



## CsPbCl<sub>3</sub> nanocrystals dispersed in the Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl matrix studied by far-infrared spectroscopy

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### ABSTRACT

The comparative far-infrared spectroscopy studies of Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl and Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl containing CsPbCl<sub>3</sub> nanocrystals between 170 and 320 K are reported. The effect of cesium lead chloride nanocrystals on the phonon modes of the host matrix, particularly manifested in different temperature behavior of LO–TO splitting and the temperature dependence of high frequency dielectric constant, are demonstrated.

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## 1. Introduction

Rb<sub>1-x</sub>Cs<sub>x</sub>Cl solid solutions crystallize in a NaCl structure when  $x < 0.33$  [1]. Introduction of lead under certain conditions may lead to the formation of CsPbCl<sub>3</sub> molecular centers and their further aggregation [2]. The driving force for the creation of aggregate phases is well known: it is the aspiration of the “matrix + impurity” system toward the state with minimal free energy. For physically real objects an equilibrium state of the “matrix + impurity” system is not always reached and, therefore, in most cases only metastable compositions are realized [3].

In the last two decades many interesting studies have been performed on a new type of microcrystals and nanocrystals, namely CsPbBr<sub>3</sub> and CsPbCl<sub>3</sub> dispersed in bulk crystals [2,4–15]. These studies are motivated by the strong expectation of their possible applications in fast scintillator and opto-electronic devices. In

particular, with an interest in fast-response detectors for gamma-rays and charged particles, scintillation characteristics of CsPbCl<sub>3</sub> have been recently evaluated in [16], while stimulated emission from microcrystalline CsPbBr<sub>3</sub> was studied in details in [17–19]. Similar phases of CsEuBr<sub>3</sub> nanocrystals in CsBr:Eu storage phosphor have been characterized in [20].

The hypothetical mechanism of CsPbCl<sub>3</sub> molecular centers formation in CsCl:Pb crystals was discussed in details in [4]. High-temperature treatment of this crystal activates the movement of anion and cation vacancies accompanied by the re-building of the coordination anionic surrounding of standalone radiative centers Pb<sup>2+</sup> – v<sub>c</sub><sup>-</sup> from eightfold to sixfold. As a consequence, the cluster of the CsPbCl<sub>3</sub> molecule type is created. The tendency of CsPbCl<sub>3</sub> molecular centers to aggregation induces the formation of nano- and then microcrystals of CsPbCl<sub>3</sub>, which are dispersed in the CsCl matrix. In practice not all single Pb<sup>2+</sup> – v<sub>c</sub><sup>-</sup> centers in the CsCl:Pb crystal are aggregating, therefore CsPbCl<sub>3</sub> nanocrystals and standalone Pb<sup>2+</sup> – v<sub>c</sub><sup>-</sup> centers coexist. Spatial confinement of excitons causes the appearance of discrete electron and hole levels. This results in the quantum-sized effect manifested in the short-wavelength shift  $\Delta E$  of the free exciton emission band in CsPbCl<sub>3</sub>

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nanocrystals with respect to the free exciton band of the same single crystals [2], and in the significant decrease of the excitonic luminescence decay time for CsPbCl<sub>3</sub> nanocrystals ( $\tau = 0.15$  ns) as compared to that of the CsPbCl<sub>3</sub> single crystal ( $\tau = 0.48$  ns).

The aggregation of CsPbCl<sub>3</sub> molecular centers in Rb<sub>1-x</sub>Cs<sub>x</sub>Cl ( $x = 0.05 - 0.2$ ) crystalline matrices, where Rb<sup>+</sup>, Cs<sup>+</sup> ions and, respectively, the impurity ion Pb<sup>2+</sup> are characterized by sixfold surrounding of Cl<sup>-</sup> anions, is expected, since the structure does not have to be rebuilt for the formation of [PbCl<sub>6</sub>]<sup>4-</sup> octahedron (unlike CsCl-type crystalline matrices, where eightfold surrounding of Cl<sup>-</sup> anions first must change to sixfold during the process of CsPbCl<sub>3</sub> molecule type cluster). [PbCl<sub>6</sub>]<sup>4-</sup> octahedron is the basis of the CsPbCl<sub>3</sub> molecular cluster and that is why its presence in the matrix promotes the formation of nano and microcrystals of CsPbCl<sub>3</sub> type in Rb<sub>1-x</sub>Cs<sub>x</sub>Cl:Pb crystals. Besides, the presence of a charge-compensative vacancy  $v_c^-$  near the activator ion Pb<sup>2+</sup> increases Pb<sup>2+</sup> ions mobility thus leading to the creation of lead-containing aggregates.

Average radius  $R_{QD}$  of the CsPbCl<sub>3</sub> type nanocrystals dispersed in Rb<sub>1-x</sub>Cs<sub>x</sub>Cl doped with 1 mol% Pb was determined according to the known relationship between the short-wavelength shift and  $R_{QD}$  [21]

$$\Delta E = \frac{\hbar^2 \pi^2}{2\mu R_{QD}^2}, \quad (1)$$

where  $\mu = 0.65m_0$  the exciton mass [22,23] in the CsPbCl<sub>3</sub> single crystal ( $m_0$  – free electron mass). The obtained values are nearly 2.3 and 4.7 nm, for Rb<sub>0.95</sub>Cs<sub>0.05</sub>Cl:Pb and Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl:Pb, respectively. Different sizes of CsPbCl<sub>3</sub> nanocrystals in Rb<sub>0.95</sub>Cs<sub>0.05</sub>Cl and Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl matrices can be explained if one considers that the decrease of Cs<sup>+</sup> ions concentration in the compound, lowers the probability of CsPbCl<sub>3</sub> nanocrystals formation in the Rb<sub>0.95</sub>Cs<sub>0.05</sub>Cl matrix. On the other hand, the increase in the concentration of Cs<sup>+</sup> ions in the Rb<sub>1-x</sub>Cs<sub>x</sub>Cl solid solution from  $x = 0.05$  up to  $x = 0.2$  leads to the formation of larger CsPbCl<sub>3</sub> nanocrystals in the Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl matrix.

As predicted theoretically, quantum-sized effect manifests itself in the aggregates with the radius  $R_{QD} < 10r_{ex}$  [24], where  $r_{ex}$  denotes exciton radius. Taking into account the numeric value of  $r_{ex}$  for CsPbCl<sub>3</sub> ( $r_{ex} = 9.8$  Å [23]), one can see that obtained above  $R_{QD}$  values satisfy the quantum-sized effect conditions.

In the present work we report the results of the far infrared spectroscopic measurements with aim to clarify the influence of CsPbCl<sub>3</sub> complexes, dispersed in the Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl matrix on the vibrational spectra of the host lattice.

## 2. Experimental details

Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl and Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl:Pb crystals (Pb concentration was 1 mol% in the melt) were grown by the Stockbarger method. In order to form the CsPbCl<sub>3</sub> nanocrystals dispersed in Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl:Pb, crystal was subjected to a prolonged (100 h) high-temperature ( $T = 200$  °C) annealing.

Far infrared reflectivity of Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl crystals was measured in the temperature range 160–320 K at the Daphne Light IR station, which is described in [25] and intensively used for nondestructive quantitative characterization of different types of the micro- and nanomaterials [25–30]. For this purpose ~5 mm thick crystals were cut. One of the sample surfaces was polished in stages (finally with a micron polishing paper) to ensure the maximum intensity of the reflected signal. The opposite edge surface was made rough to avoid parasitic reflections and, consequently, the unwanted interference fringes. Measurements were performed for unpolarized light under near normal incidence with a resolution of 1 cm<sup>-1</sup> in the frequency range from 35 to 600 cm<sup>-1</sup>. The reflectance

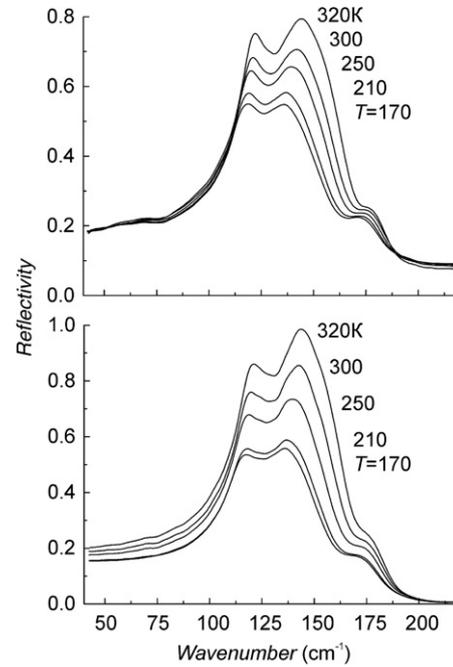


Fig. 1. Measured reflectivity of undoped Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl (top) and Rb<sub>0.8</sub>Cs<sub>0.2</sub>Cl doped with 1 mol% Pb (bottom) at various temperatures in far infrared region.

$I_{sample}(\omega)$  from the polished surface were measured at elevating temperatures, starting from 160 K with the step of 50 K. After that, the reference spectra of gold, evaporated on the sample surface  $I_{ref}(\omega)$  were taken for each respective temperature. The reflectivity was obtained as

$$R(\omega) = \ln \frac{I_{sample}(\omega)}{I_{ref}(\omega)}. \quad (2)$$

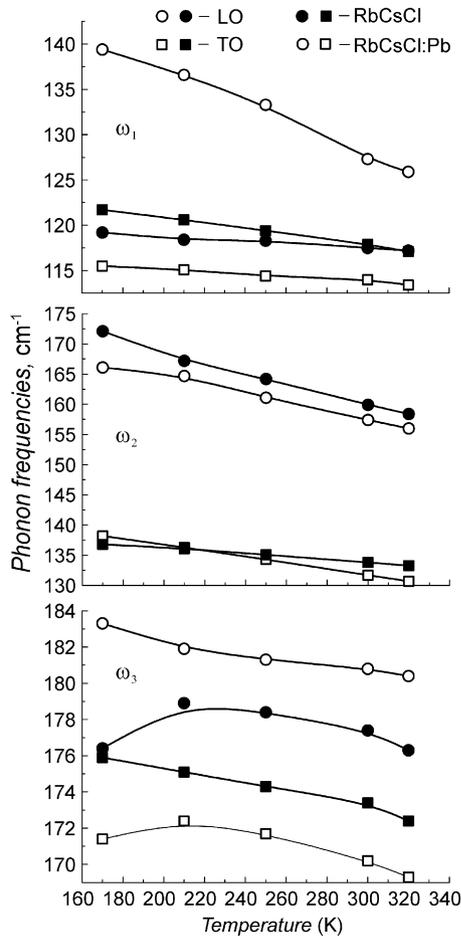
The OPUS-5.0 spectroscopic software was employed for the purpose of experiment control and data processing.

## 3. Results and discussion

Experimental results are shown in Fig. 1. The reflectivity spectrum of the undoped Rb<sub>1-x</sub>Cs<sub>x</sub>Cl (at 170 K) exhibits three intensive bands at 117, 135 and 173 cm<sup>-1</sup>. The spectrum of Rb<sub>1-x</sub>Cs<sub>x</sub>Cl:Pb at the respective temperature has similar structure, however the distinctions can be revealed when one analyzes the results of the dispersion analysis, presented below. From Fig. 1 it also follows that the reflectivity decreases upon heating while the observed bands shift to lower wavenumbers.

To the best of our knowledge, lattice dynamics of Rb<sub>1-x</sub>Cs<sub>x</sub>Cl solid solution has not yet been studied theoretically. Although RbCl structure has high symmetry, Cs atoms positions and mutual orientations determine the phonon frequencies and bandwidths, bringing much complexity to the calculations. Some basic considerations, however, can be derived from the analysis of RbCl lattice dynamics which has been extensively investigated, both theoretically and experimentally [31,32]. Thus, in RbCl two transverse optical modes are observed at 117 and 164 cm<sup>-1</sup>, both frequencies being close to those, observed experimentally in present work (see Section 2 above). Since Cs atoms are harder than rubidium ones the lower frequency band is expected to split. As one can see from Fig. 1 the splitting leads to the appearance of the additional band at ~135 cm<sup>-1</sup> in the spectra of RbCsCl crystals.

Obtained reflectivity spectra have been analyzed using FOCUS software. The analysis has been carried out for pure Rb<sub>1-x</sub>Cs<sub>x</sub>Cl as well as for Rb<sub>1-x</sub>Cs<sub>x</sub>Cl:Pb. We utilized the factorized approach,



**Fig. 2.** Temperature dependence of phonon frequencies for the LO and TO-modes in  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}$  (undoped and doped with Pb). Lines are drawn to guide the eye. From  $\omega_1$  and  $\omega_3$  curves the influence of  $\text{CsPbCl}_3$  complexes on the respective mode splitting is evident.

suggesting that complex dielectric function can be expressed in the form [33]

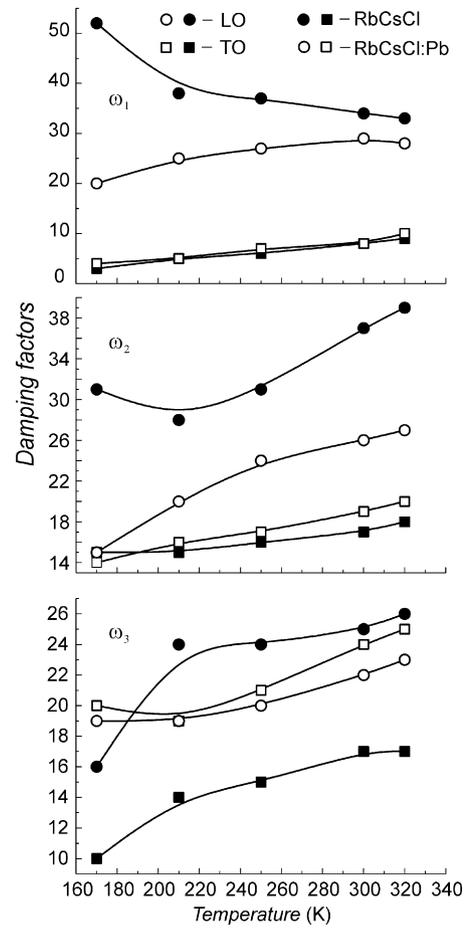
$$\varepsilon(\omega) = \varepsilon_\infty \prod_i \frac{\omega_{i\text{LO}}^2 - \omega^2 + j\Gamma_{i\text{LO}}\omega}{\omega_{i\text{TO}}^2 - \omega^2 + j\Gamma_{i\text{TO}}\omega} \quad (3)$$

and considering the relationship between the reflectivity factor  $R$  and  $\varepsilon$ , known as the Fresnel formula [34]

$$R(\omega) = \left( \frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1} \right)^2. \quad (4)$$

In order to compare the vibrational parameters of IR-active modes of the pure  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}$  crystals and crystals, containing nano-inclusions of  $\text{CsPbCl}_3$ , the frequencies of the LO- and TO-modes,  $\omega_{\text{LO}}$  and  $\omega_{\text{TO}}$ , the respective damping constants  $\Gamma_{\text{TO}}$ ,  $\Gamma_{\text{LO}}$  and the optical dielectric constant  $\varepsilon_\infty$  have been estimated for each measured temperature. For this purpose we used the non-linear least-squares fitting of the calculated reflectivity to the experimental data. The results are shown in Figs. 2–4; numerical values are presented in Table 1.

It is worth noting that the largest difference between the investigated crystals becomes apparent in the behavior of phonons corresponding to  $i = 1, 3$  while there is strong resemblance in the behavior of LO–TO splitting, phonon frequencies and  $\Gamma_{2\text{TO}}$  values for both crystals when  $i = 2$  (damping constants  $\Gamma_{2\text{LO}}$  in the latter case distinguish and behave differently). Below these modes  $\omega_{1\text{LO}}$  and  $\omega_{1\text{TO}}$  frequencies are very close (within the error



**Fig. 3.** Temperature dependence of phonon damping constants for the LO and TO modes in  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}$  (undoped and doped with Pb), demonstrating the effect of  $\text{CsPbCl}_3$  nanocrystals on the  $\Gamma_{1\text{LO}}$ ,  $\Gamma_{2\text{LO}}$ ,  $\Gamma_{3\text{TO}}$  and  $\Gamma_{4\text{LO}}$  parameters. Lines are drawn to guide the eye.

of their determination) in case of pure  $\text{Rb}_{1-x}\text{Cs}_x\text{Cl}$  whereas large splitting is observed for  $\text{Rb}_{1-x}\text{Cs}_x\text{Cl}:\text{Pb}$ , which is slightly decreasing at elevating temperatures.  $\Gamma_{1\text{TO}}(T)$  curves are almost identical for both crystals;  $\Gamma_{1\text{LO}}$  factor of  $\text{Rb}_{1-x}\text{Cs}_x\text{Cl}$  at 170 K is found to be more than 2 times larger than those of the doped crystal, however this difference almost vanishes when at  $T > 300$  K.  $\omega_{3\text{LO}} - \omega_{3\text{TO}}$  difference in case of  $\text{Rb}_{1-x}\text{Cs}_x\text{Cl}$  is about  $12 \text{ cm}^{-1}$  and varies slightly in temperature range 170–320 K. For  $\text{Rb}_{1-x}\text{Cs}_x\text{Cl}:\text{Pb}$  crystals this difference is  $\sim 6 \text{ cm}^{-1}$  at 320 K and diminishes to zero at 170 K. For this phonon mode both TO and LO damping factors exhibit different temperature behavior.

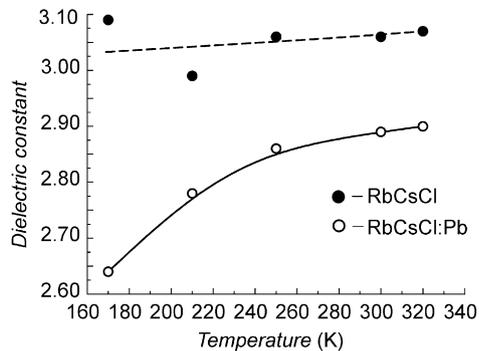
Optical dielectric constant of pure crystals, as shown in Fig. 4, falls within the range 3.0–3.1, while in case of  $\text{Rb}_{1-x}\text{Cs}_x\text{Cl}:\text{Pb}$   $\varepsilon_\infty$  increases monotonically from  $\sim 2.6$  (at 160 K) up to 2.9 at 320 K.

Summarizing the results depicted in Figs. 2–4 and values in the Table 1, one can outline several effects arising from the presence of  $\text{CsPbCl}_3$  nanocrystals in the  $\text{RbCsCl}$  host. In particular,  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}:\text{Pb}$  crystals show essentially larger LO–TO splitting of the modes at  $117 \text{ cm}^{-1}$  and  $173 \text{ cm}^{-1}$  as clearly exhibiting different temperature behaviour of phonon damping constants (except of  $\Gamma_{1\text{TO}}$  and  $\Gamma_{2\text{TO}}$ ). Besides that, the dielectric constant values at high frequency limit ( $\varepsilon_\infty$ ) for Pb-enriched material are generally lower at respective temperatures than those for undoped crystals and in case of  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}:\text{Pb}$  more pronounced non-linear temperature variation of  $\varepsilon_\infty$  is observed.

The increase of LO–TO splitting for low and high energy modes and slight decrease in the case of mode at  $\sim 135 \text{ cm}^{-1}$  cm

**Table 1**Phonon frequencies (in  $\text{cm}^{-1}$ ), damping constants and optical dielectric constants of  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}$  and  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl:Pb}$  at several temperatures.

Crystal	Temperature (K)	$\omega_{1\text{LO}}$	$\omega_{1\text{TO}}$	$\Gamma_{1\text{LO}}$	$\Gamma_{1\text{TO}}$	$\omega_{2\text{LO}}$	$\omega_{2\text{TO}}$	$\Gamma_{2\text{LO}}$	$\Gamma_{2\text{TO}}$	$\omega_{3\text{LO}}$	$\omega_{3\text{TO}}$	$\Gamma_{3\text{LO}}$	$\Gamma_{3\text{TO}}$	$\epsilon_{\infty}$
$\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}$	170	119.2	121.7	52	3	172.1	136.8	31	15	176.4	175.9	16	10	3.09
	210	118.4	120.6	38	5	167.2	136.1	28	15	178.9	175.1	24	14	2.99
	250	118.3	119.4	37	6	164.2	135.1	31	16	178.4	174.3	24	15	3.06
	300	117.5	117.9	34	8	159.9	133.8	37	17	177.4	173.4	25	17	3.06
	320	117.2	117.1	33	9	158.4	133.3	39	18	176.3	172.4	26	17	3.07
$\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl:Pb}$	170	139.4	115.5	20	4	166.1	138.2	15	14	183.3	171.4	19	20	2.64
	210	136.6	115.1	25	5	164.7	136.3	20	16	181.9	172.4	19	19	2.78
	250	133.3	114.4	27	7	161.1	134.3	24	17	181.3	171.7	20	21	2.86
	300	127.3	114.0	29	8	157.4	131.7	26	19	180.8	170.2	22	14	2.89
	320	125.9	113.4	28	10	156.0	130.7	27	20	180.4	169.3	23	25	2.90

**Fig. 4.** Temperature dependence of high frequency dielectric constant  $\epsilon_{\infty}$  for  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl}$  (pure and containing cesium lead chloride nanocrystals).

indicate the significant change in the electronic system of the material due to the variation of the dynamic charges caused by Pb atoms. Temperature dependence of LO–TO splitting could also be a manifestation of some increase of the host lattice ionicity (even considering that  $\text{RbCsCl}$  lattice is ionic) and a signature of some covalent character of unsaturated bonds. Taking into account the temperature behaviour of  $\omega_1$  and  $\omega_3$ , it is natural to assume that these two modes are related to the vibrations of cations and  $\omega_2$  frequency characterizes the vibration the anion (Cl). On the other hand, considering the masses of atoms,  $\omega_1$  should be ascribed to the vibration of Cs atoms and  $\omega_2$ —to the atoms of rubidium whereas  $\omega_3$  should correspond to Cl atoms. In the latter case (which is in better agreement with the obtained results) the splitting is increasing for the Cs–Cl bond—this is explained by the fact that the ionic radius of Cs is larger than that of rubidium and Cs–Cl bond is expected to be more covalent due to overlapping of the atomic orbitals. After introducing of Pb ion in the matrix the polarization of such bond is favorable, inducing the increase of Born effective charges, which express the integrated oscillator strength, and, consequently, leading to the larger LO–TO splitting, observed experimentally.

Lower TO frequencies in case of lead-containing crystals may result from the hydrostatic pressure; this assumption however should be verified by carrying out vibrational spectroscopy of pure  $\text{RbCsCl}$  crystals under pressure and estimation of Gruneisen parameters.

#### 4. Conclusion

Prolonged ( $\sim 100$  h) high-temperature ( $T = 200^\circ\text{C}$ ) annealing of  $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{Cl:Pb}$  crystals with the structure of NaCl type results in the formation of the  $\text{CsPbCl}_3$  nanocrystals dispersed in the corresponding matrix. In the collected FIR spectra bands corresponding to  $\text{CsPbCl}_3$  nanocrystals cannot be separated since the ranges of intrinsic absorption of the host matrix ( $\text{RbCsCl}$ ) and

$\text{CsPbCl}_3$  [35] coincide. However through the detailed analysis it has been shown that introducing of cesium lead chloride in the form of nano- and microcrystals modifies the spectral properties of the host material in the far infrared domain, being apparent in the temperature behavior of LO–TO splitting of phonons related to the vibration of the cesium and chloride atoms. Observed effects are partially due to the deformation of the host lattice.

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