 2a). The isosbestic point where the spectra intersect at 3335 cm^{-1} is formed, while the temperature of the transition calculated according to the methodology proposed in [22] is −16.3 °C. This value is very close to the one previously reported in the literature of −18.5 °C [5]. Another feature that points out to a structural change is the region of the bending vibrations of the NH$_2$ groups – δ(NH$_2$) at around 1650 cm^{-1}. Here, another isosbestic point appears between 1654 and 1655 cm^{-1}. The calculated temperature for the PT based on this point is −16.7 °C. The last, not very indicative change can be found in the

band assembly at 3425 cm^{-1} (Fig. 2a). Some of the bands that constitute this strong intensive band, change their relative intensity. Because of the overlap, it cannot be clearly distinguished at which temperature the change occurs. Also, the calculation based on the intensity of each band leads to inconclusive results. Nevertheless, these variations are an indication about a change in the structure related to the NH$_2$ groups.

3.3. Isostructural phase transition +47 → +48 °C (III → "−")

Until recently [15], the existence of this PT was not known. The indication about the presence of a new phase came from the analysis and investigations connected to the temperature dependent IR

spectra. Further employment of other methods verified this assumption [22]. The results gave an undoubtable indication for the occurrence of a new phase below +50 °C in GAPbI$_3$. According to the IUCr guidelines [23], the new phase can be denoted with hyphen ("–").

One of the most convincing indications based on the IR spectra for the phase transition was the appearance of an isosbestic point. This result is also supported by additional changes in IR spectra occurring at +47 → +48 °C temperature transition. We divided these changes in four feature groups.

1. Change in the absorption characteristics. A sudden drop in the transmittance intensity is observed in the spectra when the temperature reaches +48 °C (Fig. 3a). Afterwards, as the temperature continues to increase, the absorption coefficient stays constant (insignificant changes). These changes in the absorption coefficient are more pronounced for higher wavenumber values and less in the low wavenumber region (below 1600 cm^{-1}).

2. Band shift. The second feature is associated with a band shift (Fig. 3b) where the band assigned as asymmetric stretching vibration of the NH$_2$ groups [24,25] shifts from 3427 to 3443 cm^{-1} when increasing the temperature from +30 to +52 °C. If the relative intensities as a function of the band shift are taken into account, than the exact temperature at which the change occurs can be calculated [22]. In this case, the transition temperature was found to be +47.7 °C.

3. Isosbestic point. The most reliable and straightforward indication that leads to an undoubtable conclusion that a phase transition occurs is the appearance of an isosbestic point at 1659 cm^{-1} (Fig. 4). In this case, there is only one isosbestic point for the III → "–" phase transition and it is associated with the bands originating from the bending vibration of the NH$_2$ groups. The point appears as a result of the diminishing of the band positioned at 1655 cm^{-1} and the intensifying of the band at 1660 cm^{-1}. The change of the intensity for the 1660 cm^{-1} band is accompanied by a band shift of 3 cm^{-1} in total (to 1663^{-1} for +52 °C). It is interesting to note that while the δ(NH$_2$) are affected by the PT, the bands originating from the ν(NH$_2$) do not show any sign of disruption during this transformation. Since there are two types of changes in the vicinity of the isosbestic point, the calculation of the transition temperature can be made based on the band shift but also on the changes in
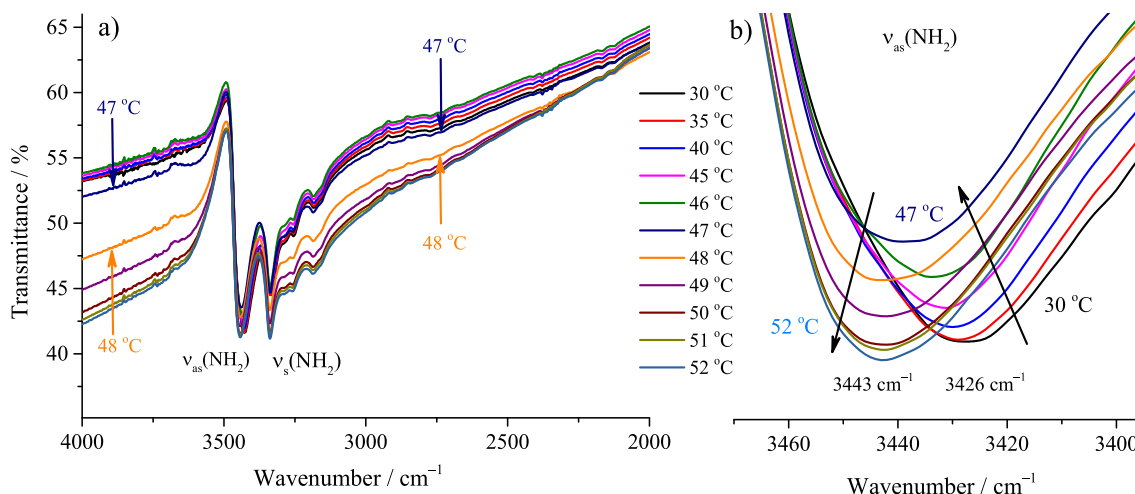
the intensities of the bands. Based on the band shift, the calculated value of the transition temperature is found to be +46.9 °C, and from the variations of the intensities, the obtained value is +47.5 °C.

4. Appearance/disappearance of bands. The last changes that can be noticed for this PT in the temperature dependent IR spectra are the changes associated with the appearance/disappearance of the bands related to the NH$_2$ rocking and wagging vibrations [16,19]. These bands appear below 1150 cm^{-1} (Figs. 5 and 6). Placing the IR spectra in order of temperature increase (Fig. 5), the interchange of the bands at 1053 and 1033 cm^{-1} may be clearly observed. While the band at 1033 cm^{-1} is visible before the phase transition and vanishes after, the band at 1053 cm^{-1} appears after the transition takes place. This indicates that there is a change in the position of the NH$_2$ group in the structure of GA$^+$ cation. If the spectra are normalized and stacked together, a formation of a double isosbestic points can be observed (Fig. 6). These points have all the features of a regular occurring isosbestic points, although they are obtained

Fig. 4. Temperature dependent isosbestic point as a clear indication of the phase transition occurring at +47 → +48 °C.

Fig. 3. Temperature dependent transmission spectra in the +30 to +52 °C region, a) significant drop in transmittance due to the absorption coefficient increase, b) band shift of the asymmetric stretching vibration of the NH$_2$ groups.
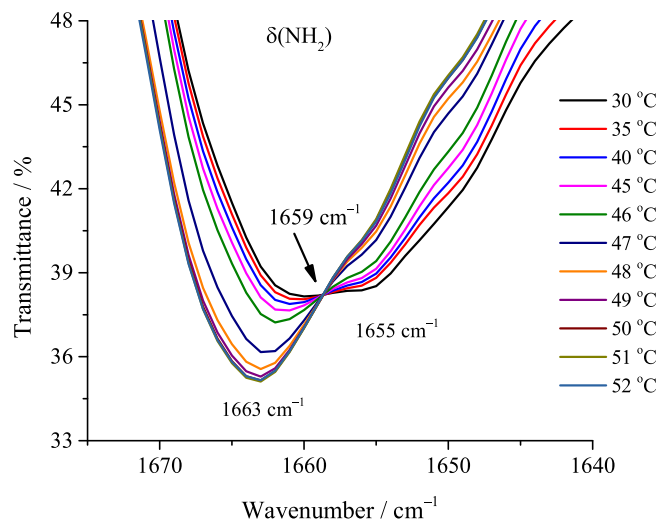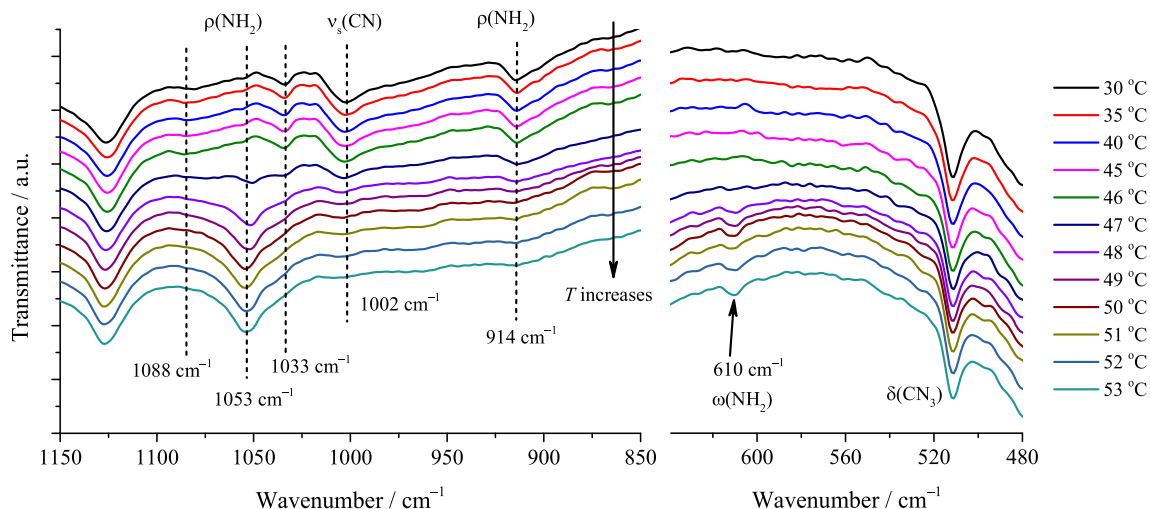
Fig. 5. Transmission IR spectra in the region of the low temperature phase transition ordered by the increase of the temperature.
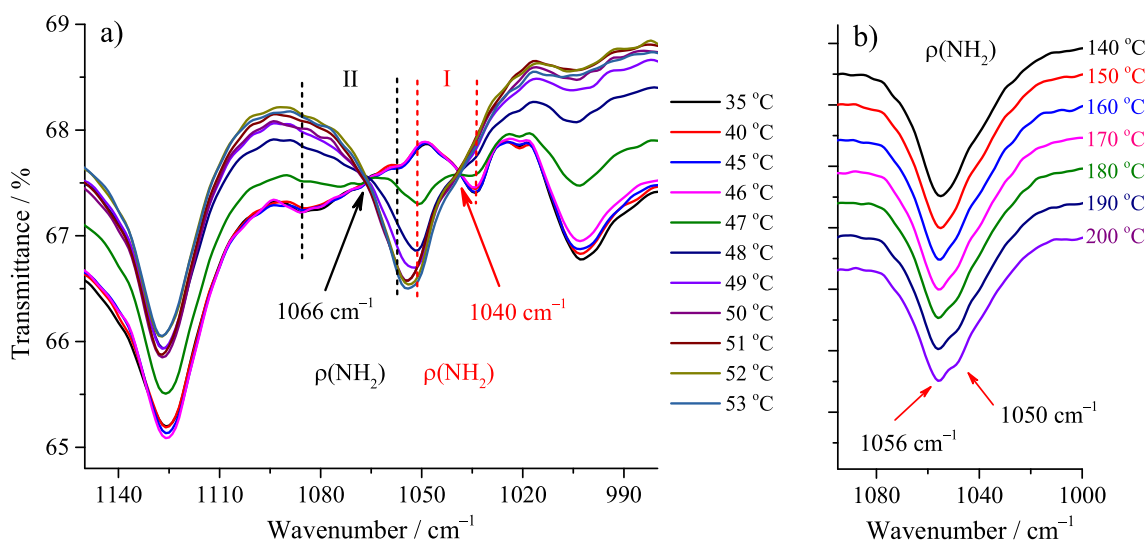

Fig. 6. a) Two isosbestic points obtained by normalization of the IR spectra in the region of the rocking vibrations of NH$_2$ groups, b) splitting of the band at 1054 cm^{-1} at higher temperatures.

by normalization. Calculations of the temperature of the phase transition are made and the obtained value is found to be +47.8 °C.

Taking into consideration the calculated and observed temperatures of the phase transition it can be concluded that the isostructural changes in the GAPbI$_3$ happen in the interval +47 → +48 °C. This temperature transition is established based on the four features described in this chapter. Also, it agrees with the temperature at which the disruption of linearity in the proton second moment function [13,17].

As it was previously mentioned that in the vicinity of the isosbestic points one band vanishes while another one appears [22,26,27]. According to this, as a result of the appearance of two isosbestic points (Fig. 6a), there are supposed to be two different sets of bands (one for the first point, and another one for the second point). At a first glance, it might not be noticed that the band at 1054 cm^{-1} consists of two bands, but the high temperature spectra show its' splitting (Fig. 6b). The two bands belong to the

two different isosbestic points. By close inspection of the bands at 1086 and 1056 cm^{-1} it can be noticed that the band at 1086 cm^{-1} diminishes while the one at 1056 cm^{-1} gains on intensity as the transition takes place and is related with the isosbestic point at 1066 cm^{-1}. On the other hand the isosbestic point at 1040 cm^{-1} correlates the bands at 1050 and 1034 cm^{-1} (Fig. 6a).

An interesting detail is the connection between the band at 914 cm^{-1} on one hand and the band at 610 cm^{-1} on the other (Fig. 5). The first one is assigned as a rocking vibration, ρ(NH$_2$) [24,28], while the other one as wagging vibration, ω(NH$_2$) [29]. The 914 cm^{-1} band diminishes and the band at 610 cm^{-1} appears (Fig. 5) as the temperature increases. The band originating from the stretching CN vibrations can confirm the relation between these bands. Namely, ν$_s$(CN) is positioned at 1002 cm^{-1} and its intensity is reduced as the ρ(NH$_2$) bands vanish and ω(NH$_2$) become active. This is due to the fact that the position of the NH$_2$ groups changes in respect to the carbon atom. This provokes increase in the symmetry of the GA$^+$. Based on this, a conclusion that the hydrogen bond strength decreases, can be drawn. The described rearrange-

ment of the band positions in the IR spectra that lead to this conclusion are clearly visible (Fig. 5). This means that the GA⁺ moves in respect to the PbI_6 octahedra.

Another proof that the changes taking place in the transition II → "–" provoke weaker hydrogen bonding can be found in the band shift at $3426 \to 3443$ cm⁻¹ accompanied by a band appearance at higher wavenumbers in respect to the isosbestic point (1663 cm⁻¹). The movement (new position) of the NH_2 groups leads to weaker hydrogen bonding and at the same time to higher symmetry of the GA⁺ ion. Due to the extension of the changes in the transmission spectra and the appearance of the isosbestic points, it can be concluded that a phase transition is certain to take place.

The results obtained by the IR investigations can be further verified by the findings from the Raman spectroscopy studies. The Raman spectra can also be used to determine the temperature dependent phase transitions [30,31] even though in this particular case they are not as straightforward as the findings from the IR investigations. The results obtained by the Raman spectra investigations can confirm the conclusions made by the IR studies.

The Raman spectra recorded using the red laser line show high fluorescence in the region above 1500 cm⁻¹ (Fig. 7). This has been observed and reported in the literature for the mixed GA-FA lead iodide perovskites [32], but also for other perovskites [12]. It is a known fact that with the temperature increase, fluorescence intensity drops. It is interesting to note that in the case of $GAPbI_3$ for temperature range between +45 °C and +50 °C (zone of phase transition) the fluorescence seizes completely. The vanishing of the fluorescence is abrupt and it is an indication of a sudden change in the structure of the $GAPbI_3$.

Additional differences in the temperature dependent Raman spectra (Fig. 7) can be found in the low frequency region (below 150 cm⁻¹) where bands origination from the PbI_6 octahedra appear. Besides the shift of the band occurring at 108 cm⁻¹ in the spectra up to +45 °C to a position of 108 cm⁻¹ in the spectra above +50 °C, there is also a change in the ratio considering the relative intensity of the bands at 106 cm⁻¹ and 92 cm⁻¹. This change is sudden when the temperature is increased from +45 to +50 °C. The band at 106 cm⁻¹ originates from the bending I–Pb–I mode and is assigned as symmetric A_g mode, the shoulder at 115 cm⁻¹ as an asymmetric B_{2g} mode, while the band at 92 cm⁻¹ is related to the convolution of the modes A_g and B_{2g} [33]. From all of the above mentioned changes and the assignment of the bands, it can be concluded that the changes in the Raman spectra are

associated with the rearrangement or reorientation of the PbI_6 octahedra in the crystal structure. Furthermore, as it has been reported previously [30], the reorientation or movement of the Pb cage can result in phase transition. This is closely associated with the position, orientation and the distance between the lead and iodine atoms in the octahedra.

3.4. High temperature phase transition +159 → +160 °C ("–" to I)

The IR spectra suggest another phase transition at +159 → +160 °C, also confirmed by other methods [14,15]. At high temperatures the IR spectra show presence of isosbestic point as well as changes in the position/intensity of some bands. It is interesting to note that even though these transition changes are accompanied by a change in the space group and the crystal system, they are not as pronounced in the spectra as the ones appearing during the isostructural phase transition (subchapter 3.3.).

The main differences in the spectra are related to the vibrations assigned to ρ(NH_2) mode that are related to the appearance of the temperature dependent isosbestic point (Fig. 8a). This point is at 1658 cm⁻¹ and is obtained by the vanishing of the band at 1659 cm⁻¹ and the appearance of the band at 1656 cm⁻¹. If a further analysis is made on band at 1656 cm⁻¹, it can be concluded that for the phase "–" one broad band exists, but if a deconvolution is made, this band can be successfully fitted by introducing two oscillators with medium strength S and low dumping constant γ [34]. The calculated value for the temperature of this PT was found to be +160.2 °C.

When the temperature reaches +160 °C, a new band appears at 1652 cm⁻¹ that was first thought to be a shift of the band existing at 1650 cm⁻¹ (Fig. 8a). The transition temperature that was calculated based on the assumption that band shift exists, gave inconsistent results. An inspection that was more thoroughly conducted lead to a conclusion that the band at 1650 cm⁻¹ does not cease to exist. Its' intensity is shaded by the appearance of previously mentioned band at 1652 cm⁻¹. This was additionally confirmed by the deconvolution of the band.

The last feature that points to a phase transition at +160 °C is the region of the bending NH_2 vibrations. A sudden disappearance of the band at 1541 cm⁻¹ and the appearance of a band at 1546 cm⁻¹, not only is an indication of a phase transition, but also suggests a change in the position i.e. orientation of the NH_2 groups when the temperature is increased from +159 to +160 °C. If normalization of the spectra is conducted, another
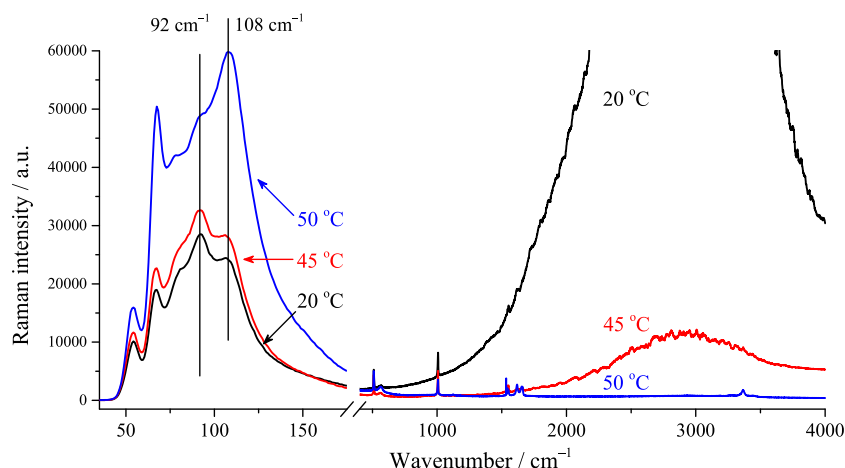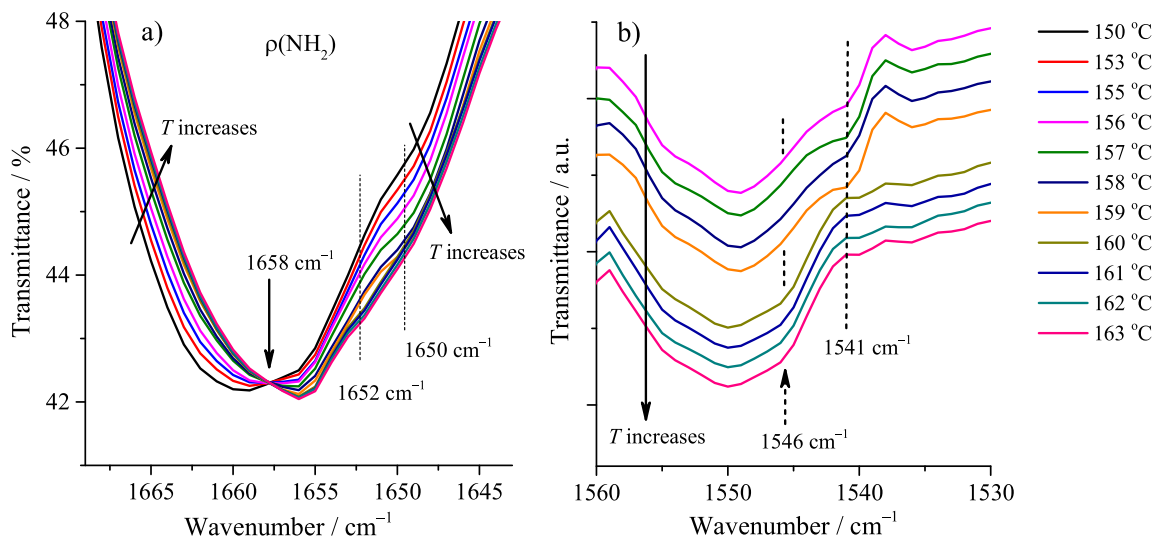

Fig. 7. Raman spectra of $GAPbI_3$ recorded at 20, 45 and 50 °C in the frequency region from 20 to 150 cm⁻¹ where the cage Pb–I vibrational bands occur and in the region of high frequencies indicating the diminishing of the fluorescence.

Fig. 8. Temperature induced isosbestic point at +160 °C as an indication for the second phase transition in GAPbI$_3$. The point is a result of a change in the rocking NH$_2$ mode.

isosbestic point can be obtained. The profile of the spectra around 1541 cm^{-1} for temperatures above +160 °C is a result of the strength and the dumping constant of the oscillators in the vicinity of the isosbestic point (new band at 1546 cm^{-1} and the band at 1535 cm^{-1}) [34].

Compared to the IPT, in this case the IR spectra (near IR region) do not show any significant change in the position of the NH$_2$ groups and the appearing differences are probably due to the change in the position of the PbI$_6$ octahedra. The structural data obtained by powder XRD [14] show change in the connectivity of the PbI$_6$ octahedra from edge sharing at room temperature to face sharing at high temperature. As a result, one of the three NH$_2$ groups becomes more attracted by the PbI$_6$ in comparison with the others. This conclusion can be confirmed by the Raman spectra.

The comparison of the temperature dependent Raman spectra reveal significant changes in the entire spectral region when increasing the temperature from +155 to +160 °C (inset Fig. 9b). In Fig. 9a the differences between the spectra associated with the changes in the PbI$_6$ octahedra are evident and they point to a phase transition. It is apparent that in this case not only the band at 107 cm^{-1} is shifted to 100 cm^{-1}, but also the band at 92 cm^{-1} vanishes. The loss of the intensity of the band at 54 cm^{-1} (Fig. 9a) assigned to I–Pb–I bending motion (A_{1g} mode) [35,36] is obvious.

As it has been reported previously [30], the reorientation or movement of the Pb cage can result in phase transition. This is closely associated with the position, orientation and the distance between the lead and iodine atoms in the octahedra. Namely, when
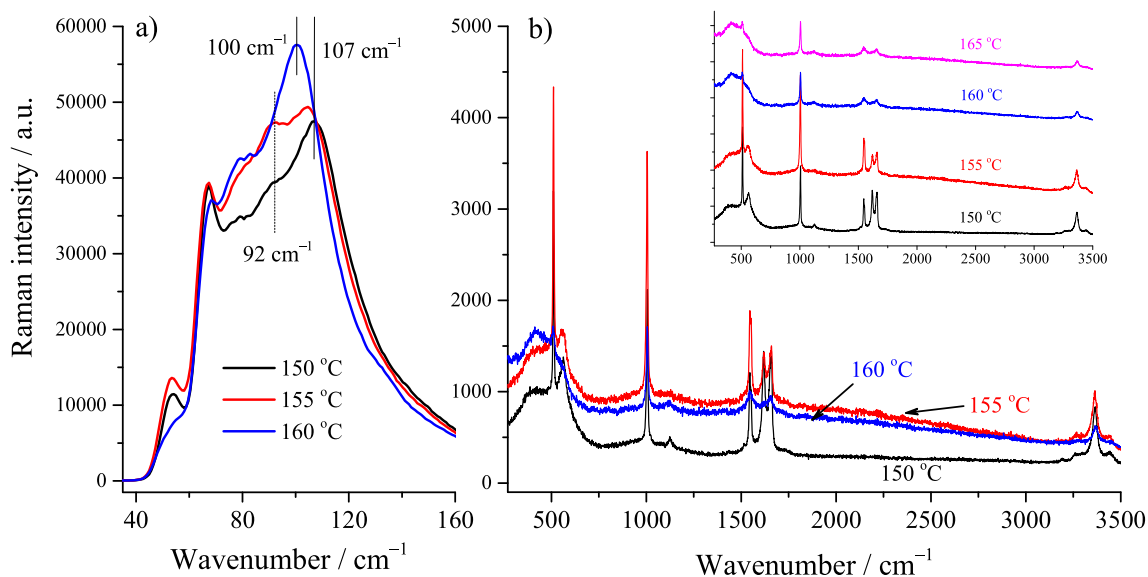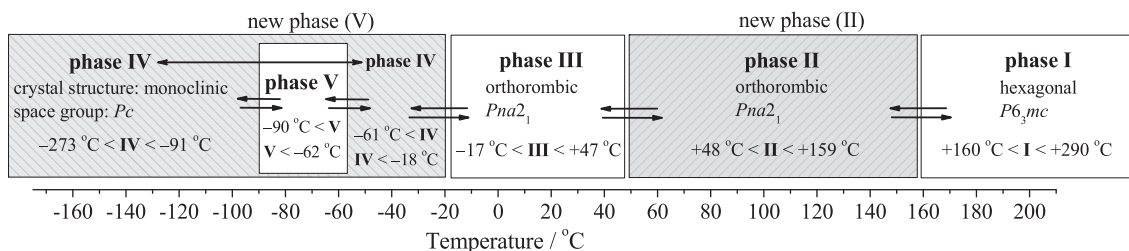

Fig. 9. Raman spectra in the temperature range around the second phase transition, a) in the spectral region of the PbI$_6$ cage vibration and b) in the region above 300 cm^{-1} where the changes in the organic cation can be followed.
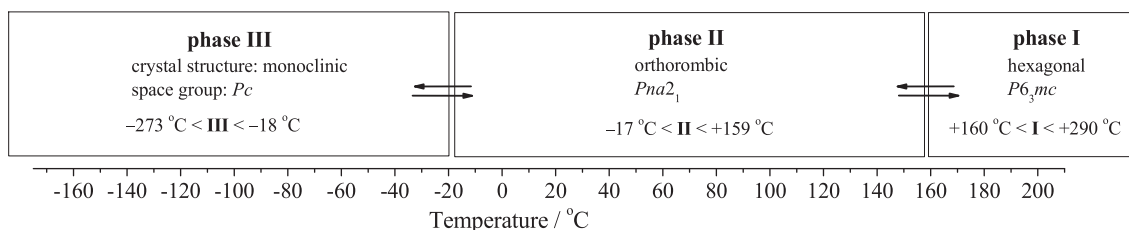
Scheme 1. Existence of different phases in GAPbI$_3$ in the temperature range from −170 to 200 °C under atmospheric pressure, before and after the discovery of a new phase.

the position of the PbI$_6$ changes, some of the Raman modes become active or inactive.

4. Redefinition and nomenclature of the phases in GAPbI$_3$

According to the recommendations from the International Union of Crystallography - IUCr [23], the six field nomenclature of all temperature dependent phases in GAPbI$_3$, including the existence of newly discovered phase, under atmospheric pressure is introduced. Also, to be consistent with the given recommendations, a redefinition of the phases is made. The four phases existing in the temperature range from LNT up to the decomposition point of the compound (−196 to +310 °C) are systematically defined and denoted:

I|<583 K|$P6_3mc$ (186)|$Z = 5$|–|decomposition above 583 K
II|321−432 K|$Pna2_1$ (33)|$Z = 4$|–|Type = $KCdCl_3$
III| 255–320 K|$Pna2_1$ (33)|$Z = 4$|– | Type = $KCdCl_3$
IV|184−210 K|Pc (7)|$Z = 1$|–|–
V|<183 K|Pc (7)|$Z = 1$|–|–

Based on the findings presented in this paper as well as the available literature data, a schematic illustration of the phase transitions that is in line with the recommendation for the nomenclature of the phases proposed by the IUCr is given in Scheme 1. The data in this scheme refers to the existence of each phase in GAPbI$_3$ as a function of temperature under constant, atmospheric pressure. Also a comparison to the previously known 3 phases (before the findings presented in [15] and this paper) is given in order to notice the upgrade of the scheme, more easily.

5. Conclusion

Infrared spectroscopy is still a powerful technique that can give answers to many questions related to the structure of the compounds and the changes that happen when the conditions (temperature, pressure) change. In this study, two new phases have been identified and characterized by the means of vibrational spectroscopy techniques (IR and Raman). The obtained results for the already known phases are in line with the ones available in the literature. By the thoroughly conducted research, it was found that

there are 3 major phase transitions happening in the temperature intervals of:

−18 → −17 °C
+47 → +48 °C
+159 → +160 °C

It has also been detected that in the temperature range from −90 °C to −62 °C an additional phase exists within the phase IV. According to this, a complete nomenclature has been proposed in agreement with the recommendations given by IUCr.

The changes that happen in the low temperature PT, according to the IR spectra, are proposed to be a result of the GA$^+$ flipping in respect to the ac plane. The indication of this movement is based on the $\omega(CN_3)$ vibrations and the changes in the region of the stretching NH$_2$ vibrations. On the other hand, the flipping of the NH$_2$ groups, observed in the next PT (occurring at −18 → −17 °C), and the change in the hydrogen bond strength are responsible for the PT. The isostructural phase transition is accompanied with changes in the position of the entire NH$_2$ group so the movement (new position) of the NH$_2$ groups leads to weaker hydrogen bonding and at the same time to higher symmetry of the GA$^+$ ion. The high temperature PT reveals small changes to the GA$^+$ but the appearance of an isosbestic point is a clear indication of a PT. The Raman spectra confirm that the changes are much more pronounced in the PbI$_6$ cage of GAPbI$_3$. The recorded Raman spectra for this temperature range reveal distortion in the position of the PbI$_6$ leading to a PT.

CRediT authorship contribution statement

M. Bukleski: Conceptualization, Data curation, Writing – original draft, Writing – review & editing, Visualization. **S. Dimitrovska-Lazova:** Investigation, Formal analysis, Writing – review & editing. **S. Aleksovska:** Resources, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] N. Pellet, P. Gao, G. Gregori, T.-Y. Yang, M.K. Nazeeruddin, J. Maier, M. Grätzel, Mixed-organic-cation perovskite photovoltaics for enhanced solar-light harvesting, Angew. Chemie - Int. Ed. 53 (12) (2014) 3151–3157, https://doi.org/10.1002/anie.201309361.

[2] Z. Wang, Z. Shi, T. Li, Y. Chen, W. Huang, Stability of Perovskite Solar Cells: A Prospective on the Substitution of the A Cation and X Anion, Angew. Chemie Int. Ed. 56 (2017) 1190–1212, https://doi.org/10.1002/anie.201603694.

[3] Y. Zhou, H. Xue, Y.-H. Jia, G. Brocks, S. Tao, N.i Zhao, Enhanced Incorporation of Guanidinium in Formamidinium-Based Perovskites for Efficient and Stable Photovoltaics: The Role of Cs and Br, Adv. Funct. Mater. 29 (48) (2019) 1905739, https://doi.org/10.1002/adfm.v29.4810.1002/adfm.201905739.

[4] C.M.M. Soe, C.C. Stoumpos, M. Kepenekian, B. Traoré, H. Tsai, W. Nie, B. Wang, C. Katan, R. Seshadri, A.D. Mohite, J. Even, T.J. Marks, M.G. Kanatzidis, New Type of 2D Perovskites with Alternating Cations in the Interlayer Space, $(C(NH_2)_3)$ $(CH_3NH_3)_nPb_nI_{3n+1}$: Structure, Properties, and Photovoltaic Performance, J. Am. Chem. Soc. 139 (45) (2017) 16297–16309, https://doi.org/10.1021/jacs.7b09096.

[5] M. Szafrański, Investigation of phase instabilities in guanidinium halogenoplumbates(II), Thermochim. Acta. 307 (2) (1997) 177–183, https://doi.org/10.1016/S0040-6031(97)00408-5.

[6] A.D. Jodlowski, A. Yépez, R. Luque, L. Camacho, G. de Miguel, Benign-by-Design Solventless Mechanochemical Synthesis of Three-, Two-, and One-Dimensional Hybrid Perovskites, Angew. Chemie Int. Ed. 55 (48) (2016) 14972–14977, https://doi.org/10.1002/anie.201607397.

[7] Z. Deng, G. Kieslich, P.D. Bristowe, A.K. Cheetham, S. Sun, Octahedral connectivity and its role in determining the phase stabilities and electronic structures of low-dimensional, perovskite-related iodoplumbates, APL Mater. 6 (2018) 1–9, https://doi.org/10.1063/1.5046404.

[8] M. Wilke, N. Casati, Insight into the Mechanochemical Synthesis and Structural Evolution of Hybrid Organic-Inorganic Guanidinium Lead(II) Iodides, Chem. - A Eur. J. 24 (67) (2018) 17701–17711, https://doi.org/10.1002/chem.201804066.

[9] Y. Kim, P. Nandi, D. Lee, H. Shin, Stabilization of 3-D trigonal phase in guanidinium $(C(NH_2)_3)$ lead triiodide $(GAPbI_3)$ films, Appl. Surf. Sci. 542 (2021) 148575, https://doi.org/10.1016/j.apsusc.2020.148575.

[10] G. Bator, R. Jakubas, J. Baran, H. Ratajczak, Infrared studies of structural phase transitions in $(CH_3NH_3)_3Bi_2I_9$ (MAIB), J. Mol. Struct. 325 (1994) 45–51, https://doi.org/10.1016/0022-2860(94)80016-2.

[11] G. Bator, R. Jakubas, J. Baran, H. Ratajczak, Infrared studies of structural phase transitions in $(NH_3CH_3)_3Sb_2I_9$, Vib. Spectrosc. 8 (3) (1995) 425–433, https://doi.org/10.1016/0924-2031(94)00073-P.

[12] M. Trzebiatowska, K. Hermanowicz, The mechanism of phase transitions and luminescence properties of azide perovskites, Spectrochim, Acta Part A Mol. Biomol. Spectrosc. 255 (2021) 119716, https://doi.org/10.1016/j.saa.2021.119716.

[13] M. Grottel, M. Szafrański, Z. Pająk, NMR study of cation motion in guanidinium iodoplumbates, Zeitschrift Fur Naturforsch. - Sect. A J. Phys. Sci. 52 (1997) 783–788. https://doi.org/10.1515/zna-1997-1105.

[14] S. Dimitrovska-Lazova, M. Bukleski, P. Tzvetkov, S. Aleksovska, D. Kovacheva, Crystal structure of the high-temperature polymorph of C(NH2)3PbI3 and its thermal decomposition, J. Alloys Compd. 864 (2021) 158104. https://doi.org/10.1016/j.jallcom.2020.158104.

[15] S. Dimitrovska-Lazova, M. Bukleski, P. Tzvetkov, M. Pecovska-Gjorgjevich, D. Kovacheva, S. Aleksovska, The mechanism of the isostructural phase transition in $C(NH_2)_3PbI_3$ as a guide for understanding the properties of the new phase, Mater. Chem. Phys. 275 (2022) 125240, https://doi.org/10.1016/j.matchemphys.2021.125240.

[16] M. Drozd, Molecular structure and infrared spectra of guanidinium cation. A combined theoretical and spectroscopic study, Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 136 (1) (2007) 20–28, https://doi.org/10.1016/j.mseb.2006.08.063.

[17] S.-E. Gima, Y. Furukawa, D. Nakamura, 1H NMR Studies on the Dynamics of Planar $[C(NH_2)_3]^+$ Cations in the Crystal of Various Guanidinium Salts, Berichte Der Bunsengesellschaft Für Phys Chemie. 88 (10) (1984) 939–946, https://doi.org/10.1002/bbpc.19840881005.

[18] M. Szafrański, A. Katrusiak, Phase transitions in the layered structure of diguanidinium tetraiodoplumbate, Phys. Rev. B - Condens. Matter Mater. Phys. 61 (2) (2000) 1026–1035, https://doi.org/10.1103/PhysRevB.61.1026.

[19] A. Katrusiak, M. Szafrański, Structural phase transitions in guanidinium nitrate, J. Mol. Struct. Theochem. 378 (3) (1996) 205–223, https://doi.org/10.1016/S0166-1280(96)90974-4.

[20] N. Sheppard, Vibrations of the Guanidinium Ion, Trans. Faraday Soc. 53 (1956) 589–600. https://pubs.rsc.org/en/content/articlelanding/1957/tf/tf9575300589#!divAbstract.

[21] E.M. Mozur, J.C. Trowbridge, A.E. Maughan, M.J. Gorman, C.M. Brown, T.R. Prisk, J.R. Neilson, Dynamical Phase Transitions and Cation Orientation-Dependent Photoconductivity in $CH(NH_2)_2PbBr_3$, ACS Mater. Lett. 1 (2) (2019) 260–264, https://doi.org/10.1021/acsmaterialslett.9b00209.

[22] M. Bukleski, S. Dimitrovska-Lazova, V. Makrievski, S. Aleksovska, A simple approach for determination of the phase transition temperature using infrared temperature-induced isosbestic points, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 231 (2020) 118118, https://doi.org/10.1016/j.saa.2020.118118.

[23] J.-C. Tolédano, A.M. Glazer, T. Hahn, E. Parthé, R.S. Roth, R.S. Berry, R. Metselaar, S.C. Abrahams, Structural phase transition nomenclature report of an IUCr working group on phase transition nomenclature, Acta Crystallogr. Sect. A Found. Crystallogr. 54 (6) (1998) 1028–1033, https://doi.org/10.1107/S0108767398008150.

[24] C.L. Angell, N. Sheppard, A. Yamaguchi, T. Shimanouchi, T. Miyazawa, S. Mizushima, The infra-red spectrum, structure, and normal vibrations of the guanidinium ion, Trans. Faraday Soc 53 (1957) 589, https://doi.org/10.1039/tf9575300589.

[25] M. Bukleski, S. Dimitrovska-Lazova, S. Aleksovska, Vibrational spectra of methylammonium iodide and formamidinium iodide in a wide temperature range, Maced. J. Chem. Chem. Eng. 38 (2019) 237–252. https://doi.org/10.20450/mjcce.2019.1940.

[26] S. Bergamasco, G. Calzaferri, Isosbestic points and vibrational levels in electronically excited states of dye molecules, J. Photochem. Photobiol. A Chem. 63 (2) (1992) 211–215, https://doi.org/10.1016/1010-6030(92)85138-K.

[27] T. Nowicka-Jankowska, Some properties of isosbestic points, J. Inorg. Nucl. Chem. 33 (7) (1971) 2043–2050, https://doi.org/10.1016/0022-1902(71)80566-3.

[28] O.D. Bonner, C.F. Jordan, The infrared and Raman spectra of guanidinium salts, Spectrochim. Acta Part A Mol. Spectrosc. 32 (5) (1976) 1243–1246, https://doi.org/10.1016/0584-8539(76)80316-9.

[29] M. Drozd, D. Dudzic, Guanidinium perchlorate ferroelectric crystal. Study of vibrational properties based on experimental measurements and theoretical calculations, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 115 (2013) 345–356, https://doi.org/10.1016/j.saa.2013.06.023.

[30] A. Maaej, M. Bahri, Y. Abid, N. Jaidane, Z.B. Lakhdar, A. Lautié, Raman study of low temperature phase transitions in the cubic perovskite $CH_3NH_3PbCl_3$, Phase Trans. 64 (1998) 179–190, https://doi.org/10.1080/01411599808207997.

[31] B. Martín-García, D. Spirito, G. Biffi, S. Artyukhin, Francesco Bonaccorso, R. Krahne, Phase Transitions in Low-Dimensional Layered Double Perovskites: The Role of the Organic Moieties, J. Phys. Chem. Lett. 12 (2021) 280–286. https://doi.org/10.1021/acs.jpclett.0c03275.

[32] O. Nazarenko, M.R. Kotyrba, S. Yakunin, M. Aebli, G. Rainò, B.M. Benin, M. Wörle, M.V. Kovalenko, Guanidinium-Formamidinium Lead Iodide: A Layered Perovskite-Related Compound with Red Luminescence at Room Temperature, J. Am. Chem. Soc. 140 (11) (2018) 3850–3853, https://doi.org/10.1021/jacs.8b0019410.1021/jacs.8b00194.s00110.1021/jacs.8b00194.s002.

[33] C. Quarti, G. Grancini, E. Mosconi, P. Bruno, J.M. Ball, M.M. Lee, H.J. Snaith, A. Petrozza, F. De Angelis, The raman spectrum of the $CH_3NH_3PbI_3$ hybrid perovskite: Interplay of theory and experiment, J. Phys. Chem. Lett. 5 (2) (2014) 279–284, https://doi.org/10.1021/jz402589q.

[34] M. Bukleski, V. Ivanovski, V.M. Petruševski, IR specular reflectance spectra of $KHSO_4$ single crystal - Dispersion analysis, Vib. Spectrosc. 57 (2011), https://doi.org/10.1016/j.vibspec.2011.04.003.

[35] J. Satta, C. Melis, C.M. Carbonaro, A. Pinna, M. Salado, D. Salazar, P.C. Ricci, Raman spectra and vibrational analysis of $CsPbI_3$: A fast and reliable technique to identify lead halide perovskite polymorphs, J. Mater. 7 (1) (2021) 127–135, https://doi.org/10.1016/j.jmat.2020.08.004.

[36] M.A. Pérez-Osorio, R.L. Milot, M.R. Filip, J.B. Patel, L.M. Herz, M.B. Johnston, F. Giustino, Vibrational Properties of the Organic-Inorganic Halide Perovskite $CH_3NH_3PbI_3$ from Theory and Experiment: Factor Group Analysis, First-Principles Calculations, and Low-Temperature Infrared Spectra, J. Phys. Chem. C. 119 (46) (2015) 25703–25718, https://doi.org/10.1021/acs.jpcc.5b07432.