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SPECTROSCOPIC AND THERMAL STUDIES OF SILICATE-PHOSPHATE GLASS

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The structure of silicate-phosphate glass containing the different amounts of phosphorus, magnesium and calcium cations, acting as macroelements was examined by FTIR, XRD and thermal (DTA/DSC) methods.

It has been found that in the structure of silicate-phosphate glass modified by an addition of Mg^{2+} and Ca^{2+} there are formed domains characterized by certain degree of ordering of the units present in their composition, while the structure of the newly formed domains is similar to the structure of the crystal compounds formed during crystallization of these glasses.

The changing character of domains structure may be the reason of different chemical activity of glass acting as glassy fertilizers.

Keywords: *DTA, FTIR, glass crystallization, glass structure, silicate-phosphate glass*

Introduction

Silicate-phosphate glass was applied as bioactive materials on account of the content of phosphorus which is one of the elements important for the functioning of living organisms. An original type of glasses is silicate-phosphate glass containing K, Mg, Ca and microelements in its composition which demonstrates an ability to release them selectively in the biological soil environment, in a form available for plants. Earlier investigations showed that increasing content of phosphorus and potassium in the structure of silicate-phosphate glass is responsible for a distinct increase of their solubility [1], however the effect of presence of Mg and Ca on the chemical activity of these glasses was found to be more complex [2]. It was assumed that the explanation of the differentiated influence of these elements on the chemical activity of the glassy fertilizers should be related to the nature of the structure of these glasses.

According to [3–5] it is assumed that the structure of silicate-phosphate glass is composed of tetrahedra, combined at random with each other, forming a three-dimensional, disordered lattice in which every silicon atom is bound with four other silicon or phosphorus atoms by means of oxygen bonds (e.g. Si–O–Si, Si–O–P), whereas each phosphorus atom has only three bridging bonds. In the four edges of the tetrahedron $[PO_4]$ there is a non-bridging oxygen atom bound with the central phosphorus atom by a double bond (O=P). This oxygen atom does not form an oxygen bridge with another tetrahedron and thereby it does not participate in the formation of polymerized phosphate anions. It can, however, form a bond with a cation-modifier, the result of which is the formation of the bond of the type $M–O–PO_3$, where *M* is the modifying cation.

Introduction of the modifying oxides of RO and RO_2 type (where R=K^+, Na^+, Mg^{2+}, Ca^{2+} etc.) into the structure of the silicate-phosphate glass results in the breaking of some part of the chemical bonds, occurring in the oxygen bridges of the type: Si–O–Si, Si–O–P and P–O–P [6] and as a consequence in the formation of terminal oxygens of the type $Si–O^-$ and $P–O^-$, and thereby to depolymerization of the silicate-phosphate network [5–9].

Basing on the investigation results of ^{31}P MAS-NMR it has been found that the phosphate lattice of silicate-phosphate glass containing a modifier in the form of the cations K^+ is formed only of monophosphate complexes (PO_4^{3-}), whereas the introduction into their structure modifiers in the form of Mg^{2+} or Ca^{2+} cations is accompanied by the occurrence in the phosphate lattice additional diphosphate complexes ($P_2O_7^{4-}$). Increase of the content of these cations causes depolymerization and increase of the content of the monophosphate groups. The results confirmed also the depolymerizing effect of the cation modifiers (Mg^{2+}, Ca^{2+}) on the silicate network [10].

The aim of the present study was the explanation of the differentiated effect of the content of P, Ca and Mg on the structure of the model silicate-phosphate glass basing on the FTIR, XRD and DTA/DSC methods.

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Experimental

The compositions of batches of the examined glasses from the systems SiO_2–P_2O_5–CaO–K_2O and SiO_2–P_2O_5–MgO–K_2O are presented in Table 1 and the method of their preparation is given in [10]. To investigate the course of the crystallization process of the glasses there were used the DTA/DSC methods (Perkin-Elmer thermoanalyser DTA-7). The structural investigations of the glasses were based on infrared absorption spectrophotometry (Digilab FTS-60 MVPC spectrometer, Bio-Rad), and for identification of the crystal phases the X-ray analysis – XRD (X'Pert PRO, Phillips) was used.

Because of the complex character of the obtained absorption spectra of the silicate-phosphate glasses which are the object of the present study, it was necessary to carry out the process of their decomposition into the constituent bands. Basing on the hypothesis of similarity between the structure of an amorphous material and the structure of its devitrificate [11, 12], the examined glasses were subjected to the process of isothermal heating for 1 h at temperatures resulting from DTA/DSC measurements, which allowed to obtain crystalline materials each time.

Mathematical decomposition of the absorption spectra of selected glasses and their crystal equivalents was carried out using SpectraCalc^{TM}.

Table 1 The chemical composition of silicate-phosphate glass

No.	Chemical composition/mol%				
	SiO_2	P_2O_5	K_2O	MgO	CaO
1	76	2	6	16	–
2	69	2	6	23	–
3	63	2	6	29	–
4	57	2	6	35	–
5	51	2	6	41	–
6	80	2	6	–	12
7	74	2	6	–	18
8	68	2	6	–	24
9	63	2	6	–	28
10	72	6	6	16	–
11	57	6	6	31	–
12	51	6	6	37	–
13	45	6	6	43	–
14	69	7	6	–	18
15	63	7	6	–	24
16	57	7	6	–	30
17	51	7	6	–	36

Results and discussion

FTIR study

The FTIR spectra were interpreted at the assumption that the structure of silicate-phosphate glass contains Si–O bonds, occurring in the amorphous SiO_2 and P–O bonds present in the amorphous P_2O_5. Selected FTIR spectra of silicate-phosphate glass modified by addition of Mg^{2+} and Ca^{2+} cations are shown in Figs 1 and 2.

FTIR spectra of the examined glasses are characterized by main absorption bands at: 900–1200, 750–810 and 460–480 cm^{-1}, as well as an additional band in the range 570–650 cm^{-1}, better visible in the case of glasses containing the Ca^{2+} ions as modifier of the structure. The most intensive bands at 900–1200 cm^{-1} are related to the presence of stretching vibrations of Si–O and P–O bands [13, 14]; bands at 750–810 cm^{-1} are related to the presence of a combination of vibrations of Si–O–Si, Si–O–P and P–O–P bridges [14]; the next group of bands at 570–650 cm^{-1} have been connected with P–O vibrations or pseudo-lattice vibrations of groups of phosphate tetrahedra [12, 14–16]. The last group of bands, at 460–480 cm^{-1} has been ascribed to the combination of bending vibrations of O–Si–O and O–P–O bonds

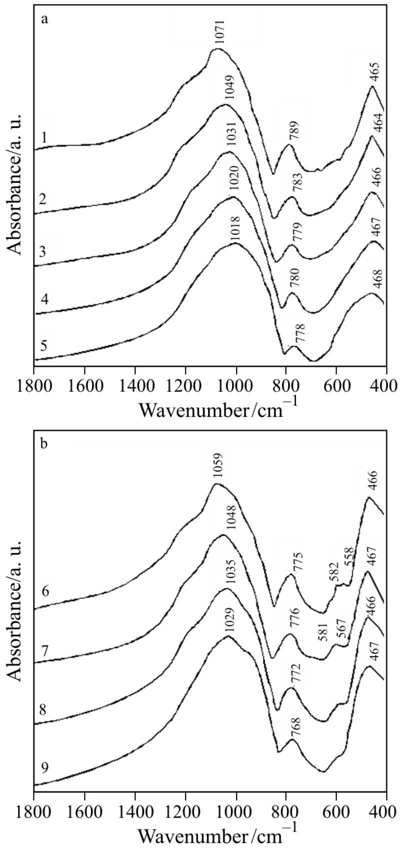

Fig. 1 FTIR spectra of silicate-phosphate glass with 2 mol% P_2O_5, containing a – magnesium and b – calcium cations as modifiers

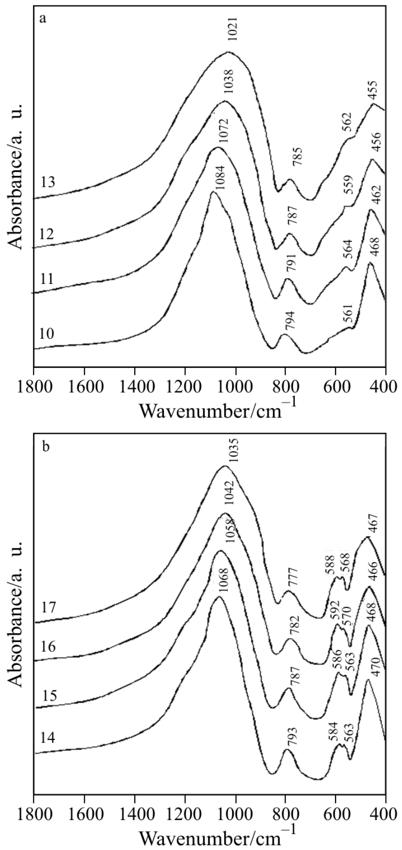

Fig. 2 FTIR spectra of silicate-phosphate glass with 6–7 mol% P_2O_5, containing a – magnesium and b – calcium cations as modifiers

[13, 15]. It should be noted that P=O bond at 1300 cm^{-1} did not appear in any group of examined glass.

It should be noted that the silicate-phosphate glass containing a greater amount of P_2O_5 in comparison with glasses containing 2 mol% of P_2O_5 has not revealed the presence of any additional absorption bands which might be evidence of a different influence of the higher content of P_2O_5 on the structure of the considered glass (Figs 1 and 2).

On the basis of the decomposition of glass spectra (Figs 3a–8a) it has been found that within the range of the most intensive band at 900–1200 cm^{-1} there are present additional absorption bands, situated in the ranges: 900–970 and 1100–1200 cm^{-1}.

The first of these bands are derived from a combination of stretching vibrations of P–O groups in P–O–P bridges and from terminal vibrations of Si–O$^-$ groups formed as a result of breaking Si–O–Si bridges [17]. With increasing content of the modifiers in the structure of glasses their position becomes evidently shifted towards lower wavenumbers (Figs 3a and 4a), which suggests the increase of the degree of depolymerization of the structure of the amorphous material. On the other hand, the bands situated within the range of higher vibration frequencies can be assigned to terminal vibrations of Si–O$^-$ or Si=O bonds [15, 18, 19].

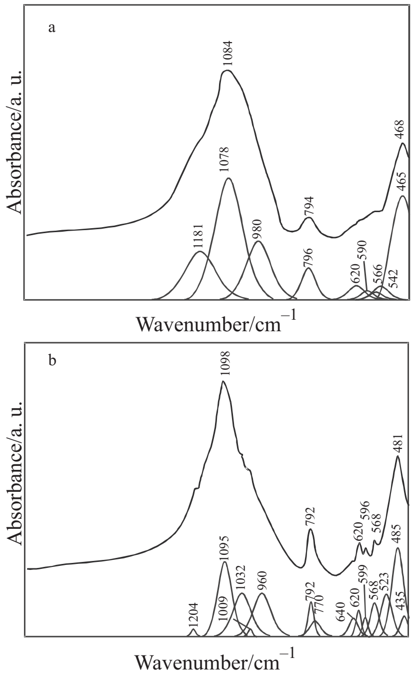

Fig. 3 The decomposition of MIR spectra of silicate-phosphate glass containing a – 16 mol% MgO and b – its devitrificate

The process of decomposition of the absorption bands in the range 570–650 cm^{-1}, occurring in glasses with the lowest content of Mg^{2+} cations indicated the existence of four constituent bands at 620, 590, 566 and at about 544 cm^{-1} (Fig. 3a). According to [19] the last three bands are connected with the occurrence of the earlier mentioned bending vibrations of P–O bonds and the pseudo-lattice vibrations of the groups of [PO_4] tetrahedra, whereas the band at 620 cm^{-1} is characteristic for vibrations of Si–O bonds, occurring in cristobalite. It should be noted that the decomposition process of the absorption bands of devitrificate enabled to characterize also other bands (Fig. 3b).

With increasing content of MgO in the structure of silicate-phosphate glass, at simultaneous reduction of SiO_2 content, the character of the constituent absorption bands within the examined range of wavenumbers is changed. There appear bands at about 880 and 510 cm^{-1} (Fig. 4a), corresponding to vibrations of Si–O bonds, characteristic of magnesium orthosilicate (forsterite) (Fig. 4b) [20]. The presence of orthosilicate of this type has been confirmed in the devitrificates by X-ray method.

The analysis of the constituent absorption bands of silicate-phosphate glass containing the modifier in the form of CaO and their devitrificates indicate the occurrence of three bands situated at 590, 566 and 530 cm^{-1} (Fig. 5a), and of bands lying at 610, 587 and 560 cm^{-1} (Fig. 6a).

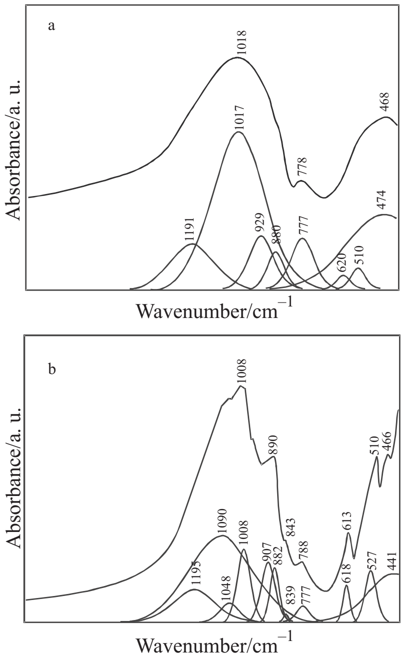

Fig. 4 The decomposition of MIR spectra of silicate-phosphate glass containing a – 41 mol% MgO and b – its devitrificate

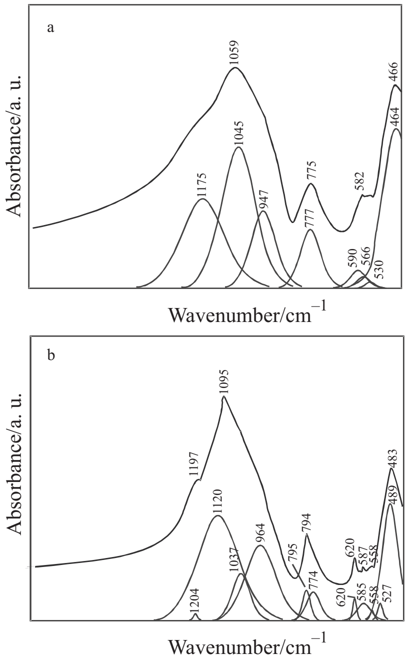

Fig. 5 The decomposition of MIR spectra of silicate-phosphate glass containing a – 12 mol% CaO and b – its devitrificate

In the absorption spectra of recrystallized glasses these bands are much more distinct (Figs 5b and 6b) and their positions correspond to the vibrations of P–O bonds occurring in calcium phosphate – $Ca_3(PO_4)_2$ [20]. It should be noted that in the absorption spectra of the devitrificates of the glasses there are also present the absorption bands at about 795 and 620 cm^{-1}, illustrating the presence of vibrations of Si–O bonds, occurring in cristobalite [20].

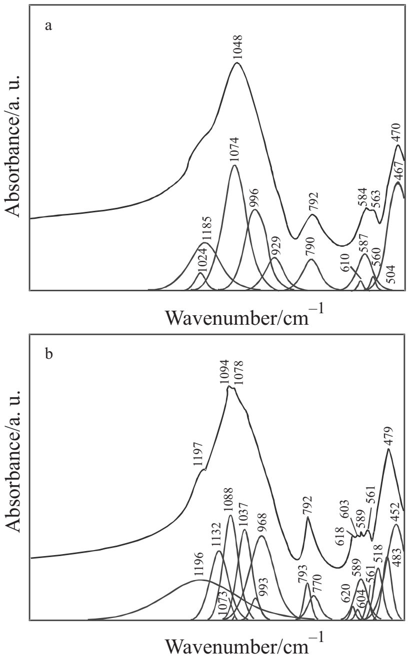

Fig. 6 The decomposition of MIR spectra of silicate-phosphate glass containing a – 18 mol% CaO and b – its devitrificate

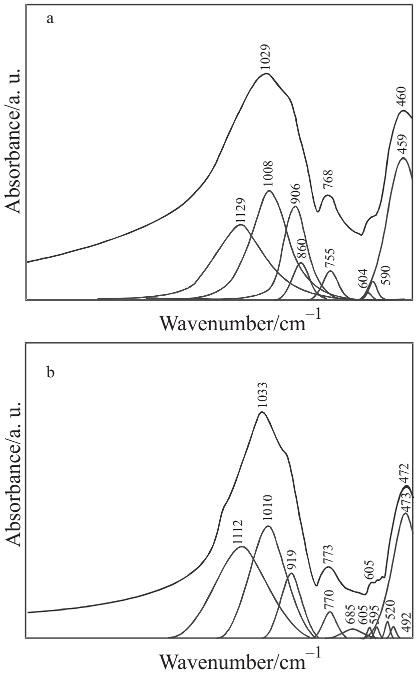

Fig. 7 The decomposition of MIR spectra of silicate-phosphate glass containing a – 28 mol% CaO and b – its devitrificate

With further increase of the amount of CaO in the structure of silicate-phosphate glass, the absorption bands characteristic for bonds occurring in cristobalite (at about 620 cm^{-1}) disappear (Figs 7a and 8a). The analysis of the component absorption bands present in glass containing 28 mol% of CaO with a lower content of P_2O_5 indicates the presence of absorption bands at about 590 and 860 cm^{-1} which are connected with the

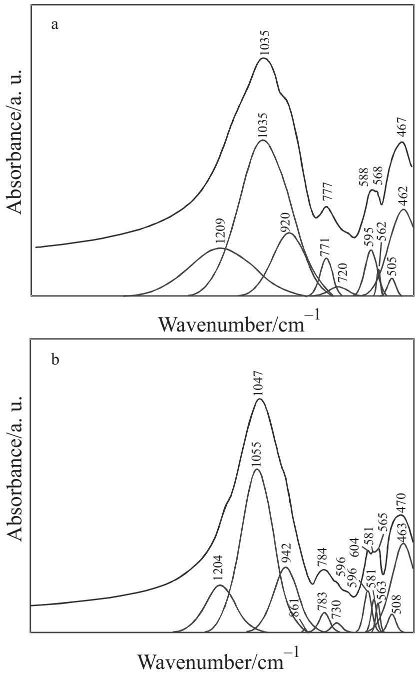

Fig. 8 The decomposition of MIR spectra of silicate-phosphate glass containing a – 36 mol% CaO and b – its devitrificate

vibrations of Si–O bonds in calcium silicate of γ-Ca_2SiO_4 type (Fig. 7) [20]. On the other hand, the absorption bands at about 604 and 568 cm^{-1}, whose equivalents appear in the spectra of recrystallized glasses (Fig. 8b) indicate the presence of a mixture of calcium phosphate $Ca_3(PO_4)_2$ and calcium silicate Ca_2SiO_4.

The above results, obtained for the model silicate-phosphate glass of both lower and higher content of P_2O_5 indicate that with the change of the modifier (MgO, CaO) in their structure, there are formed domains characterized by a certain degree of the ordering of the structural units present in their composition, while the structure of the newly formed domains is similar to the structure of crystal compounds formed from glass with the same chemical composition.

The increasing amount of MgO in the structure of silicate-phosphate glass causes the formation of groupings (domains) the structure of which changes from the structure of crystobalite type to the structure corresponding to silicate of Mg_2SiO_4 type.

Depending on the change in the CaO content in the structure of the glass, the newly forming groupings of silicon-oxygen and phosphorus-oxygen units change the character of the structure from that typical for cristobalite through one similar to the calcium orthophosphate $Ca_3(PO_4)_2$, to attain, at appropriately high content of CaO, the structure corresponding to calcium silicates Ca_2SiO_4.

Thermal study

The results of thermal investigations of the silicate-phosphate glasses enabled to determine the following parameters of crystallization (Table 2):

- the temperatures of crystallization, determined by the maximum temperature of crystallization (T_{cryst}).
- values of the enthalpy of crystallization (ΔH).

On the basis of the obtained results it has been found that silicate-phosphate glass with both lower and higher content of P_2O_5, containing in their composition a single modifier in the form of calcium or magnesium cations, show a relatively small ability to crystallize, manifested by high values of the crystallization temperatures and low values of the crystallization enthalpy (Table 2).

In the case of the group of glass containing 2 mol% of P_2O_5 and the modifier in the form of magnesium cations the ability to crystallize appears not earlier than at the molar ratio $MgO/SiO_2>0.6$, whereas in case of glasses with increased content of P_2O_5 this ability is shifted to $MgO/SiO_2>0.9$. Both groups of glass are characterized by increasing ability to crystallize with increasing content of Mg^{2+} cations in their structure, and this ability is smaller in the case of glasses with a higher content of phosphorus present in the structure. Crystallization has a one-stage character and its product is the silicate of Mg_2SiO_4 type.

Table 2 Thermal and X-ray characteristics of silicate-phosphate glass

No.		T_{cryst}/ °C	ΔH/J g^{-1}	Type of cryst. comp.
	MgO/SiO_2			
1	0.21	–	–	–
2	0.33	–	–	–
3	0.46	–	–	–
4	0.61	1053	35.41	Mg_2SiO_4
5	0.80	1000	67.44	Mg_2SiO_4
	CaO/SiO_2			
6	0.15	–	–	–
7	0.24	1015	12.07	$Ca_3(PO_4)_2$
8	0.35	926	15.10	$Ca_3(PO_4)_2$+ Ca_2SiO_4
9	0.44	904	34.30	Ca_2SiO_4
	MgO/SiO_2			
10	0.22	–	–	–
11	0.54	–	–	–
12	0.73	–	–	–
13	0.96	990	38.80	Mg_2SiO_4
	CaO/SiO_2			
14	0.26	–	–	–
15	0.38	–	–	–
16	0.53	1055	35.4	$Ca_3(PO_4)_2$
17	0.71	835	12.5	$Ca_3(PO_4)_2$+ Ca_2SiO_4

On the other hand, in the case of glasses with a lower content of P_2O_5, containing the modifier in the form of calcium cations, the ability to crystallize appears already at $CaO/SiO_2>0.2$. Increased content of P_2O_5 in the structure of the examined glasses is accompanied by the reduction of their ability to crystallize at $CaO/SiO_2>0.5$. In both these groups of glasses crystallization has also a one-stage character, whereas the crystallization products are more differentiated (Table 2). Calcium phosphates of $Ca_3(PO_4)_2$ type crystallize first. When in the composition of the glass the value $CaO/SiO_2>0.35$ (2 mol% of P_2O_5) and $CaO/SiO_2>0.71$ (6 mol% of P_2O_5) product of crystallization process is the mixture of $Ca_3(PO_4)_2$ and Ca_2SiO_4. Silicate-phosphate glass containing higher content of CaO crystallizes in the Ca_2SiO_4 form.

The ability for crystallization, its course and the type of the forming phases, in case of model silicate-phosphate glass modified by MgO or CaO additions, depends on the mutual proportions between the components forming the glassy structure (MgO/SiO_2, CaO/SiO_2). It is modified by the content of P_2O_5. On the other hand, the type of the crystal phases forming in the course of heating the silicate-phosphate glass has been found to be in agreement with the character of the domains occurring in the examined glass, confirmed by spectroscopic methods.

Conclusions

On the basis of FTIR, XRD and DTA/DSC investigations the structure of silicate-phosphate glass acting as glassy fertilizers was described. It has been found that in the structure of silicate-phosphate glass modified by an addition of increasing amounts of Mg^{2+} or Ca^{2+} cations there are formed domains characterized by certain degree of ordering of the units present in their composition, while the structure of the newly formed domains is similar to the structure of the crystal compounds formed during crystallization of these glasses.

The increasing amount of MgO in the structure of silicate-phosphate glasses causes the formation of groupings (domains) the structure of which changes gradually from a structure of the cristobalite type to a structure corresponding to forsterite type.

Depending on the change in the CaO content in the structure of silicate-phosphate glasses the newly formed groupings of silicon-oxygen and phosphorus-oxygen units change their structure from a structure typical for cristobalite through one similar to the calcium orthophosphate, to a structure corresponding to calcium silicates.

Character of domains structure which formed in the considered glass may be the reason of their different chemical activity. Formation of domains with structure corresponding of silicates causes the increase of chemical activity of glasses. However, formation of domains with structure similar to orthophosphates, which are characterized by lower solubility in comparison with solubility of silicates reduces chemical activity of glasses in biological solutions.

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