DECOMPOSITION OF BROAD IR ABSORPTION BANDS OF WATER IN VITREOUS METAPHOSPHATES OF METALS FROM Li TO Ba

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Abstract All phosphate glasses genetically contain a certain amount of residual water. The broad absorption bands of water in the IR region about $3.0\ \mu\text{m}$ are well known. This paper presents decomposition of 2 broad integral absorption bands (the broader and complicate one at about $3000\ \text{cm}^{-1}$ and the stronger and stabler one at about $2300\ \text{cm}^{-1}$) in phosphate glasses into 8 components. The investigation was carried out on vitreous metaphosphates of metals of the I-II Groups of the Periodical System (Li, Na, Mg, Ca, Sr, Ba) and ultraphosphate $\text{CaO} \cdot 2\text{P}_2\text{O}_5$. All the Gaussian bands show high stability of their position and dispersion for all the cations, but the ratio of the bands' intensities differ remarkably for various samples.

INTRODUCTION

All phosphate glasses genetically contain a certain amount of residual water. The broad absorption bands of water in the IR region about $3.0\ \mu\text{m}$ are well known. For a longtime this absorption band ca. $3000\ \text{cm}^{-1}$ was attributed to the absorption of P-OH bond. However, water, especially in high contents, can be present in various forms: OH-groups, protons, H_3O^+ , bonded molecular water and «free» molecular water. Each form has its own spectral manifestation in the integral absorption spectrum. The development of new high resolution set-ups for absorption recording allow distinction of a number of sharper absorption bands within those broader. The first paper [1] proposed a decomposition of the absorption band only about $3000\ \text{cm}^{-1}$. The later investigations of phosphate glasses structure [2,3] and the interaction of phosphate glasses with water and hydrogen [4] have given us a possibility to make a new attribution of «private» absorption bands in the range $1800\text{-}3500\ \text{cm}^{-1}$. We use also the analogy with widely investigated silicate glasses. This paper presents decomposition of 2 broad integral absorption bands (the broader and complicate one at about $3000\ \text{cm}^{-1}$ and the stronger and stabler one at about $2300\ \text{cm}^{-1}$) in phosphate glasses into 8 components. Each of the

mentioned broad absorption bands was decomposed into 4 components. In the frequency range about 3000 cm^{-1} the experimental and literature data were used for the decomposition, parameter s about 120 cm^{-1} . In the frequency range about 2300 cm^{-1} our experimental data only were used, parameter s about 80 cm^{-1} . For a number of samples, a quantitative analysis of the water content was carried out.

EXPERIMENTAL PROCEDURE

The investigation was carried out on vitreous metaphosphates of metals of the I-II Groups of the Periodical System (Li, Na, Mg, Ca, Sr, Ba) and ultraphosphate $\text{CaO} \cdot 2\text{P}_2\text{O}_5$. Some samples (Mg, Sr, Ba) were melted in fused silica crucibles in air in Germany, the other - in vitreous carbon crucibles in Ar-riched atmosphere in Russia.

The spectra records were fulfilled by means of spectrophotometer PE 983 in 5000-1800 cm^{-1} interval by the standard method with maximal resolution.

The absolute contents of water in samples was determined by the method of nuclear microanalysis (by detecting recoiled protons) with the use of ^4He ions [5].

The decomposition of complex absorption bands was carried out on computer by selection of the equation $\alpha = \alpha_{\text{max}} \exp(-((\nu - \nu_0)^2 / 2\sigma^2))$, where α is the Gaussian ordinate, ν is the position of the band maximum (for α_{max}), and s is the dispersion, up to minimal difference from the experimental curve.

RESULTS AND DISCUSSION

The optimal results of the decomposition have been achieved with the use of 8 basic Gaussian curves. Their positions, halfwidths and intensities differ from those in [1]. All results are shown in Table 1, one example of decomposition is shown in Fig.1 (for NaPO_3).

All the Gaussian bands show high stability of their position and halfwidth for all the cations, but the ratio of the bands' intensities differ remarkably for various metaphosphates. Red/ox conditions of melting and the cations valence have not

the significance. So, all the absorption bands are caused by the vibration of the phosphate chains and water.

Table 1. Gaussian Parameters for decomposition of the broad absorption band in ca. 3000 cm⁻¹ in phosphate glasses.

Samples	Parameters	Line 1	Line 2	Line 3	Line 4	Line 5	Line 6	Line 7	Line 8	[H ₂ O]
LiPO ₃	ν	2000	2180	2338	2503	2745	2990	3200	3425	
	σ	75	75	75	90	120	120	120	120	
	$\alpha_{\max}$	13.0	13.7	15.2	13.5	14.1	12.9	9	4.5	
NaPO ₃	ν	1985	2195	2377	2547	2775	2985	3205	3420	
	σ	75	72	70	77	120	120	120	120	
	$\alpha_{\max}$	9.5	11.2	25.0	8.0	8.2	8.4	3.8	1.7	
Mg(PO ₃) ₂	ν	1980	2191	2407	2550	2770	3000	3205	3423	
	σ	85	90	87	85	120	120	120	120	
	$\alpha_{\max}$	5.1	6.8	10.2	4.4	0.9	1.2	1.3	1.5	
Ca(PO ₃) ₂ -1	ν	2015	2200	2377	2540	2758	2985	3195	3420	0.06
	σ	80	80	80	85	120	120	120	120	
	$\alpha_{\max}$	13.9	17.7	21.5	11.8	15.4	15.2	11.5	8.4	
Ca(PO ₃) ₂ -2	ν	2022	2205	2382	2550	2765	2985	3205	3420	0.12
	σ	83	83	83	95	120	125	120	120	
	$\alpha_{\max}$	22.9	25	24.8	20	28.8	24.0	17.0	9.0	
Ca(PO ₃) ₂ -3	ν	2016	2200	2377	2551	2770	2985	3200	3435	0.31
	σ	75	75	78	80	120	120	120	120	
	$\alpha_{\max}$	26	35	55	20	11.2	12.7	9.5	7.8	
CaO·2P ₂ O ₅	ν	2018	2183	2330	2498	2711	2963	3185	3420	5.2
	σ	80	80	80	87	123	122	120	120	
	$\alpha_{\max}$	62	59	52	53.5	68.7	60	43	11	
Ba(PO ₃) ₂ - -rus	ν	2030	2205	2370	2560	2755	2985	3205	3420	4.7
	σ	80	73	77	86	110	120	120	120	
	$\alpha_{\max}$	56.0	60	63	43	57	38	20	11	
Sr(PO ₃) ₂	ν	1990	2195	2402	2553	2775	2990	3210	3425	
	σ	90	90	90	80	125	120	120	12	
	$\alpha_{\max}$	8.2	10	15	9	6.1	8.1	9.5	8	
Ba(PO ₃) ₂ - -ger	ν	1995	2175	2350	2520	2747	2945	3205	3420	
	σ	75	75	75	75	120	120	120	120	
	$\alpha_{\max}$	13.3	16.3	31	13.3	16.5	15.6	8.7	4.2	
Middle value	ν	2005.2	2193.4	2371	2537	2757	2981	3202	3423	
	σ									

In [4] it is proved, that the shortest wavelength absorption band about 3400 (our 3420) cm⁻¹ is connected with the vibrations of molecular water implanted into the glass network. The additional evidence of this suggestion is the increase of this band intensity for phosphates with very big water contents only (see Table 1). The next by wavelength absorption band about 3200 cm⁻¹ in [4] is connected with P-OH. We propose that this band and also three next ones (up to 2537 cm⁻¹) are connected with the bond P-OH vibrations. According to [2], there are 4 types of tetrahedra [PO₄] in phosphate glasses distinguished by the number of bridging bonds (Q⁰ - Q³). It is consistent to propose that 4 closely placed absorption bands correspond to them. These 4 bands compose the broad absorption band about 3000 cm⁻¹ attributed earlier to the absorption of P-OH bond. Q¹ and Q² tetrahedra, which are most frequent in phosphate chains, have higher intensities (bands at 2981 and 2757

Fig.1 The decomposition of broad water absorption band in IR region by components for NaPO_3

cm⁻¹ accordingly in Table 1). The strong absorption band near 2371 cm⁻¹ we attribute as corresponding to the P-H bond [6,7]. This position differ strongly from that proposed in [1], but our suggestion is confirmed by analogy with silicate glasses (see, for example, [8], Si-H: 2260 cm⁻¹). The band about 2200 cm⁻¹ is assumed to refer to the existence of H₃O⁺-groups in glasses (see also [4]). The longest wavelength absorption band (2000 cm⁻¹) perhaps corresponds to vibrations of «free» molecular water, i.e. similar to the crystallization water not having a chemical bond with vitreous network. This absorption band is the nearest to n₂ of molecular water (1660 cm⁻¹, [1]), their intensity increase only for glasses with very big water content.

Unfortunately, the available literature data on the absorption bands of water-containing groups (including the given work) are not enough to offer a rather accurate method of determination of water content by measurements of absorption spectra in phosphate glasses.

SUMMARY

Basing on experimental spectral measurements and literature data we propose a model for decomposition of broad absorption band in region 3000 cm⁻¹.

ACKNOWLEDGMENT

The authors would like to thank Prof. Dr. D.Stachel (Jena, Germany) for providing of samples for investigations.

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