



INFRARED SPECTROSCOPIC STUDY OF PHASE TRANSITIONS IN NEW FERROELASTOELECTRIC $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$ CRYSTAL DOPED WITH COPPER

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Infrared spectroscopic investigations of $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$ crystal doped with copper (IPACCC) have been done in a wide temperature range covering the ferroelastoelectric phase in order to get more information about the nature of the phase transitions. The structure of the doped IPACCC crystal was found to be close to the structure of the initial one (IPACC). The Cu^{2+} ion in the IPACCC crystal statistically replaces Cd^{2+} ion in the anionic complex consisting of three “metal-halogen” octahedra with different orientation of their axes relatively to the main crystallographic directions. The phase transitions have been confirmed at $T_1 = 358$ K, $T_2 = 293$ K and $T_3 = 253$ K. These changes were clearly detected by the shifts or jumps of wavenumbers and intensities of modes mostly connected with internal vibration within isopropylammonium cation.

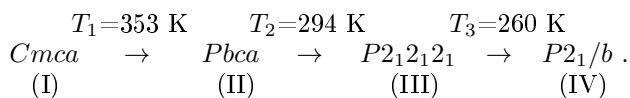
Key words: transition metal, infrared spectroscopy, crystal structure, phase transitions, isomorphous substitution, molecular interactions.

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I. INTRODUCTION

The IR spectra are an important source of information on interactions and molecular dynamics and usually are used to study phase transitions in newly grown crystals. Such an approach was used for the recently synthesized initial crystal of tetra (isopropylammonium) decachlorotricadmate (II) with chemical formula $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$ (IPACC) [1]. Their structure is built of the two dimensional network of $\text{Cd}_3\text{Cl}_{10}$ units interconnected by isopropylammonium cations. Taking into account that the related hybrid organic–inorganic compounds show unusual structural architectures of the halogenocadmate (II) complexes and chemical flexibility, it is possible to create different crystal structures to optimize their physical properties [2, 3]. These hybrid organic–inorganic crystals containing different organic cations and inorganic anions exhibit structural phase transitions of various types and they are a subject of numerous investigations [4–18].

IPACC exhibits several temperature-dependent phase transitions and therefore the structures of the individual phases were studied. Dielectric, dilatometric, X-ray, differential scanning calorimetry (DSC), birefringence and heat capacity studies [18–20] revealed three phase transitions presented in the scheme below (T_1 , T_2 and T_3 indicate the phase transitions temperatures):



The phase transition at 353 K is associated with the distortion of the anionic sublattice and is displacive in character, whereas the remaining transformations are dominated by the order-disorder phenomena of the cationic sublattice.

Phase transitions in the IPACC crystal have been studied by different methods of vibrational spectroscopy in a wide temperature range. The temperature changes of the bands parameters were analyzed in order to clarify cationic and anionic contributions to the phase transitions mechanism. The current results derived from DSC and infrared measurements revealed an additional phase transition at $T_4=120$ K [1].

One can suppose that the partial substitution of the cadmium ion with copper would affect the phase transitions in IPACC crystal, first of all, their temperatures, since the inorganic anions influence the dynamics of the organic cations, that are responsible, at least, for the two low temperature phase transitions. Moreover, it is necessary to note that due to doping with Cu^{2+} ions, new $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}:\text{Cu}$ (IPACCC) compounds become of special interest to scientists, since they could reveal principally new magnetic properties and possible magnetoelectric coupling. Indeed, the related crystals with an alkylammonium cation and transition metal ions in their structure were found to be multiferroics since they are characterized by the coexistence of ferroelectric and magnetic ordering [21–23]. Besides, it has been shown that the partial isomorphous replacement of Al^{3+} ion with transition metal Cr^{3+} is followed by a drastic change of magnetic and electric properties in the paramagnetic ferroelectric $\text{NH}_2(\text{CH}_3)_2\text{Al}_{1-x}\text{Cr}_x(\text{SO}_4)_2 \times 6\text{H}_2\text{O}$ in comparison with an initial diamagnetic crystal with $x = 0$. Moreover, it was demonstrated that by varying the rate of the replacement ($x = 0.065$; $x = 0.20$) one can induce and even tune a sign of the magnetoelectric interactions that were found to be among the largest in the family of the known multiferroics [24]. Therefore, one can conclude that the effective interaction between magnetic moments and electric charges, which is considered to



be an important phenomenon in the modern solid state physics and spin electronics, would be realized in the organometallic compounds by means of isomorphous substitution of transition metal ions [24].

On the other hand, the compounds of such a type could be also interesting for nonlinear optics applications [25–26]. Doping these crystals with transition metal ions raises a possibility of quite large photoinduced effects, for example, a second harmonic generation.

For the first time, the properties of doped IPACCC crystals were reported in [27, 28]. The EDX analysis showed that the amount of Cu doping did not exceed 0.5%. It was suggested that the sequence of phases and their structure in IPACCC is very similar to those in the initial crystals and some Cd atoms are statistically replaced with Cu atoms in anionic complex $[\text{Cd}_3\text{Cl}_{10}]^{4-}$. This conclusion is confirmed by the data of X-ray diffraction, heat capacity and the crystal field spectra study of IPACCC crystals [27]. Besides it was shown that the temperatures of corresponding phase transitions in the doped crystals are somewhat shifted compared to the initial one:

$$\begin{array}{ccccccc} T_1=358 \text{ K} & & T_2=293 \text{ K} & & T_3=253 \text{ K} & & \\ Cmca & \rightarrow & Pbcn & \rightarrow & P2_12_12_1 & \rightarrow & P2_1/b . \\ \text{(I)} & & \text{(II)} & & \text{(III)} & & \text{(IV)} \end{array}$$

Phase III was found to be ferroelastoelectric since the corresponding domain structure was visualized using the different modes of the atomic force microscopy [28]. The analysis of the temperature dependence of the optical birefringence increment showed that the phase transition at $T_2 = 293 \text{ K}$ would be related to the first order close to the second order ones [28]. The investigated compounds can be considered as a secondary ferroic with a ferroelastoelectric phase. Their investigations are of special interest, since only a few specific examples of high order ferroics are currently known. This is because they are difficult to identify. Under such circumstances, the IR studies at different temperatures have been undertaken to study the molecular interactions' contribution to the phase transition mechanisms. Since the low temperature phase transitions in the IPACCC crystal are due to the change in the dynamical states of isopropylammonium cations $[(\text{CH}_3)_2\text{CHNH}_3]^+$, this should be related to the modifications of positions and shapes of the IR bands corresponding to the internal vibrations of these cations.

II. EXPERIMENTAL

Light yellow $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}:\text{Cu}$ (IPACCC) crystals were grown at $T=304 \text{ K}$ from an aqueous solution of $\text{CdCl}_2 \times 4\text{H}_2\text{O}$, CuCl_2 and $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ salts taken in the stoichiometric ratio with a small excess of HCl. The crystals were easily grown and they exhibited a distinct cleavage plane perpendicular to the b axis. Large and good quality crystals were obtained after about 4 weeks.

The Cd to Cu ratio in the samples was examined by SEM using a REMMA-102-02 (SEMI, Sumy, Ukraine)

scanning electron microscope. EDX was carried out by using an energy-dispersive X-ray analyzer with the pure elements as standards for Ag and Ge, ZnS for S, and KBr for Br (the acceleration voltage was 20 kV; K - and L - lines were used). The EDX analysis showed that the amount of Cu doping does not exceed 0.5 %. On the other hand, the pronounced yellowish color of the samples clearly indicates that Cu^{2+} ions are incorporated into the crystal structure [27].

Temperature dependent IR spectra were recorded with the resolution of 2 cm^{-1} in the range $50\text{--}4000 \text{ cm}^{-1}$ using a Bruker IFS-88 Fourier transform infrared (FT-IR) spectrometer. IR measurements were made on the basis of polycrystals in Nujol. The samples were measured between KBr windows in the temperature range of their phase transitions $400\text{--}240 \text{ K}$. An APD Cryogenics closed cycle helium cryogenic system (DE201) was used to control the temperature below room temperature. For the measurements of the IR spectra above room temperature, the Variable Temperature Cell SPECAC was used. The FIR spectrum was measured with Bruker IFS-88 applying polyethylene windows. For the spectroscopic data analysis, the multifunctional Galactic GRAMS/386 program was used. The error range for the determination of the peak position was $\pm 0.5 \text{ cm}^{-1}$ after the accumulation of the data and the fitting procedure.

III. RESULTS AND DISCUSSION

A. Infrared spectra of IPACCC crystals

The Fourier-transform infrared (FT-IR) spectra of IPACCC crystals were measured in the range of $50\text{--}4000 \text{ cm}^{-1}$ at 300 K (Fig.1).

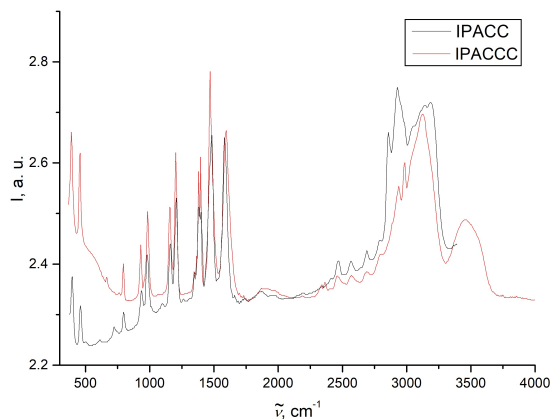


Fig. 1. Comparison of IR spectra of IPACC and IPACCC crystals in the range $300\text{--}4000 \text{ cm}^{-1}$ at 300 K

The factor group analysis of the fundamental modes in phase II (Table 1) was performed by analogy with the initial IPACC crystal [1]. On the basis of the data of the XRD study [27], one can assume that Cu^{2+} ions statistically replace Cd^{2+} ions in their anionic complex. Classification of the fundamental modes in other phases also would be performed by analogy with the case of the IPACC crystal [1].

	A_c	Lattice mode			Internal modes			Selection rules	
		IPA		$[\text{Me}_3\text{Cl}_{10}]^{4-}$	IPA1	IPA2	$[\text{Me}_3\text{Cl}_{10}]^{4-}$	IR	Raman
		L	T						
D_{2h}									
A_g		6	6	3	36	36	15	i	zx, yy, zz
B_{1g}		6	6	3	36	36	15	i	xy
B_{2g}		6	6	3	36	36	15	i	zx
B_{3g}		6	6	3	36	36	15	i	yz
A_u		6	6	3	36	36	18	i	i
B_{1u}	1	6	6	2	36	36	18	Z	xy
B_{2u}	1	6	6	2	36	36	18	Y	xy
B_{3u}	1	6	6	2	36	36	18	X	xy

Table 1. Classification of the fundamental modes for the IPACCC crystal (phase II). Abbreviation: A_c – acoustic modes, T – translational modes lattice modes, L – librational type lattice modes, i – inactive

The wavenumbers, relative intensities and proposed assignments of the internal vibrations at 300 K in IPACCC were compared with those in the initial IPACC crystal (Table 2). These characteristics were obtained for both crystals in Nujol, whereas the assignment of the modes for IPACC in the low frequency range was performed also taking into account the data obtained in Fluorolube mulls (the corresponding data are marked by stars in Table 2).

The assignments of the modes proposed in Table 2 have been based on the comparison with the IR spectra of isopropylammonium cations [14, 29, 30] and the vibrational spectra of the isopropylamine molecule [31].

As follows from the X-ray diffraction data [18] for the initial crystal, one can suppose that IPACCC is characterized by a disorder of the isopropylamine cations in all phases. The C–C (between 1.634 and 1.35Å) and C–N (between 1.405 and 1.529Å) distances in the IPACC crystal indicate disorder. According to the structural parameters of an isolated isopropylamine molecule [32], those distances should be 1.522Å (for CC) and 1.466Å (CN), correspondingly. The disorder observed using the X-ray structure analysis of the initial crystal may be checked by the vibrational spectra of IPACCC. Thus, the presence of IPA cations with different structures should lead to the splitting of some bands arising from internal modes of IPA cations. The most useful for this purpose seem to be those internal modes in which the skeleton vibrations play the most important role, and those internal modes which give rise to the bands appearing in the regions free from other vibrations. The analysis of the IR spectra shows that such conditions are fulfilled by the band appearing at 800 cm^{-1} , corresponding to the symmetric skeletal stretching vibration $\nu_s(\text{CCC})$ [31, 32]. At 300 K, a single band at 796 cm^{-1} was observed, slightly asymmetric from the low wavenumbers side. This observation clearly shows that the IPA cations are not statistically disordered and moreover, all cations are structurally identical, at least from the skeleton point of view.

Most of the bands for both crystals coincide in frequency that testifies to their similar structure. In this case, the anionic complex has the same symmetry and consists of three “metal-halogen” octahedra of two types

[27]. The octahedron of the first type is more distorted along the Z-axis, whereas in the octahedra of type II the distances of the “metal-ligand” in the equatorial plane and along the Z-axis are closer [27].

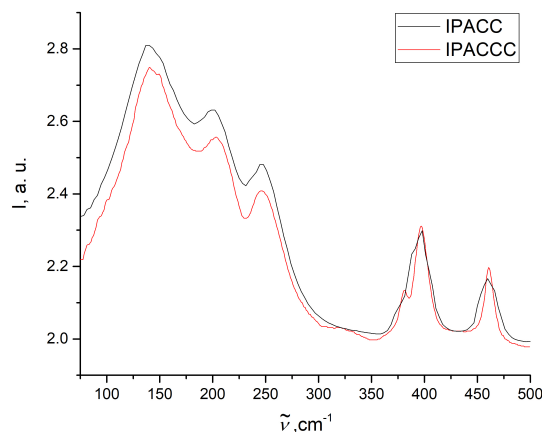


Fig. 2. The infrared spectra of IPACCC crystals at 300 K in the range 50–500 cm^{-1}

It is known that the internal vibrations of the metal-halogen complex as well as the skeletal vibrations of the organic cation manifest themselves in the low-frequency region of the spectrum. Taking into account that the isomorphous substitution first of all affects these types of vibrations, let us compare the IR spectra of both compounds in the spectral range of 50–600 cm^{-1} in detail (Fig. 2). One can note the appearance of a clear additional band in IPACCC at 381 cm^{-1} . It is connected with the splitting of $\delta_s(\text{CCC})$ skeletal mode due to the interaction of the IPA groups with the octahedra containing Cu^{2+} and Cd^{2+} , respectively. Besides, a new very weak band with a maximum at 320 cm^{-1} appears in the IR spectrum of IPACCC. It would be identified as $\nu_3(\text{Cu-Cl})$ vibrational mode in the octahedron. Besides, the replacement with Cu^{2+} ion is followed by the splitting of the band at 140 cm^{-1} with the appearance of a new shoulder at 149 cm^{-1} . This new band corresponds to $\nu_2(\text{Cu-Cl})$ vibrational mode of the octahedron, which is shifted toward higher frequencies comparing to the analogous mode $\nu_2(\text{Cd-Cl})$.

IPACC IR in nujol $T=300$ K	IPACCC IR $T=300$ K	Assignment
	3461	Intra-ions transition of Cu^{2+}
3186 vs		$\nu_a(\text{NH}_3^+)$
3140 vs	3131	$\nu_a(\text{NH}_3^+)$
3105 s,sh		$\nu_s(\text{NH}_3^+)$
3045 s,sh		$\nu_s(\text{NH}_3^+)$
2983 s*	2981	$\nu_a(\text{CH}_3)$
2936 s*	2935	$\nu_a(\text{CH}_3)$
2888 s,sh		$\nu(\text{CH}_3)$
2852 vs		$\nu_s(\text{CH}_3)$
	2802	$\nu(\text{CH})$
2787 vw		
2687 vw	2689	
2640 vw,sh	2640	
2562 vw	2566	
2475 vw, sh		
2461 vw	2462	
2408 vw	2407	
2359 vw*	2361 w	
	2340 w	
2333 vw*		
	2321	
2281 vw*		
2194 vw	2193	
	1946	
	1873	
1860 vw		
1800 vw	1790 vw	
	1716	
1697 vw	1690 vw	
	1652 vw	
1623 s, sh		$\delta(\text{NH})$
1617 s, sh		
1584 vs, sh	1580	$\delta_a(\text{NH}_3^+)$
1579 vs		$\delta_a(\text{NH}_3^+)$
1483 vs		$\delta_a(\text{NH}_3^+)$
	1476	$\delta_s(\text{NH}_3^+)$
1470 s, sh		$\delta_s(\text{NH}_3^+)$
1462 m*		$\delta_a(\text{CH}_3)$
1449 w*		$\delta_a(\text{CH}_3)$
1401 m	1396	
1383 m	1382	$\delta_s(\text{CH}_3)$
1374 nm, sh		$\delta_a(\text{CH}_3)$
1366 nw, sh		
1348 w		$\delta(\text{CH})$
1303 vw, sh		
1205 m	1202	$\nu(\text{NH}_3^+)$
	1162	
1158 m		$\nu_a(\text{CCC})$
994 w, sh	991	
	984	
979 m		$\nu(\text{CH})$
	960	$\varrho(\text{CH}_3)$
956 vw		$\varrho(\text{CH}_3)$
938 w		$\varrho(\text{CH}_3)$
	932	
928 vw, sh		$\varrho(\text{CH}_3)$
893 vw, sh		
	797	$\nu_s(\text{CCC})$
	668	$\delta(\text{CCN})$
460 m	460	$\delta(\text{CCN})$
	431	$\delta(\text{CCN})$
396 m	397m	$\delta_s(\text{CCC})$
	381 w	$\delta_s(\text{CCC})$
	325 vw	$\nu_3 \text{ Cu-Cl}$
247 m*	246 m	$\nu_1 \text{ Me-Cl}$
202 m*	203 m	$\nu_4 \text{ Me-Cl}$
	149 s, sh	$\nu_2 \text{ Cu-Cl}$
140 vs*	141vs	$\nu_2 \text{ Cd-Cl}$
101 m,*	101 m	$\nu_5 \text{ Me-Cl}$
	76	trans CCN
	62	

* – IR bands of IPACC crystal in Fluorolube+FIR at 300 K

Table 2. Experimental wavenumbers (cm^{-1}), relative intensities and assignments of the bands observed in the IR spectra of $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$ [1] and $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}:\text{Cu}$ crystals.

B. Temperature evolution of IR spectra IPACCC crystals

In general, the IR spectra in the low temperature range are considerably different from those at 300 K and high temperatures (i.e. at 400 K). The temperature evolution of the bands attributed to internal vibrations of CH_3 , NH_3^+ groups of IPA molecule and their overtones, including phases I, II, III and IV, when the samples cooled down to 248 K, is depicted in Fig. 3.

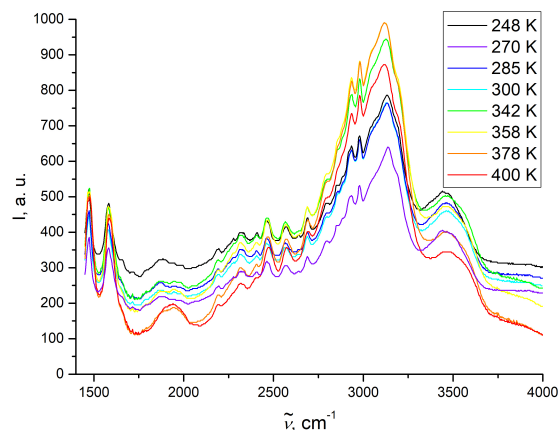


Fig. 3. IR spectra of IPACCC crystal at different temperatures

Unfortunately, the number of temperatures, at which the measurements were performed, was limited. As a result, we hardly could determine the exact temperatures of the phase transitions on the basis of the observed temperature changes of IR spectra, but it is possible to draw conclusions about the trends of structural changes in certain phases. The exact temperatures of phase transitions were taken from the previous calorimetric and optical-spectral studies [27, 28].

Compared to the initial crystal [1], a wide asymmetric band arises in IPACCC with a maximum at 3464 cm^{-1} . The band was reported in paper [27] and was related to the intra-ion transitions of Cu^{2+} ion. It has been shown that this complex band consists of two elementary contours corresponding to the allowed and forbidden electronic transitions from the ground at the excited state of $3d^9$ configuration of Cu^{2+} ion in the octahedral complexes of low symmetry. The position and intensity of this complex band are considerably dependent on temperature. The most noticeable changes of both parameters are observed at cooling below the phase transition point $T_2 = 293 \text{ K}$, when the entire band is shifted toward lower values of the wave number and its intensity (oscillator strength) decreases. The latter parameter considerably decreases also above $T_1 = 358 \text{ K}$. Such a behavior reflects considerable changes in the level of distortion of the metal-halogen octahedra. The band is characterized by a maximal intensity in phase II lying between T_1 and T_2 . The increase in intensity would be related to a partial removal of the selection rule by parity due to the distortion of the metal-halogen complexes.

According to the data of [27], this concerns first of all the second type of octahedra which was found to be the most tetragonally distorted in phase II.

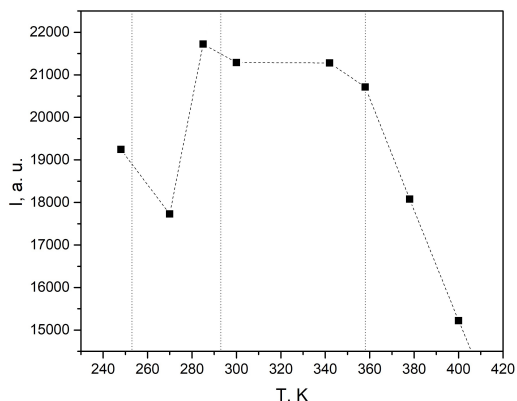


Fig. 4. Temperature dependence of the area under the contour of the asymmetric band with a maximum at 3464 cm^{-1} proportional to the oscillator strength

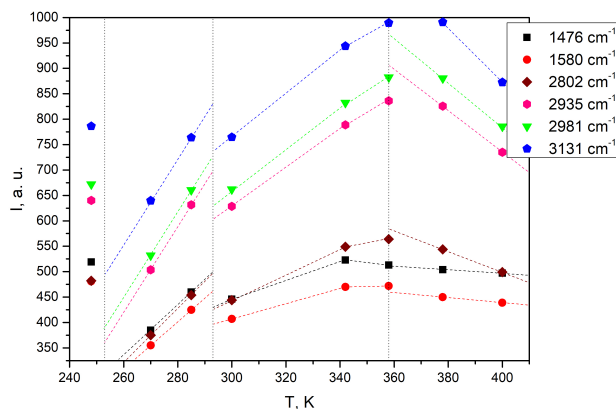


Fig. 5. Temperature evolution of IR bands intensity of IPACCC crystal in the ranges $1380\text{--}1600\text{ cm}^{-1}$ and $2800\text{--}3140\text{ cm}^{-1}$

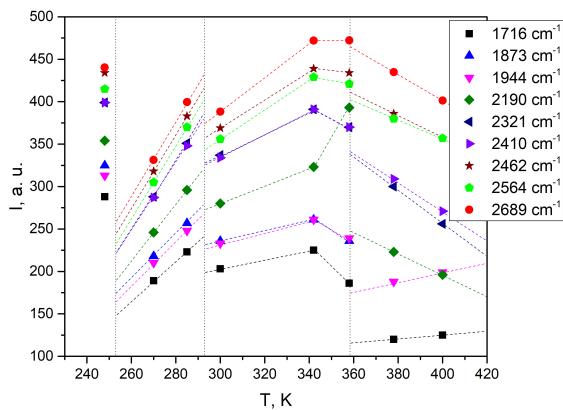


Fig. 6. Temperature evolution of IR bands intensity of IPACCC crystal in the range $1715\text{--}2690\text{ cm}^{-1}$

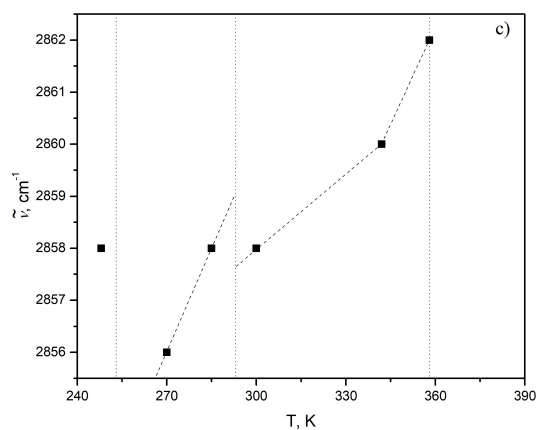
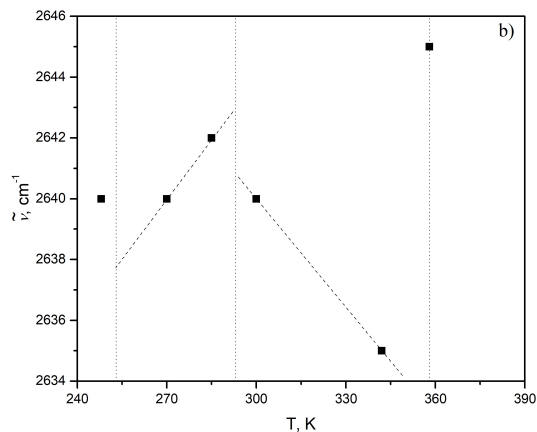
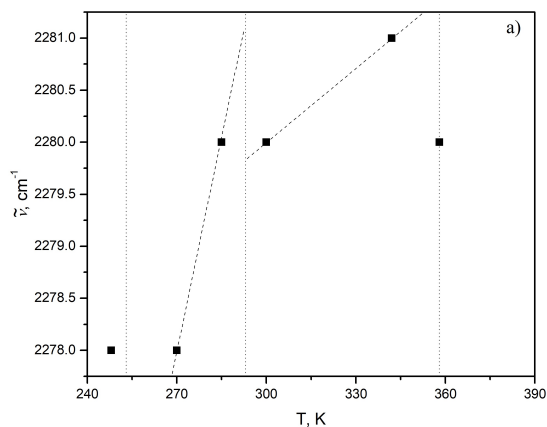


Fig. 7. Temperature evolution of wavenumbers positions for the bands at: a) – 2280 cm^{-1} ; b) – 2640 cm^{-1} ; c) – 2857 cm^{-1}

Please note, that the dashed lines in Figs.4–7 and 9 show the trend of corresponding changes within a certain phase and are used only to guide the eye. The dotted lines indicate phase transition temperatures.

Other bands identified in Table 2 would be considered as vibrational modes. Their intensity and wavenumbers positions undergo substantial changes with temperature

due to the phase transitions. Let us consider in detail the modes most sensitive to the phase transitions.

We took into account that the temperature changes of the metal-halogen polyhedra at the phase transitions were carefully studied on the basis of the analysis of the crystal field spectra [27]. On the other hand, the temperature evolution of the skeletal modes of IPA group in IPACC was discussed in [1]. We do not expect any difference in their behavior in IPACCC in respect to the initial crystal. Under such circumstances we will analyze in detail the temperature changes of the bands lying at higher frequencies (wavenumbers).

Fig. 5, 6 present the temperature evolution of the intensity of the bands observed in the IPACCC crystal in the range of 1470–3200 cm^{-1} . In Fig. 5, there are the data concerning the modes that correspond to the internal vibrations of the ammonium head and methyl groups and were found to be sensitive to the phase transitions. First of all, it is necessary to mention the anomalous behavior of the modes around 1476 and 1576 cm^{-1} corresponding to the symmetric and asymmetric bending vibrations of NH_3^+ group, respectively. They are effectively not sensitive to the high temperature phase transition at T_1 , while manifesting considerable changes at the low temperature ones at T_2 and T_3 . Their behavior correlates with corresponding structural changes. The phase transition at T_1 is associated with the distortion of the anionic sublattice and is displacive in character, whereas the remaining transformations are dominated by the order-disorder phenomena of the cationic sublattice [18-20]. That is why the phase transitions at T_2 and T_3 mostly affect the bending vibrations of NH_3^+ group. It is necessary to take into account that the ammonium head participates in the formation of the hydrogen bonds and the latter are changed at the low temperature transitions of the order-disorder type. Such a difference is less pronounced for the stretching vibrations of NH_3^+ and CH_3 groups (2935–3135 cm^{-1}) although the low temperature phase transition is followed by a very sharp change of the corresponding modes intensity.

Fig. 6 presents the temperature change of the bands observed in the region of 2000–3200 cm^{-1} . Although these modes are identified as the overtones in respect to the skeletal vibrations of IPA and different types of vibrations of ammonium and methyl groups, they were found to be sensitive to phase transitions. The sharpest jump in intensity was observed in the vicinity of the PT at $T_1 = 358 \text{ K}$ for the band at 2190 cm^{-1} . It means that IPA cations are involved in the transition of the displacive type. The intensities of this mode as well as of the other presented in Fig. 7 also are changed at the low temperature phase transitions connected with the organic cations ordering, which looks reasonable.

The temperature dependence of the wavenumbers positions of some bands found in the range between 2280 and 2860 cm^{-1} (Fig. 7) looks more sensitive to the influence of the phase transitions. Most of them are considered as the overtones of the different vibrations within the organic complex. In particular, the modes at 2280 cm^{-1} (overtone of $\nu_a(\text{CCC})$ stretching mode), 2640

cm^{-1} (overtone of $\delta(\text{CH})$) and 2857 cm^{-1} (overtone of $\delta(\text{CH}_3)$) appear only at cooling below T_1 temperature.

The most pronounced manifestation of the high temperature phase transition at T_1 was observed for the band in the range of 1850–1970 cm^{-1} designated as an overtone to the stretching $\nu_s(\text{CCC})$ mode at 797 cm^{-1} . The temperature evolution of this band is shown in Fig. 8. In phase I only one band with a maximum at 1940 cm^{-1} was observed. At T_1 (I–II) it is split. In phases II and III already two bands at 1869 cm^{-1} and 1944 cm^{-1} are observed.

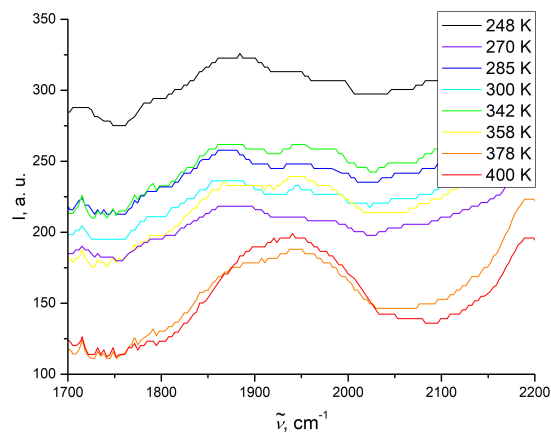


Fig. 8. Temperature evolution of IR spectra of IPACCC crystal in vicinity of the band at 1940 cm^{-1}

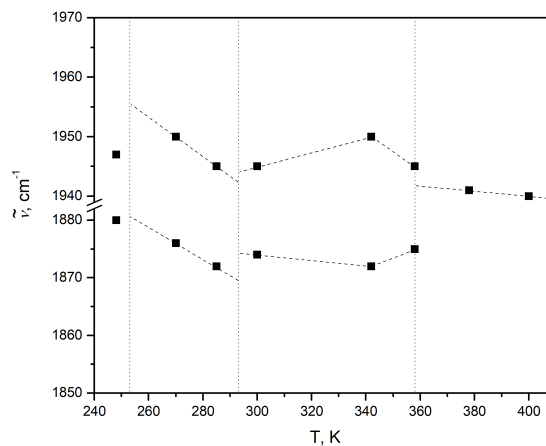


Fig. 9. Temperature evolution of vibrational band at 1940 cm^{-1}

The observed splitting correlates well with the data of previous investigations of the IPACC crystal [1]. The IR studies showed that the $\nu_a(\text{CCC})$ asymmetric stretching and $\delta(\text{CH}_3)$ modes of internal vibrations of the isopropylammonium cation are observable in the whole temperature range as well as exhibit temperature anomalies in the vicinity of the critical point temperatures T_1 , T_2 and T_3 . This means that the changes

in the dynamical state of the cation are noticeable. The intensity of these bands decreases with a decrease of temperature. This is due to the fact that in phase III two groups of cations are arranged — these are cations IPA-B and IPA-C. Such behavior is also observed in the ferroelastoelectric phase III in IPACCC (see Fig. 5).

The presence of different numbers of distinct IPA cations, depending on the particular phase, leads to a different degree of Davydov splitting of the bands that are associated with internal vibrations of these cations. This alteration shows that not only the $\nu_s(\text{CCC})$ modes but also the corresponding overtones are very sensitive to the temperature changes.

As follows from the analysis of the IR spectra temperature evolution for IPACCC crystals (Figs 3–9), in the vicinity of the temperatures $T_1 = 358$ K, $T_2 = 293$ K and $T_3 = 253$ K, which can be attributed to the PT, there are anomalies in the parameters of the vibrational modes, first of all of isopropylammonium groups, which are responsible for the phase transitions.

IV. CONCLUSIONS

Wide temperature range vibrational analyses have been done in order to get more information about the role of the cation contributions to the mechanism of the phase transitions in IPACCC crystals. The structure of IPACCC crystal was found to be close to the structure of IPACC initial crystal. In this case, the anionic complex possesses the same symmetry and consists of three “metal–halogen” octahedra with different orientation of their axes relatively to the main crystallographic directions. The Cu^{2+} ion in the IPACCC crystal statistically replaces the Cd^{2+} ion.

In comparison with initial IPACC the new wide

asymmetric band with a maximum at 3464 cm^{-1} has been detected. It was related to intra-ion transition in Cu^{2+} . It is shown that the temperature evolution of its intensity and position reflects the change of distortion level of the metal-halogen polyhedra and correlates with the conclusions made on the basis of analysis of the crystal field spectra [27].

In the range of $100\text{--}600\text{ cm}^{-1}$ there appear the three additional modes. The two of them have to be related to $\nu_2(\text{Cu-Cl})$ and $\nu_3(\text{Cu-Cl})$ vibrational modes in the octahedron. The third band at 381 cm^{-1} would be considered as a result of $\delta_s(\text{CCC})$ mode splitting and is caused by interaction of IPA cation with the polyhedra containing Cu^{2+} and Cd^{2+} respectively.

Besides, a detailed analysis of frequencies and intensities of the vibration modes has been made, mainly at temperatures close to the temperatures of the phase transitions. The results obtained in these investigations are in good agreement with the previous study of IPACC and IPACCC crystals [1, 27, 28].

The parameters of spectra presented in Figs. 3–8 reflect significant transformations of the crystal structure at the phase transition points. The transitions have been confirmed at $T_1 = 358$, $T_2 = 293$ K and $T_3 = 253$ K. These changes are clearly seen as shifting or jumping of wavenumbers and band intensities.

In particular, the high-temperature PT of a displacive type ($T_1 = 358$ K) is clearly manifested in the infrared spectra by appearance of additional modes corresponding to cation internal vibrations and their overtones. It has been found that the band at 1940 cm^{-1} splits into two modes at 1869 cm^{-1} and 1944 cm^{-1} at this phase transition. The low-temperature phase transitions are followed by the considerable variation of the vibration modes parameters reflecting the ordering of organic complexes.

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ВИВЧЕННЯ ФАЗОВИХ ПЕРЕХОДІВ У НОВОМУ СЕГНЕТОЕЛАСТОЕЛЕКТРИЧНОМУ КРИСТАЛІ $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$, ЛЕГОВАНОМУ МІДДЮ, МЕТОДОМ ІНФРАЧЕРВОНОЇ СПЕКТРОСКОПІЇ

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Стаття присвячена дослідженню впливу легування міддю кристалів $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$ на особливості їхньої структури. Крім цього, методами інфрачервоної спектроскопії досліджено структурні зміни під час фазових переходів у кристалах $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$, легованих міддю (ІРАССС). Їхні інфрачервоні спектри вивчали в широкому діапазоні температур, щоб отримати більше інформації про природу фазових переходів, зокрема в сегнетоеластоелектричну фазу. На основі порівняльного аналізу отриманих даних встановлено, що структура легованого кристала ІРАССС близька до структури вихідного кристала $[(\text{CH}_3)_2\text{CHNH}_3]_4\text{Cd}_3\text{Cl}_{10}$ (ІРАСС). Порівняно з вихідним кристалом виявлено нову широку асиметричну смугу з максимумом 3464 см^{-1} . Вона пов'язана з внутрішньйонними переходами в йоні Cu^{2+} . Йон Cu^{2+} в кристалі ІРАССС статистично замінює йон Cd^{2+} в аніонному комплексі, що складається з трьох здеформованих “метал-галогенних” октаєдрів з різною орієнтацією їхніх осей відносно основних кристалографічних напрямів. Крім цього, проведено детальний аналіз змін частот та інтенсивностей коливних мод, головню за температур, близьких до температур фазових переходів. Підтверджено наявність фазових переходів за $T_1 = 358\text{ К}$, $T_2 = 293\text{ К}$ і $T_3 = 253\text{ К}$. Ці зміни були чітко виявлені за змінами хвильових чисел та інтенсивностей мод, пов'язаних із внутрішніми коливаннями в катіоні ізопропіламонію (ІРА). Підтверджено, що два низькотемпературні переходи, що обмежують сегнетоеластоелектричну фазу, пов'язані з упорядкуванням органічних комплексів ІРА. Високотемпературний фазовий перехід типу зміщення ($T_1 = 358\text{ К}$) супроводжується появою додаткових смуг в інфрачервоному спектрі, які відповідають внутрішнім коливанням катіонів та їхнім обертонам. Встановлено, що під час цього фазового переходу смуга за 1940 см^{-1} розщеплюється на дві — за 1869 см^{-1} та 1944 см^{-1} .

Ключові слова: перехідні метали, інфрачервона спектроскопія, кристалічна структура, фазові переходи, ізоморфне заміщення, молекулярні взаємодії.