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SYNTHESIS AND PROPERTIES OF A SOLID SOLUTION FORMED IN THE $CrVMoO_7$–$AlVMoO_7$ SYSTEM

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Abstract

It has been shown by the methods of X-ray powder diffraction (XRD), differential thermal analysis (DTA) and infrared spectroscopy (IR) that solid solutions of a formula $Cr_{1-x}Al_xVMoO_7$, where $x \in (0–0.65)$, are formed in the system $CrVMoO_7$–$AlVMoO_7$. The obtained research results have proven that the ions Al^{3+} are incorporated into the crystal lattice of $CrVMoO_7$ instead of Cr^{3+}, which causes a contraction of the lattice and a shift of IR absorption bands towards higher values of wavenumbers. The phases $Cr_{1-x}Al_xVMoO_7$ melt incongruently in the temperature range from 710°C (for $x=0.65$) to ~820°C in the case of x close to zero.

Keywords: $CrVMoO_7$–$AlVMoO_7$ system, $Cr_{1-x}Al_xVMoO_7$, DTA, IR, phase equilibria, XRD

Introduction

Literature information implies that binary and ternary metal oxide systems have been for a number of years an interesting subject of comprehensive and intensive investigations, whereas quaternary oxide systems are rarely under research and this is incomplete, first of all in the aspect of searching for novel, hitherto unknown phases with interesting catalytic, electric, magnetic, optical or other properties. To such systems the investigated hereby $CrVMoO_7$–$AlVMoO_7$ system belongs, it being one of intersections of a quaternary metal oxide system, namely Cr_2O_3–V_2O_5–MoO_3–Al_2O_3. The oxides Cr_2O_3, Al_2O_3, V_2O_5 and MoO_3 and compounds formed in some systems built by the oxides find many applications, first of all, as catalysts [1–6].

$CrVMoO_7$ and $AlVMoO_7$ are compounds formed in respective lateral ternary systems of the investigated quaternary system, i.e. Cr_2O_3–V_2O_5–MoO_3 and V_2O_5–MoO_3–Al_2O_3 [7–17]. The structure and basic properties of these compounds are known. $CrVMoO_7$ crystallises in the triclinic system (space group P–1, $Z=2$) and melts incongruently at 820°C with a deposition of Cr_2O_3 as a solid product of meritectic reaction [7–10]. It is known from our earlier investigations that $CrVMoO_7$

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forms with $FeVMoO_7$, its isotype, a continuous solid solution of a formula $Cr_{1-x}Fe_xVMoO_7$ [11]. The solid product of its incongruent melting for $x<0.5$ is $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ and for $x>0.5$ – solid solutions of the types $Fe_{2-z}Cr_z(MoO_4)_3$ and $Fe_{2-u}Cr_uO_3$ [11].

$AlVMoO_7$ is not isostructural with $CrVMoO_7$, but it crystallizes in the orthorhombic system (space group Pmcn, $Z=4$) and the solid products of its melting at 690±10°C are $Al_2(MoO_4)_3$ and Al_2O_3 [12–15]. It seemed therefore interesting to find out within this work whether compounds of the same type of chemical formula, but possessing different structures, that is $CrVMoO_7$ and $AlVMoO_7$, form with each other a solid solution and if it is so – what the range of their mutual solubility is.

Experimental

The reagents used for research were: V_2O_5 a.p. (POCH Gliwice, Poland), MoO_3 p. (POCH Gliwice, Poland) Al_2O_3 p., calcined (POCH Gliwice, Poland) and Cr_2O_3 p. (Aldrich, Germany). $CrVMoO_7$ and $AlVMoO_7$ were obtained from respective oxides by methods described in the works [7, 12].

The DTA/TG measurements were conducted in air, in quartz crucibles, at a heating rate of $10°C\cdot min^{-1}$ and in the range 20÷1000°C. The investigations were performed by using an apparatus of Paulik–Paulik–Erdey type (MOM Hungary).

The powder diffraction patterns of obtained samples were registered with the aid of the diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia) using the radiation CoK_{α}/Fe. Results of investigations by XRD and DTA methods allow a determination of composition of samples as well as an establishing of their melting temperatures and finally, constructing the phase diagrams [7, 8, 11–14, 16, 18–21].

The IR spectra were recorded in the wave-number range of $1400\div250\ cm^{-1}$ by means of the spectrometer Specord M80, product of Carl Zeiss, Jena, Germany. A technique of pressing pellets with KBr at a mass ratio of 1:300 was applied.

For the research 11 samples were prepared from the oxides Cr_2O_3, Al_2O_3, V_2O_5 and MoO_3 with their compositions enabling the investigation of the system $CrVMoO_7$–$AlVMoO_7$ in the whole component concentration range. The content of V_2O_5 and MoO_3 in the oxide mixtures was always constant and amounted to 25.00 and 50.00 mol%, respectively. Selected samples were additionally prepared from the compounds $CrVMoO_7$ and $AlVMoO_7$. The composition of the samples prepared for investigations is listed in Table 1.

The oxide mixtures weighed at appropriate components ratios and $CrVMoO_7$ with $AlVMoO_7$ were homogenised by grinding in an agalite mortar and next heated in a syllite furnace in the atmosphere of air for several stages enabling an equilibrium state to be attained, i.e. 600°C(2×24 h)+650°C(24 h)+680°C(2×24 h). The samples Nos 1, 3, 5 and 8 (Table 1) prepared from the compounds $MVMoO_7$ (where M=Al, Cr) were subjected to an additional calcination at 680°C for 48 h. After each heating cycle the preparations were cooled down in the furnace to room temperature, ground and examined by X-ray phase analysis. Preparations after the last calcination cycle were investigated also with the use of the DTA/TG method and infrared spectroscopy.

Table 1 The composition of the initial oxide mixtures and the results of XRD analysis of the samples from the system $CrVMoO_7$-$AlVMoO_7$ after the last heating cycle

No.	Composition of initial mixtures mol%				Contents of samples in terms of $CrVMoO_7$–$AlVMoO_7$ system's components	Phases detected after last heating cycle
	Cr_2O_3	Al_2O_3	V_2O_5	MoO_3	$AlVMoO_7$ mol%	
1	22.50	2.50	25.00	50.00	10.00*	$Cr_{0.90}Al_{0.10}AlVMoO_7$
2	20.00	5.00	25.00	50.00	20.00	$Cr_{0.80}Al_{0.20}VMoO_7$
3	18.75	6.25	25.00	50.00	25.00*	$Cr_{0.75}Al_{0.25}VMoO_7$
4	17.50	7.50	25.00	50.00	30.00	$Cr_{0.70}Al_{0.30}VMoO_7$
5	15.00	10.00	25.00	50.00	40.00	$Cr_{0.60}Al_{0.40}VMoO_7$
6	12.50	12.50	25.00	50.00	50.00*	$Cr_{0.50}Al_{0.50}VMoO_7$
7	10.00	15.00	25.00	50.00	60.00	$Cr_{0.40}Al_{0.60}VMoO_7$
8	8.75	16.25	25.00	50.00	65.00*	$Cr_{0.35}Al_{0.65}VMoO_7$
9	7.50	17.50	25.00	50.00	70.00	$Cr_{0.35}Al_{0.65}VMoO_7$ $AlVMoO_7$
10	5.00	20.00	25.00	50.00	80.00*	$Cr_{0.35}Al_{0.65}VMoO_7$ $AlVMoO_7$
11	2.50	22.50	25.00	50.00	90.00	$Cr_{0.35}Al_{0.65}VMoO_7$ $AlVMoO_7$

* – Samples prepared both from oxides and from the compounds $CrVMoO_7$ and $AlVMoO_7$

Within this work three samples of the solid solution $Cr_{2-x}Al_x(MoO_4)_3$ for x=0.5, 1.0 and 1.5 were prepared. The synthesis of this solid solution was performed using weighed portions of the oxides Cr_2O_3, Al_2O_3, and MoO_3 in appropriate ratios, by calcining them in the following cycles: 600°C(24 h)+650°C(24 h)+700°C(24 h).

Results and discussion

Phase compositions of preparations prepared both from single oxides and from the compounds $CrVMoO_7$ and $AlVMoO_7$ representing the investigated system $CrVMoO_7$–$AlVMoO_7$, after the last heating cycle, i.e. in equilibrium state, are presented in Table 1. The composition of obtained products was the same regardless of the way of preparation.

Powder diffraction patterns of the preparations 1–8 after the last calcination cycle, containing up to 65.00 mol% $AlVMoO_7$ in a mixture with $CrVMoO_7$, were similar to one another and to the diffractogram of $CrVMoO_7$ both with respect to the number and to the mutual intensity relations of the recorded diffraction lines. The angular positions of these lines was shifted with increasing the Al_2O_3 content in initial oxide mixtures towards higher angles 2θ, in comparison with the diffractogram of pure $CrVMoO_7$, i.e. they corresponded to smaller interplanar distances d. The obtained results indicated that in the investigated system $CrVMoO_7$–$AlVMoO_7$ solid solution is formed by an incorporation of the ions Al^{3+}(r=0.535 Å) into the crystal lattice of $CrVMoO_7$ instead of Cr^{3+}(r=0.61 Å), thus a substitutional solid solution of a general formula $Cr_{1-x}Al_xVMoO_7$ is formed. The formulae of obtained solid solution were evaluated from the content of initial oxides. Phase analysis of final preparations implies that maximal solubility of $AlVMoO_7$ in $CrVMoO_7$ at ambient temperature amounts at least to 65.00 mol% $AlVMoO_7$. In terms of the oxides contents (Table 1), such solid solution contains 16.25 mol% Al_2O_3 and 8.75 mol% Cr_2O_3, which means that 65 mol% of the Cr^{3+} ions in the lattice of $CrVMoO_7$ was substituted by Al^{3+}. This phase is described therefore by the formula $Cr_{0.35}Al_{0.65}VMoO_7$ (Table 1, sample 8).

Phase analysis of the samples representing the remaining component concentration range of the investigated system $CrVMoO_7$–$AlVMoO_7$, i.e. containing more than 65 mol% $AlVMoO_7$ in a mixture with $CrVMoO_7$, showed that they were two-phase and contained beside the solid solution $Cr_{0.35}Al_{0.65}VMoO_7$, i.e. the one with maximal extent of Al^{3+} incorporation into the structure of $CrVMoO_7$, also the phase $AlVMoO_7$. In subsequent preparations the intensity of diffraction reflections characteristic for $AlVMoO_7$ increases and for $Cr_{0.35}Al_{0.65}VMoO_7$ decreases with increasing the content of $AlVMoO_7$ in initial mixtures. Positions of the diffraction lines recorded in diffraction patterns of these samples, the lines characteristic for $AlVMoO_7$, do not change, which proves additionally that the Cr^{3+} ions are not incorporated into the structure of $AlVMoO_7$.

In a further part of research, powder diffraction patterns of selected monophase samples of the obtained solid solution were indexed (program Refinement) and the calculated unit cell parameters and unit cell volumes are presented in Table 2. An analysis of the data compiled in Table 2 allows us to confirm the conclusion that in the system $CrVMoO_7$–$AlVMoO_4$ a solid solution of $Cr_{1-x}Al_xVMoO_7$ type with the structure of $CrVMoO_7$ is formed. With increasing the incorporation extent of the smaller Al^{3+} ions into the $CrVMoO_7$ structure a distinct contraction of crystal lattice is observed, a measure of which can be the decreasing unit cell volume of the subsequent solid solution samples.

Table 2 The unit cell parameters and unit cell volumes of the $CrVMoO_7$ (x=0), $AlVMoO_7$ (x=1.0) and selected samples of the $Cr_{1-x}Al_xVMoO_7$ type solid solution

Formula	Content of $AlVMoO_7$ mol%	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/Å^3
$CrVMoO_7$	0	5.536	6.584	7.865	96.13	89.87	101.94	278.81
$Cr_{0.90}Al_{0.10}VMoO_7$	10	5.517	6.579	7.861	96.19	89.87	101.92	277.47
$Cr_{0.75}Al_{0.25}VMoO_7$	25	5.502	6.567	7.853	96.23	89.85	101.94	275.91
$Cr_{0.50}Al_{0.50}VMoO_7$	50	5.479	6.535	7.839	96.36	89.84	101.96	272.84
$Cr_{0.35}Al_{0.65}VMoO_7$	65	5.463	6.523	7.833	96.38	89.81	101.96	271.32
$AlVMoO_7$	100	5.383	8.175	12.743	90.00	90.00	90.00	560.77

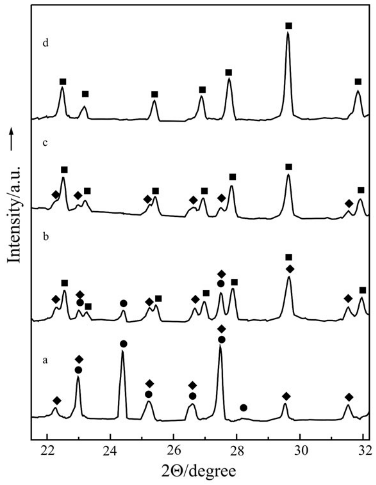

Fig. 1 The changes in powder diffraction patterns on selected stages of the ■ – $Cr_{1-x}Al_xVMoO_7$, ◆ – synthesis reaction from $CrVMoO_7$ and ● – $AlVMoO_7$ in their equimolar mixture; a – initial mixture of $CrVMoO_7$ and $AlVMoO_7$; b – after heating at 600°C(24h); c – after heating at 600°C(2x24 h); d – after additional heating at 650°C(24 h) and 680°C(4x24 h), pure $Cr_{0.5}Al_{0.5}VMoO_7$

A much slower course of synthesising the $Cr_{1-x}Al_xVMoO_7$ solid solution from the ready prepared phases $MVMoO_7$ (where M=Al, Cr) enabled us to follow the mechanism of this process. Figure 1 presents powder diffraction patterns of the preparation comprising in its initial mixture 50 mol% $AlVMoO_7$ and 50 mol% $CrVMoO_7$ before beginning the synthesis (curve a), after the first heating stage at 600°C (curve b), after the second heating stage at 600°C (curve c) and after the fourth heating stage at 680°C (curve d), the pure phase $Cr_{0.5}Al_{0.5}VMoO_7$. After the first heating stage at 600°C (Fig. 1 curve b) the diffractogram revealed beside the diffraction reflections characteristic for pure phases $AlVMoO_7$ and $CrVMoO_7$ also a set of lines characteristic for $Cr_{0.35}Al_{0.65}VMoO_7$, (x=0.65) that is to say the solid solution with the maximal possible extent of Al^{3+} incorporation into the structure of $CrVMoO_7$. In the diffractogram of the preparation after the second heating stage at 600°C (Fig. 1 curve c) two sets of diffraction reflections were recorded, characteristic for $CrVMoO_7$ and the solid solution $Cr_{1-x}Al_xVMoO_7$ - the reflections of which lay at lower angles than it was after the first stage of synthesis at 600°C. In the diffractogram of the preparation after the fourth heating stage at 680°C (Fig. 1 curve d) a set of diffraction reflections characteristic only for $Cr_{0.5}Al_{0.5}VMoO_7$ was recorded, so they were shifted still more towards lower angles 2Θ than it was after the second heating stage. The results of such conducted XRD investigations proved that the synthesis process of the $Cr_{1-x}Al_xVMoO_7$ type phases with the use of the pure phases $MVMoO_7$ leads at an early stage to obtaining a solid solution with the maximal possible extent of $AlVMoO_7$ incorporation into $CrVMoO_7$. Next, the non-reacted $CrVMoO_7$ reacts with the solid solution $Cr_{0.35}Al_{0.65}VMoO_7$ yielding a solid solution of a composition intermediate between $Cr_{0.35}Al_{0.65}VMoO_7$ and $Cr_{0.5}Al_{0.5}VMoO_7$. This process leads on using up the whole excessive $CrVMoO_7$ to obtaining the phase of the assumed composition $Cr_{0.5}Al_{0.5}VMoO_7$.

The obtained preparations after the last heating cycle, i.e. monophase and containing only the solid solution $Cr_{1-x}Al_xVMoO_7$, as well as the two-phase ones containing additionally $AlVMoO_7$ were subjected to DTA investigation. In the DTA curves of samples containing only the solid solution two endothermic effects were recorded up to 1000°C. The beginning temperature of the first distinctly pronounced effect decreased with increasing x in the phases $Cr_{1-x}Al_xVMoO_7$ from 810°C for the sample where x=0.1 to 710°C for the sample where x=0.65. The second effect recorded in DTA curves of monophase preparations began at 905°C for x=0.1, and its onset temperature, decreasing for subsequent samples with increasing x, amounted to 865°C for x=0.65. The second effect was always much smaller than the first and for the majority of samples it was registered as a poorly pronounced remnant effect. Figure 2 presents exemplary DTA curves for the samples containing $CrVMoO_7$ (curve A), $AlVMoO_7$ (curve B), $Cr_{0.35}Al_{0.65}VMoO_7$ (curve C) and DTA curve of mixture of $Cr_{0.35}Al_{0.65}VMoO_7$ and $AlVMoO_7$, sample containing 80 mol% of $AlVMoO_7$ in terms of the components of the system $CrVMoO_7$–$AlVMoO_7$ (curve D).

In order to explain the nature of these endothermic effects and first of all to establish the way of melting the solid solution $Cr_{1-x}Al_xVMoO_7$, the samples of solid solution for x=0.1; 0.25; 0.40 and 0.65 were additionally heated for 3 h at 850°C (x=0.1 and x=0.25) and 820°C (x=0.4 and x=0.65), i.e. at temperatures close to the extremum temperatures of the first endothermic effect registered in the DTA curves of these preparations. After heating these samples they were cooled rapidly to ambient temperature. Phase analysis of the preparations partially melted at these tempera-

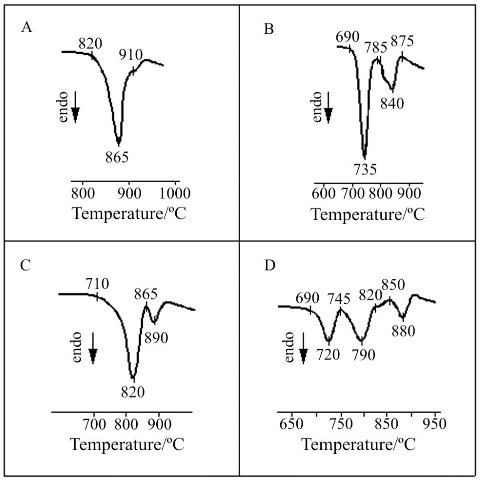

Fig. 2 DTA curves of A – $CrVMoO_7$, B – $AlVMoO_7$, C – $Cr_{0.35}Al_{0.65}VMoO_7$, D – mixture of $Cr_{0.35}Al_{0.65}VMoO_7$ and $AlVMoO_7$, sample containing 80 mol% of $AlVMoO_7$ in terms of the components of the system $CrVMoO_7$ – $AlVMoO_7$

tures showed that they comprised a mixture of the solid solution $Cr_{2-z}Al_z(MoO_4)_3$ with $V_9Mo_6O_{40}$ and V_2O_5. Taking into account that both $V_9Mo_6O_{40}$ and V_2O_5 at temperatures the heating of samples was conducted at do not exist already as solid phases [16], so they crystallise from the liquid, it was concluded that the investigated solid solution $Cr_{1-x}Al_xVMoO_7$ melt incongruently and their solid product of melting is the solid solution $Cr_{2-z}Al_z(MoO_4)_3$ [17]. Analysis of reflections positions characteristic for such thermally treated samples of solid solution in comparison with diffractograms of separately obtained samples containing only the solid solution $Cr_{2-z}Al_z(MoO_4)_3$ for z=0.5; 1.0 and 1.5 allowed us to state moreover that with increasing the amount of Al^{3+} in the $CrVMoO_7$ crystal lattice the extent of incorporating these ions into the solid melting product of these solid solution, *i.e.* into $Cr_{2-z}Al_z(MoO_4)_3$, increases as well.

The DTA investigations of samples at equilibrium that were two-phase and contained beside $Cr_{0.35}Al_{0.65}VMoO_7$ also variable amounts of $AlVMoO_7$ allowed it to be established that these phases remain at equilibrium with each other in the solid state up to 690°C, which was evidenced by the beginning temperature of the first endothermic effect recorded in DTA curves of these samples (Fig. 2 curve D).

The pure phases $CrVMoO_7$, $AlVMoO_7$ as well as the solution phases $Cr_{1-x}Al_xVMoO_7$ were also subjected to an investigation with the use of infrared spectroscopy (IR).

Figure 3 presents the IR spectra of $CrVMoO_7$, (curve a), $Cr_{0.75}Al_{0.25}VMoO_7$ (curve b), $Cr_{0.35}Al_{0.65}VMoO_7$ (curve c) and $AlVMoO_7$ (curve d). The IR spectrum of $AlVMoO_7$ (curve d) differs distinctly from the remaining spectra of the phases $Cr_{1-x}Al_xVMoO_7$ (curves a, b and c) that are very similar to one another. In the case of

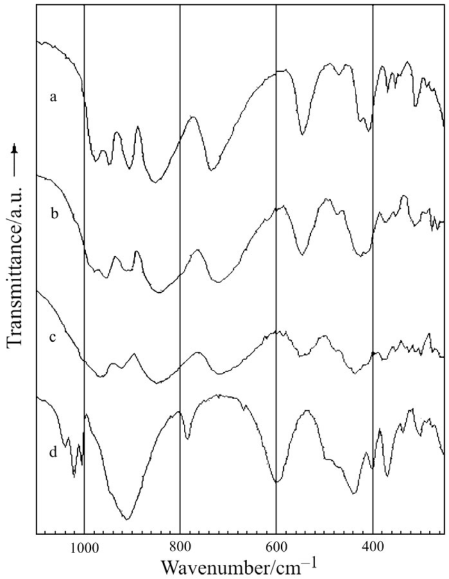

Fig. 3 IR spectra of: a – $CrVMoO_7$, b – $Cr_{0.75}Al_{0.25}VMoO_7$, c – $Cr_{0.35}Al_{0.65}VMoO_7$, d – $AlVMoO_7$

the solid solution $Cr_{1-x}Al_xVMoO_7$ with increasing the $AlVMoO_7$ content an evident broadening of the absorption bands corresponding respectively to each other is observed in comparison to the IR spectrum of $CrVMoO_7$. This is undoubtedly due to an appearance of numerous M–O bonds with their lengths smaller than those occurring in the structure of $CrVMoO_7$.

The IR spectrum of the phase with the formula $Cr_{0.35}Al_{0.65}VMoO_7$ (x=0.65) reveals the presence of absorption bands with their maxima at 964, 922, 848, 716, 540 and 438 cm^{-1}. With increasing the incorporation extent of the lighter and smaller Al^{3+} ions into the structure of $CrVMoO_7$ a shift of the respective absorption bands towards higher wavenumbers is observed. The most evident shift of an absorption band is observed in the case of the band with its maximum registered in the IR spectrum at 438 cm^{-1} (in the IR spectrum of pure $CrVMoO_7$ at 405 cm^{-1}). Therefore one may suppose that this band is associated with stretching vibrations within the MO_6 octahedra (M=Cr, Al) building up the structure of $Cr_{1-x}Al_xVMoO_7$ together with the tetrahedra VO_4 and MoO_4 [9–11, 13, 20].

Conclusions

The research conducted within this work and the obtained results allow us to draw the following conclusions:

- In the quaternary oxide system Cr_2O_3–V_2O_5–MoO_3–Al_2O_3 a solid solution with limited solubility of $AlVMoO_7$ in $CrVMoO_7$ is formed with its general formula $Cr_{1-x}Al_xVMoO_7$.
- The Al^{3+} ions are incorporated into the crystal lattice of $CrVMoO_7$ instead of Cr^{3+} and the maximal solubility of $AlVMoO_7$ in $CrVMoO_7$ amounts at least to 65 mol%.
- With increasing the value of x in the phases $Cr_{1-x}Al_xVMoO_7$ a contraction of crystal lattice occurs together with a shift of absorption bands towards higher wavenumbers.
- The solid solution $Cr_{1-x}Al_xVMoO_7$ melts incongruently with a dependence on the value of x in the temperature range from 710°C for x=0.65 to 810°C for x=0.10. The solid melting product is a solid solution of the general formula $Cr_{2-z}Al_z(MoO_4)_3$.

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