Optical absorption and resonance Raman scattering spectra of Lead Phthalocyanine (PbPc) and Chloroaluminum Chlorophthalocyanine (ClAlClPc) thin films

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Abstract.

The optical absorption (within 500 - 950 nm) and resonant Raman spectra (within 100 - 3000 cm^{-1}) of thin solid films of lead phthalocyanine (PbPc) and chloroaluminum chloro phthalocyanine (ClAlClPc) with thickness of 190 and 220 nm respectively were studied. The films were applied on silica substrates by thermal evaporation in a vacuum of 6.5 mPa. The optical absorption changes for ClAlClPc and PbPc films indicate that under annealing in these films undergo a phase transition from monoclinic to triclinic crystal phase. The resonant Raman spectra of the second order in the region of 1700–3050 cm^{-1} of PbPc and ClAlClPc films were obtained and analyzed. This has been done the first time for ClAlClPc films. It is shown that the Raman spectra of the second-order PbPc and ClAlClPc films are mainly formed by overtones and combinations of the first-order bands with symmetry B$_1$. The region 2550 - 2950 cm^{-1} of Raman scattering together with the vibrations of the fundamental modes in the range of fingerprints (within 1350 – 1550 cm^{-1}) for PbPc and ClAlClPc can be used to identify these substances in heterostructures and composites.

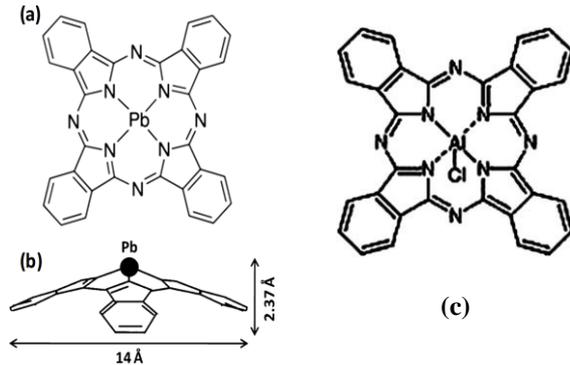# Monoclinic-triclinic phase transition in PbPc and ClAlClPc films during their thermal annealing.

Fig.1. The structures of PbPc molecule: (a) frontal and (b) lateral projections [1] and of ClAlPc molecule: (c) frontal projection [2].

Fig.2. The normalized absorption spectra of the long-wave Q- band of PbPc films with a thickness of 190, 200 and 100 nm (respectively, curves 1, 5 and 6, solid lines). Curves 2, 3 and 4 (Fig. 2a) and 7, 8 and 9 (Fig. 2b) show the results of fitting the Q -band with 3 Gaussian functions, and curves 1 and 6 cumulative forms of this band (dashed lines). The vertical arrows indicates the energy of the laser quanta (1.959 eV) to excite the Raman scattering spectra of these films.
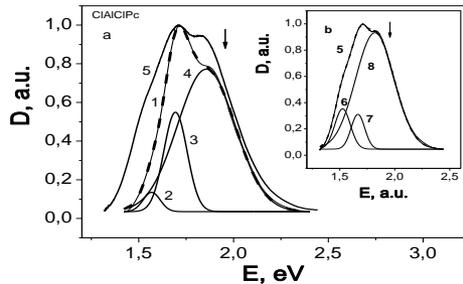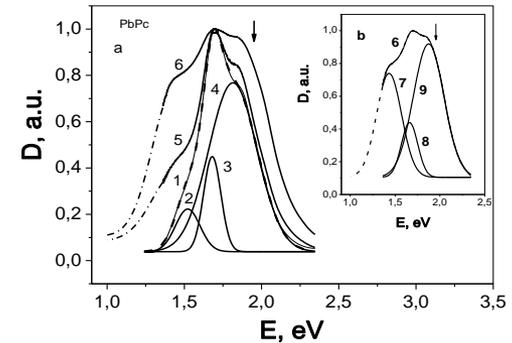

Fig.3. The normalized absorption spectra of the long-wave Q – band of ClAlClPc films with a thickness of 220 and 160 nm (respectively curves 1 and 5, solid lines). Curves 2, 3 and 4 (Fig. 3a) and 6, 7 and 8 (Fig. 3b) show the results of fitting the Q -band with 3 Gaussian functions, and curves 1 and 5 show the cumulative forms of this band (the dashed lines). The designation of the vertical arrows is the same as in Fig.2.

Figures 2a (PbPc)and 3a (ClAlClPc).
Curves 1 - not annealed films, T_{sub} = 303K.
Curves 5 – films annealed for 20 min at T_{sub} = 323K.
Curve 6 - PbPc film annealed for 40 min at T_{sub} = 343K.

[1] K.P. Madhuri et al. *Beilstein J. Nanotechol.*,**11**, p.814 (2020).
[2] M-T.S. Chani et al. *Physica E*, **45**, p.77 (2012).

Monoclinic-triclinic phase transition in PbPc and ClAlClPc films during their thermal annealing.

Table 1. The fitting parameter of structural Q-bands of the ClAlClPc and PbPc films with the 3 Gaussian functions

Compound	Energy of peaks of Gauss bands , eV.			Gauss bands width, eV			Area of Gauss bands, a.u.			Height of Gauss bands, a.u.		
	E_1	E_2	E_3	W_1	W_2	W_3	A_1	A_2	A_3	H_1	H_2	H_3
ClAlClPc 220 нм 303 K	1,57	1,69	1,86	0.11	0.15	0.36	0,01	0,08	0,28	0,10	0,51	0,73
ClAlClPc 160 нм 323 K	1,53	1,66	1,82	0.17	0.15	0.41	0,05	0,04	0,39	0,31	0,27	0,88
PbPc 190 нм 303 K	1,52	1,68	1,82	0.19	0.13	0.37	0,04	0,06	0,29	0,18	0,41	0,72
PbPc 200 нм 323 K	1.45	1.68	1.81	0.37	0.12	0.39	0.12	0.03	0.32	0.30	0.27	0.77
PbPc 100 нм 343 K	1.43	1.66	1.87	0.33	0.22	0.40	0.22	0.08	0.35	0.63	0.33	0.81

Conclusion

It is established that with increasing the substrate temperature of PbPc and ClAlClPc films from 303K to 323K, the intensity of the first low-energy Gaussian band increases and the intensity of the next Gaussian band decreases (areas A_1 and A_2, respectively). This indicates that during thermal annealing in PbPc and ClAlClPc films there is a phase transition from monoclinic to triclinic crystalline phase.

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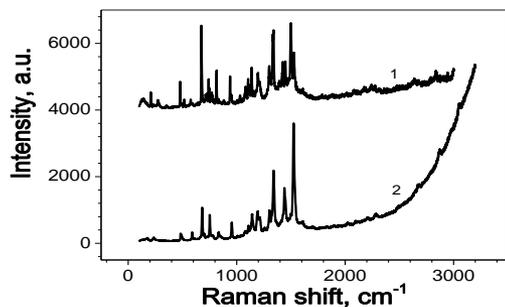# The spectra of resonant Raman scattering of PbPc and ClAlClPc films.

Fig.4. The original resonant Raman spectra of unannealed PbPc films (curve 1) and ClAlClPc (curve 2) with thickness of 190 and 220 nm, respectively.
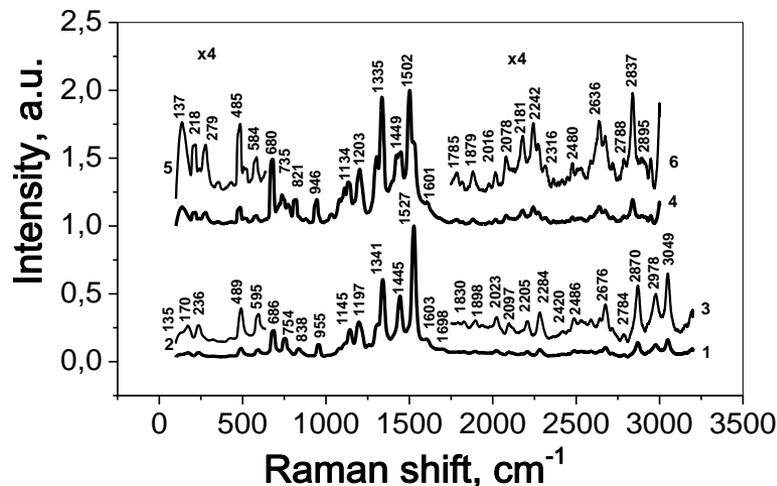

Fig.5. The resonance Raman scattering spectra of ClAlClPc films (curves 1, 2 and 3) and PbPc (curves 4, 5 and 6) with a thickness of 220 and 190 nm, respectively, after smoothing and subtraction of the baseline. To facilitate the analysis, the ordinates of the modified spectra were increased 4 times at the spectral sections of 100 - 640 cm^{-1} (curves 2 and 5) and 1700 - 3000 cm^{-1} (curves 3 and 6).
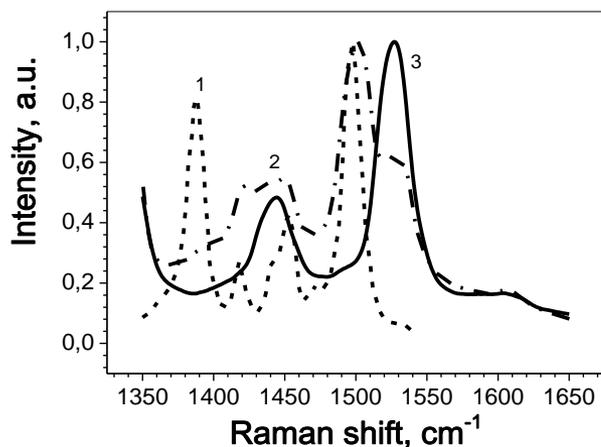

Fig.6. The resonance Raman spectra of PbPc films (curve 2) and ClAlClPc (curve 3) with thickness respectively of 190 and 220 nm in the fingerprints range. For comparison, the Raman spectra of PbPc powder (curve 1 [3]) are given.

[3] D.R. Tackley et al. *Phys. Chem. Chem. Phys.*, **3**, p.1419 (2001).

The spectra of resonant Raman scattering of PbPc and ClAlClPc films in the fundamental region 100 – 1700 cm⁻¹.

Table 2. The peak positions (cm⁻¹) and normalized intensities (in parentheses) of fundamental Raman bands and their assignment to molecular vibrations for different samples.

PbPc This work Film 632.8 nm	ClAlClPc This work Film 632.8 nm	ClAlPc [6] Film 488 nm	ZnPc [8] Powder 1064 nm	PbPc [7] Film 632.8 nm	Assignment [4 - 10]
137 (0.14)	135 (0.02)		146, B_1		Macrocycle out of plane deformation
	170 (0.04)			184, B_1	In-phase motion of isoindole groups
218 (0.10)			229, B_2	206, B_1	Isoindole ring deformation
279 (0.10)	236 (0.04)	252, B_1	252, A_1	229, A_1	M-N_1 stretching
485 (0.14)	489 (0.07)	489, E	476, B_2	482, B_1	Isoindole ring deformation
584 (0.08)	595 (0.06)	590, A_1	583, A_1	566, A_1	Benzene ring deformation
680 (0.49)	686 (0.20)	679, A_1	666, A_1	681, A_1	Macrocycle breathing
735 (0.23)	754 (0.14)	749, E	735, B_1	723, B_2	Macrocycle deformation
		776, B_2	764, B_1	797, A_1	Macrocycle deformation
821 (0.20)	838 (0.07)	830, A_1	828, A_1	889, B_1	Macrocycle ring stretching
946 (0.20)	955 (0.10)	952, B_1	925, B_2	1008, B_1	Benzene breathing
1034 (0.09)	1081 (0.07)	1104, E	1098, B_2	1025, E	C–H bending
1134 (0.32)	1145 (0.21)	1132, B_2	1134, B_1	1141, B_2	Pyrrole ring breathing
	1197 (0.26)	1186, A_1			C–H bending
1203 (0.42)		1210, E	1189, B_2	1194, E	C–H bending
1335 (0.95)	1341 (0.58)	1335, A_1	1361, B_1	1335, E	Pyrrole ring stretching
1449 (0.55)	1445 (0.45)		1438, B_1	1451, B_1, E	Isoindole ring stretching
		1472, B_2			Isoindole ring stretching
1502 (1.00)			1516, B_1	1511, -	C-N_2 aza-group stretching
	1527 (1.00)	1526, B_2	1573, A_1		C-N_1 pyrrole stretching
1601 (0.18)	1603 (0.14)	1608, E	1595, B_2		Benzene ring stretching

The positions of the peaks of the relevant fundamentals Raman bands ClAlClPc (column 2) compared to PbPc (column 1) are mainly shifted to the high frequency range. At the same time the relatives peak intensities of ClALClPc bands is a lower than those for PbPc.

[4] R. Aroca et al. *Spectrochimica Acta A*, **42** (9), p.991 (1986)
[5] L. Tao et al. *Chin. Phys. Lett.,* **43** (6), p.725 (1987)
[6] T. V. Basova et al. *Chemical Physics*, **380**, p.40 (2011)
[7] L. Xi et al. *Acta Phys.-Chin. Sin*., **28** (10), p.2355 (2012)
[8] D. R. Tackley et al. *Phys. Chem. Chem. Phys*., **2**, p.3949 (2000)
[9] R. Aroca et al. *Spectrochimica Acta A*, **39** (10), p.847 (1983)
[10] C. Jennings et al. *Spectrochimica Acta A*, **41** (9), p.1095 (1985)

Overtones and combinations of fundamental vibrational modes of PbPc and ClAlClPc molecules.

Table 3. Possible assignment of the second-order Raman bands for PbPc thin solid film to overtones and combinations of fundamental modes

No.	Fundamental vibrational modes, cm^{-1}		Overtones and combinations, cm^{-1}	
	ν_1	ν_2	$\nu_1+\nu_2$	ν_{exp}
1	584 *(0.08)*, A$_1$*	1203 *(0.42)*, B$_2$	1787	1785 *(0.05)*
2	680 *(0.49)*, A$_1$	1203 *(0.42)*, B$_2$	1883	1879 *(0.05)*
3	680 *(0.49)*, A$_1$	1335 *(0.95)*, B$_1$	2015	2016 *(0.05)*
4	946 *(0.20)*, B$_2$	1134 *(0.34)*, B$_1$	2080	2078 *(0.08)*
5	1502 *(1.00)*, B$_1$	680 *(0.49)*, A$_1$	2182	2181 *(0.12)*
6	1502 *(1.00)*, B$_1$	735 *(0.23)*, B$_1$	2237	2242 *(0.14)*
7	1502 *(1.00)*, B$_1$	821 *(0.20)*, A$_1$	2323	2316 *(0.06)*
8	1335 *(0.95)*, B$_1$	1134 *(0.89)*, B$_1$	2469	2480 *(0.07)*
9	1502 *(1.00)*, B$_1$	1134 *(0.34)*, B$_1$	2636	2636 *(0.14)*
10	1449 *(0.55)*, B$_1$	1335 *(0.95)*, B$_1$	2784	2788 *(0.07)*
11	1335 *(0.95)*, B$_1$	1502 *(1.00)*, B$_1$	2837	2837 *(0.19)*
12	**1449 *(0.55)*, B$_1$**	**1449 *(0.55)*, B$_1$**	**2898**	**2895 *(0.08)***
13	1449 *(0.55)*, B$_1$	1502 *(1.00)*, B$_1$	2951	2947 *(0.07)*

Table 4. Possible assignment of the second-order Raman bands for ClAlClPc thin solid film to overtones and combinations of fundamental modes

No.	Fundamental vibrations modes, cm^{-1}		Overtones and combinations, cm^{-1}	
	ν_1	ν_2	$\nu_1+\nu_2$	ν_{exp}
1	686 *(0.20)*, A$_1$*	1145 *(0.21)*, B$_1$	1831	1830 *(0.04)*
2	754 *(0.14)*, B$_1$	1145 *(0.21)*, B$_1$	1899	1898 *(0.05)*
3	686 *(0.20)*, A$_1$	1341 *(0.47)*, B$_1$	2027	2023 *(0.05)*
4	754 *(0.14)*, B$_1$	1341 *(0.58)*, B$_1$	2095	2097 *(0.04)*
5	754 *(0.14)*, B$_1$	1445 *(0.45)*, B$_1$	2199	2205 *(0.04)*
6	838 *(0.07)*, A$_1$	1445 *(0.45)*, B$_1$	2283	2284 *(0.05)*
7				2420 *(0.03)*
8	1145 *(0.21)*, B$_1$	1341 *(0.47)*, B$_1$	2486	2486 *(0.05)*
9	1145 *(0.21)*, B$_1$	1527 *(1.00)*, B$_1$	2672	2676 *(0.07)*
10	1341 *(0.58)*, B$_1$	1445 *(0.45)*, B$_1$	2786	2784 *(0.02)*
11	1341 *(0.58)*, B$_1$	1527 *(1.00)*, A$_1$	2868	2870 *(0.11)*
12	1445 *(0.45)*, B$_1$	1527 *(1.00)*, A$_1$	2972	2978 *(0.09)*

*Note: The symmetry of vibrational modes for the ZnPc molecule was calculated in work [8].

[8] D.R. Tackley et al. *Phys. Chem. Chem. Phys.,* **2**, p.3949 (2000)

Conclusions

1. It is established that with increasing the substrate temperature of PbPc and ClAlClPc films from 303K to 323K, the intensity of the first low-energy Gaussian band increases and the intensity of the next Gaussian band decreases. This indicates that during thermal annealing in PbPc and ClAlClPc films there is a phase transition from monoclinic to triclinic crystalline phase.

2. The resonant Raman spectra of the second order in the region of 1700–3050 cm^{-1} of PbPc and ClAlClPc films with thicknesses of 190 and 220 nm, respectively, were obtained and analyzed. This was done for ClAlClPc films for the first time. These spectra of sufficient quality and with reliably established values of frequencies of the Raman bands were measured due to resonance amplification with use of the He-Ne laser line 1.959 eV as an excitation source.

3. It is shown that the Raman spectra of the second-order PbPc and ClAlClPc films are mainly formed by overtones and combinations of first-order bands with B_1 symmetry.

4. The range 2550 - 2950 cm^{-1} together with the fundamental vibrations in the region of fingerprints for PbPc and ClAlClPc (within 1350 – 1550 cm^{-1}) can be used to identify these substances in heterostructures and composites.