IR ABSORPTION AND RAMAN SCATTERING OF WATER IN PHOSPHATE GLASSES: SIMILARITY AND DIFFERENCES

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ABSTRACT. The broad absorption band of water in phosphate glass near 3000 cm^{-1} contains several components belonging to different bonds of water ions. To determine the relation of these components, IR absorption spectra in a broadened interval (up to 1400 cm^{-1}) and Raman scattering spectra of the same samples were measured. All the measurements were collated with quantitative determinations of water content in the studied glasses that was done by means of nuclear microanalysis methods. A pilot decomposition of Raman band of water in vitreous LiPO_3 was done using the same procedure as for the IR spectra. The calculated components show that the positions of the hydrogen-containing groups are similar in the Raman and the IR spectra, however, their intensities being in inverse dependence. Furthermore, the Raman scattering bands are clearly different in the meta- and poly-phosphate regions. Of great importance is also the kind of the metal cation in the phosphate.

Water ions have various possibilities for incorporating into phosphate glassforming matrix for different $\text{MeO/P}_2\text{O}_5$ ratios and different kinds of metal. These differences become clear in decomposition of broad absorption band of water near 3000 cm^{-1} [Polak¹, Efimov²]. This work proposes a version of decomposition of this band in a broadened interval $4500\text{-}1500\text{ cm}^{-1}$, i. e. up to the frequencies of the basic phosphate matrix. Specially recorded new absorption spectra and their decomposition coincide very well with earlier published data in $4000\text{-}2000\text{ cm}^{-1}$ [Smirnova³] because the decomposition in the interval of $2000\text{-}1500\text{ cm}^{-1}$ seems to be reliable (Table 1). The intensities of decomposition components were collated with quantitative determinations of water content in the studied glasses that was done by means of nuclear microanalysis methods [Ilchamov⁴]. For glasses containing the maximal amount of water and, accordingly, having the highest absorption near 3000 cm^{-1} the Raman scattering spectra were recorded – for $\text{Ba(PO}_3)_2$ (ger.) (about 0.45 % wt. of water), $\text{CaO} \cdot 2\text{P}_2\text{O}_5$ (about 5.2 % wt. of water) and LiPO_3 (about 0.6% wt. of water). The latter spectrum came out the most distinct because we did the pioneer decomposition of the Raman spectrum of water in the glass. The method of decomposition is the same for IR and Raman spectra. The calculated components show that the positions of the hydrogen-containing groups are

TABLE 1. Parameters of Gaussiana's for decomposition of the IR absorption band in area 1400-3500 cm^{-1} in phosphate glasses.

Samples	Parameter	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	N11
LiPO ₃	ν , cm^{-1}			1828	2012	2195	2350	2518	2763	3000	3215	3442
	σ , cm^{-1}	*	*	80	80	78	78	95	120	120	120	120
	α_{max}			16,7	13	13,8	14,8	14	14,5	13	9,5	4,8
Mg(PO ₃) ₂	ν	1400	1658	1826	2010	2195	2401	2540	2785	3000	3202	3446
	σ	100	80	77	82	90	86	82	120	120	120	120
	α_{max}	65	40	36	5	7,6	11,1	6,2	2	1,6	1,8	2,2
Ca(PO ₃) ₂ (Ca16-1)	ν	1400	1640	1795	2012	2200	2366	2540	2779	2993	3198	3460
	σ	100	80	80	80	80	80	82	120	120	120	120
	α_{max}	38	31	26,5	10,4	12,3	18,5	9,6	9,2	8,8	6,8	5,2
CaO 2P ₂ O ₅ (Ca-U)	ν				2018	2183	2330	2498	2711	2963	3185	3420
	σ				80	80	80	87	123	122	120	120
	α_{max}				62	59	52	53,5	68,7	60	11	11
Ba(PO ₃) ₂ (Ba-rus)	ν	1400	1628	1790	2018	2196	2364	2558	2772	2992	3202	3415
	σ	100	80	80	79	76	77	93	105	112	112	115
	α_{max}	75	71	65	41	47	60	36	45	34	20	11,5
Ba(PO ₃) ₂ (Ba-ger)	ν			1830	2098	2210	2390	2609	2809	3000	3200	3450
	σ	*	*	80	85	90	90	100	99	97	100	100
	α_{max}			7	5,8	6	6	6	5,7	4	3	1,5

In Tables 1,2: *) – not measured

TABLE 2. Parameters of Gaussiana's for decomposition of the Raman scattering' band in area 1400-3500 cm^{-1} in LiPO₃.

LiPO ₃	Parameter	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	N11	N12
Raman scattering	ν , cm^{-1}		1610	1830	2010	2205	2350	2520	2770	3015	3200	3510	4005
	σ , cm^{-1}	*	(300)	300	300	300	300	300	300	290	290	290	290
	I, arb. u.		(0,105)	0,015	0,055	0,08	0,08	0,095	0,21	0,105	0,205	0,30	0,365

FIGURE 1. Decomposition of the Raman scattering band in area 1400-3500 cm^{-1} in LiPO_3

similar in Raman and IR spectra, and the intensities have an inverse dependence (Table 2). These results should be expected keeping in mind the alternative selection rule. Furthermore, the fitting of the decomposition spectrum made us add a new absorption band near 4005 cm^{-1} , which is absent in the IR spectra. In Fig.1 is shown the Raman spectrum of LiPO_3 and its decomposition into components that are visible mostly in the original spectrum. The intensities of water-related bands in Raman scattering spectra are clearly different in meta- and poly-phosphate regions. The intensities of Raman scattering in $\text{CaO} \cdot 2\text{P}_2\text{O}_5$ and $\text{Ba}(\text{PO}_3)_2$ distinguish more than 10 times. This fact corresponds to water content in these glass. But the water-related bands in $\text{CaO} \cdot 2\text{P}_2\text{O}_5$ have the intensities comparable with those of main phosphate vibrations, and in $\text{Ba}(\text{PO}_3)_2$ they are negligible small. Of great importance is also the kind of the metal cation in the phosphate. For example, metaphosphates of Li (coordination number $\text{CN} = 4$) and Ba ($\text{CN} = 8$) contain remarkably different symmetrical vibrations of water in the Raman spectra while the asymmetrical vibrations of water in these glasses (IR spectra) and water content are similar (Table 1).

The Raman scattering spectra were recorded by means of spectrophotometer Spex Ramalog 5 (Ioffe Physical Technical institute, St.-Petersburg, Russia). The authors gratefully appreciate K. Kober for making the spectra.

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