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Synthesis and characterization of phosphates in molten systems $Cs_2O–P_2O_5–CaO–M^{III}_2O_3$ (M^{III}—Al, Fe, Cr)

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ABSTRACT

The crystallization of complex phosphates from the melts of $Cs_2O–P_2O_5–CaO–M^{III}_2O_3$ (M^{III}—Al, Fe, Cr) systems have been investigated at fixed value Cs/P molar ratios equal to 0.7, 1.0 and 1.3 and Ca/P=0.2 and $Ca/M^{III}=1$. The fields of crystallization of $CsCaP_3O_9$, β-$Ca_2P_2O_7$, $Cs_2CaP_2O_7$, $Cs_3CaFe(P_2O_7)_2$, $Ca_9M^{III}(PO_4)_7$ (M^{III}—Fe, Cr), $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ and $CsCa_{10}(PO_4)_7$ were determined. Obtained phosphates were investigated using powder X-ray diffraction and FTIR spectroscopy. Novel whitlockite-related phases $CsCa_{10}(PO_4)_7$ and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ have been characterized by single crystal X-ray diffraction: space group *R3c*, $a=10.5536(5)$ and 10.5221(4) Å, $c=37.2283(19)$ and 37.2405(17) Å, respectively.

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1. Introduction

Synthesis of new compounds and functional materials is a long-term strategy of modern chemistry. Among a great variety of inorganic solids the compounds containing phosphate anions keep an interest due to a number of crystal structure and properties. In particular, complex caesium-containing phosphates are widely investigated for possible usage of them as ferroelectric materials [1–3] and as crystalline matrices for the storage of radioactive isotope wastes.

The caesium phosphates that are actually known up to nowadays can be tentatively divided accordingly the condensation degree of phosphate anions into following groups: orthophosphates ($CsM^{II}PO_4$ (M^{II}—Mn, Co, Zn) [1–3], $CsLi_{0.5}Al_{0.5}PO_4$ [4], $CsM^{II}M^{III}(PO_4)_2$ [5]), diphosphate ($CsVP_2O_7$ [6]), threephosphates ($Cs_2M^{III}P_3O_{10}$ (M^{III}—Al, Ga) [7] and $CsAl_3(P_3O_{10})_2$ [8]), and compounds with cyclic phosphate anions ($Cs_3M^{III}_3P_{12}O_{36}$ (M^{III}—Fe, Ga, V) [9–11], $Cs_2M^{II}_2P_6O_{18}$ (M^{II}–Mg, Zn) [12] and $CsM^{II}M^{III}P_6O_{18}$ (M^{II}—Mg, Co, Zn, Mn; M^{III}—Al, Ga, V, Fe) [13]). These compounds were synthesized applying solid state technique [1–8] or from polyphosphate acids [9–15]. In our previous works it was shown that complex caesium-containing phosphates could be obtained during slow crystallization in multicomponent molten caesium phosphates. For instance, langbeinite-related phosphates $Cs_{1+x}Ln_xZr_{2-x}(PO_4)_3$ (Ln=Sm–Lu) were synthesized in the melts of $Cs_2O–P_2O_5–LnF_3–ZrF_4$ systems [16]. Double orthophosphate $Cs_3In_3(PO_4)_4$ was prepared in the self-flux of $Cs_2O–P_2O_5–CuO–In_2O_3$ system [17].

We reported here the results of phase formation investigations in the melts of $Cs_2O–P_2O_5–CaO–M^{III}_2O_3$ (M^{III}—Al, Fe, Cr) systems at fixed values of Cs/P molar ratios equal to 0.7, 1.0 and 1.3 at constant ratios of Ca/P=0.2 and $M^{III}/Ca=1$. Obtained compounds have been characterized by powder X-ray diffraction and FTIR spectroscopy. Crystal structures of $CsCa_{10}(PO_4)_7$ and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ were determined by single crystal X-ray diffraction.

2. Experimental

2.1. Synthetic procedure

The interactions in the $Cs_2O–P_2O_5–CaO–M^{III}_2O_3$ (M^{III}—Al, Fe, Cr) systems were performed using crystallization of the homogenous melts. $CsOH·H_2O$, H_3PO_4, CaO (all reagent grade), Al_2O_3, Fe_2O_3 and Cr_2O_3 (all extra pure grade) were used to prepare precursors (for example $CsPO_3$ from $CsOH·H_2O$ and H_3PO_4) and initial mixtures at appropriate ratios for melts. Fluxes of the $Cs_2O–P_2O_5–CaO–M^{III}_2O_3$ (M^{III}—Al, Fe, Cr) systems with following ranges of the ratios at point of homogeneity were investigated: Cs/P=0.7–1.3 at constant ratios of Ca/P=0.2 and $M^{III}/Ca=1.0$.

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Two techniques of the melts preparation were applied depending starting Cs/P ratio. At Cs/P < 1 calculated amounts of $CsPO_3$, CaO and $M^{III}_2O_3$ were grinded, put into platinum crucible and then necessary amount of H_3PO_4 was added. The crucibles were put into the cold furnace and slowly heated up (approximately at a rate of 200 K/h) to 1073 K. At this temperature the flux was exposed during 40–50 min to reach homogeneity. The crystallization was performed at a rate of 30–50 K/h down to 943–923 K. For the melts with Cs/P ≥ 1 calculated amounts of previously prepared caesium phosphate glass (with constant Cs/P ratio equal to 1.3), $CsPO_3$, CaO and $M^{III}_2O_3$ were grinded in an agate mortar. Then the resulting charge in a platinum crucible was directly placed into hot furnace (1273–1323 K) and kept at this temperature for 30 min. The crystallization was carried out in a manner described above for the fluxes with Cs/P < 1. The completeness of the dissolving of oxides was controlled by observing the melt and by picking up of the melts with a platinum stirrer which were examined by optical microscopy. At the final temperature of crystallization the remaining flux were purred out from the solids. The crystals were washed up by cold water.

2.2. Identification

Chemical compositions of the samples were verified by ICP-AES method with Shimadzu ICPE-9000 spectrometer after appropriate sample preparation (wet digestion with nitric acid).

Phase composition was investigated by powder XRD (diffractometer Shimadzu XRD-6000, curved pyrolitic graphite counter monochromator, Cu$K\alpha$ radiation $\lambda = 1.54184$ Å, $2\theta = 5$–90°).

IR-spectra of the synthesized compounds were recorded using FTIR spectrometer Nicolet Nexus 470 at wavelengths range of 400–4000 cm^{-1}. Measurements were performed for the samples pressed into the pellets of KBr.

2.3. Crystal structure determination

Prismatically shaped crystals of $CsCa_{10}(PO_4)_7$ and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ were selected for structure determination. Oxford Diffraction "XCalibur 3" diffractometer equipped with 2048 × 2048 K (4 MPixel) CCD detector was used for data collection (Table 1). The structures were solved with SHELXS-97 [18] by direct method. The sites of caesium, calcium and phosphorus were defined during structure solution. Remaining oxygen atoms were found from difference Fourier maps. According to the chemical composition found the second compound contains iron. As this structure type contains three kinds of calcium polyhedra there was assumed, that iron can occupy only one type of the calcium site. This site is six coordinated which form octahedron [Ca1O_6]. At the same time shortened (in comparison with pure Ca–O bond lengths in the corresponding [Ca1O_6] octahedra of $CsCa_{10}(PO_4)_7$) calculated length of M–O bond in this octahedron only makes possibility for partial substitution of calcium by iron. The iron was placed into Ca1 position. The coordinates and anisotropic displacement parameters of Ca1 and Fe1 were constrained. The occupancies of Cs1, Ca1 and Fe1 were refined with restrained as fully occupied Ca1/Fe1 position. Restriction of the charge equal to 3 was applied also to keep the electroneutrality of the compound. Structure refinement was performed with SHELXL-97 [19]. The refined chemical composition was found to be close to that determined by chemical analyses.

The detailed results of the structure determination can be found at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +(49) 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-380395 for $CsCa_{10}(PO_4)_7$ and CSD-380393 for $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$.

3. Results and discussions

3.1. Crystallization in the melts

The crystallization of three kinds of crystalline compounds $CsCaP_3O_9$, β-$Ca_2P_2O_7$ and $Cs_2CaP_2O_7$ in the fluxes of Cs_2O–P_2O_5–CaO system were reported previously [20]. Only one type of compound with general composition $CsM^{III}P_2O_7$ crystallizes from the melts Cs_2O–P_2O_5–$M^{III}_2O_3$ (M^{III}—Fe, Cr) [21]. In the caesium aluminium phosphate melts any crystallines cannot be obtained due to a wide region of the vitrification [21].

The crystallization of the compounds was observed at a temperature range of 1323–773 K in the investigated sections of the Cs_2O–P_2O_5–CaO–$M^{III}_2O_3$ (M^{III}—Al, Fe, Cr) systems. The presence of the CaO in the melts has an influence on the dissolution of threevalent metal oxides, especially on Cr-containing one. In the system Cs_2O–P_2O_5–Cr_2O_3 (section at ratios Cs/P = 0.7–1.5, Cr/P = 0.11) homogenization of the melts can be reached only after 4–6 h at a temperature of 1323 K [21]. At the same time with the presence of CaO in the system for the same ratios Cs/P and Cr/P a complete homogenization of the melt was observed after 20–30 min at 1273 K. This fact may be connected with increasing of basicity in the Cs_2O–P_2O_5–CaO–$M^{III}_2O_3$ systems comparing with Cs_2O–P_2O_5–$M^{III}_2O_3$ (M^{III}—Al, Fe, Cr) (the same Cs/P ratios). In the Al- and Fe-containing systems the dissolution of the oxides it takes two times shorter period (approx. 20 min.) comparing with the systems without CaO. A slow cooling of the homogenous melts results in crystallization of several compounds, depending the initial Cs/P ratio and the nature of threevalent metal.

3.1.1. Cs_2O–P_2O_5–CaO–Al_2O_3 system

A complete dissolution of CaO–Al_2O_3 oxides mixture in the caesium phosphate melts with Cs/P ratio equal to 0.7 is observed at a temperature of 1023 K. Further cooling of this melt down to 773 K leads to crystallization of plate-shaped colourless crystals $Ca_2P_2O_7$. Phase analysis of XRD powder pattern confirmed that obtained compound belongs to β-polymorph of $Ca_2P_2O_7$ (PDF2 01-081-2257). The melts with initial Cs/P ratio equal to 1.0 vitrify after cooling without formation of crystalline compounds. The crystallization of the fluxes with Cs/P = 1.3 at temperatures below 923 K results in formation of prismatically shaped colourless crystals. Phase analysis of obtained compound showed, that it is isostructural to $KCa_{10}(PO_4)_7$ (PDF2 00-045-0138). Element composition of the obtained phosphate corresponds to $CsCa_{10}(PO_4)_7$ (mass %: Cs 11.21–found, 11.09–calc.; Ca 33.44–found, 33.41–calc.; P 17.98–found, 18.09–calc.). The structure of $CsCa_{10}(PO_4)_7$ was investigated by single crystal X-ray diffraction.

3.1.2. Cs_2O–P_2O_5—CaO–Fe_2O_3 system

Regions of crystallization of diphosphates and orthophosphates were found in the investigated area of ratios. Light pink plate-like crystals of triple caesium calcium iron (III) diphosphate $Cs_3CaFe(P_2O_7)_2$ are formed in the melts at Cs/P = 0.7 and temperature range of 1073–923 K. The structure of $Cs_3CaFe(P_2O_7)_2$ was reported previously [22]. Almost colourless hexagonal plates of double orthophosphate $Ca_9Fe(PO_4)_7$ can be synthesized by crystallization of the melts with Cs/P = 1.0 at a temperature range of 1123–873 K. This compound belongs to rhombohedral system with the cell parameters: $a = 10.3614(1)$ and $c = 37.2339(5)$ Å.

Increasing of Cs/P ratio in the initial melts strongly influents on the element composition of the crystallized phases which is

Table 1
Crystallographic data and structure refinement parameters for $CsCa_{10}(PO_4)_7$ and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$.

	$CsCa_{10}(PO_4)_7$	$Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$
Crystal data		
Crystal system	trigonal	trigonal
Space group	*R3c*	*R3c*
Cell parameter (Å) $a=$	10.5536(5)	10.5221(4)
$c=$	37.2283(19)	37.2405(17)
V (Å^3)	3590.9(3)	3570.7(3)
Z	6	6
$\rho_{calc.}$ (g/cm^3)	3.325	3.222
Crystal dimensions (mm)	$0.10\times0.09\times0.07$	$0.10\times0.08\times0.05$
Data collection		
Apparatus	XCalibur-3	XCalibur-3
Wavelength (Å)	0.71073	0.71073
Monochromator	Graphite	Graphite
Scan mode	φ and ω	φ and ω
μ (mm^{-1})	4.287	3.885
Absorption correction	multi-scan	multi-scan
T_{min}; T_{max}	0.6328; 0.7152	0.6835; 0.7532
Number of reflections	12,663	14,569
Independent reflections	3482	3489
Reflections with $>2\sigma(I)$	2325	3109
$\theta_{min.;\ max.}$ (deg.)	3.3; 35.0	3.1; 35.0
R_{int}	0.0627	0.045
$h=$, $k=$, $l=$,	$-12\rightarrow17$; $-17\rightarrow15$; $-60\rightarrow59$	$-16\rightarrow16$; $-16\rightarrow16$; $-60\rightarrow60$
Solution and refinement		
Primary solution method	direct	direct
Weighting scheme	$w=1/[\sigma(F_o^2)+0.0446P)^2]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma(F_o^2)+0.0484P)^2]$, where $P=(F_o^2+2F_c^2)/3$
R_1(all)	0.0799	0.0435
wR_2	0.0979	0.086
S (Goof)	0.902	1.107
Number of parameters	140	143
$(\Delta\rho)_{max.\ min}$ (e/Å^{-3})	2.798; −2.546	1.343; −1.534
Flack parameter	0.50(3)	0.75(2)

connected with inclusion of caesium into framework of $Ca_9Fe(PO_4)_7$. Resulting compounds belongs to solid solutions of $Ca_9Fe(PO_4)_7$ and $CsCa_{10}(PO_4)_7$. Their chemical composition can be specified as $Cs_xCa_{9+x}Fe_{1-x}(PO_4)_7$, where $0\le x\le1$. The phosphate which belongs to denoted above solid solutions with a general composition $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ (mass %: Cs 7.21–found, 7.25–calc.; Ca 33.36–found, 33.41–calc.; Fe 1.81–found, 1.79–calc.; P 18.52–found, 18.76–calc.) was isolated from the fluxes with Cs/P=1.3 at a temperatures below 1073 K and its crystal structure was investigated.

3.1.3. Cs_2O–P_2O_5–CaO–Cr_2O_3 system

Three types of distinct compounds were obtained in the system: $CsCaP_3O_9$, $Ca_9Cr(PO_4)_7$ and $Cs_2CaP_2O_7$. The cooling of the melts with Cs/P=0.7 from 1023 to 973 K is accompanied by crystallization of colourless crystals of $CsCaP_3O_9$. The same can be observed during cooling of the system without chromium [20]. Light green prisms of $Ca_9Cr(PO_4)_7$ can be synthesized by cooling of the fluxes with Cs/P=1.0 at a temperature range of 1273–923 K. Increasing of Cs/P ratio up to 1.3 does not initiate a formation of solid solution with a general composition $Cs_xCa_{9+x}Cr_{1-x}(PO_4)_7$, where $0\le x\le1$, in contrast to iron-containing system. At these conditions $Cs_2CaP_2O_7$ can be crystallized only. The structures of these compounds were reported previously [20,23–24].

3.2. Whithlockite-related structures

The compounds obtained in the system with element compositions $Ca_9Fe(PO_4)_7$, $Ca_9Cr(PO_4)_7$, $CsCa_{10}(PO_4)_7$ and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ derive from the β-$Ca_3(PO_4)_2$ which crystallizes in whitlockite mineral structure type [25,26]. The relations between β-$Ca_3(PO_4)_2$ and synthesized compounds lie in aliovalent substitution of calcium atoms in β-$Ca_3(PO_4)_2$. The framework of β-$Ca_3(PO_4)_2$ consists of 5 kinds of [CaO_n] polyhedra linked by 3 kinds of orthophosphate tetrahedra [PO_4]. Two atoms of Ca in 18*b* positions are surrounded by 8 oxygen atoms, one Ca atom in 18*b* site is coordinated by 7 oxygen atom and one Ca atom (6*a*) lies in the centre of octahedron (the range of distance Ca–O 2.2–2.8 Å), and the fifth type of Ca is situated in large cavity of the framework (three contacts Ca–O 2.53 Å, the distance of other one is more 3.1 Å). 2[CaO_8], [CaO_7], [CaO_6] and 3[PO_4] share their vertices and edges forming $[Ca_{10}(PO_4)_7]^-$ anionic sublattice. In case of β-$Ca_3(PO_4)_2$ the negative charge of the framework is compensated by additional Ca atoms, which are situated in cavity positions 6*a* with only half occupancy factor. Thus, the crystallographic formula can be shown as $Ca_{0.5}[Ca_{10}(PO_4)_7]$. The position of Ca in a cavity is suitable for substitution by alkaline metal, which is described in examples of $M^ICa_{10}(PO_4)_7$ (M^I—Li, Na, K) [27–29]. In our investigation the charge of the framework is compensated by "large" cations of caesium in $CsCa_{10}(PO_4)_7$.

Aliovalent substitution of Ca atoms by threevalent metal in β-$Ca_3(PO_4)_2$ is possible in [CaO_6] octahedra. That leads to appearance of the vacancies in cavity Ca position. This kind of substitution is observed for a wide range of threevalent metals solids with a general composition $Ca_9M^{III}(PO_4)_7$ (M^{III}—Cr, Fe, Ga, In) [29–32].

The crystallization of the whitlockite-related compounds in the Cs_2O–P_2O_5–CaO–Fe_2O_3 system results in $Ca_9Fe(PO_4)_7$ formation and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$. In latter case mixed substitution of calcium atoms in octahedral and cavity positions is realized. Both Ca positions liable to aliovalent substitution lie on three-fold axis in the whitlockite-like framework (Fig. 1(a)). In $CsCa_{10}(PO_4)_7$ caesium occupies completely Ca sites in the cavities of the

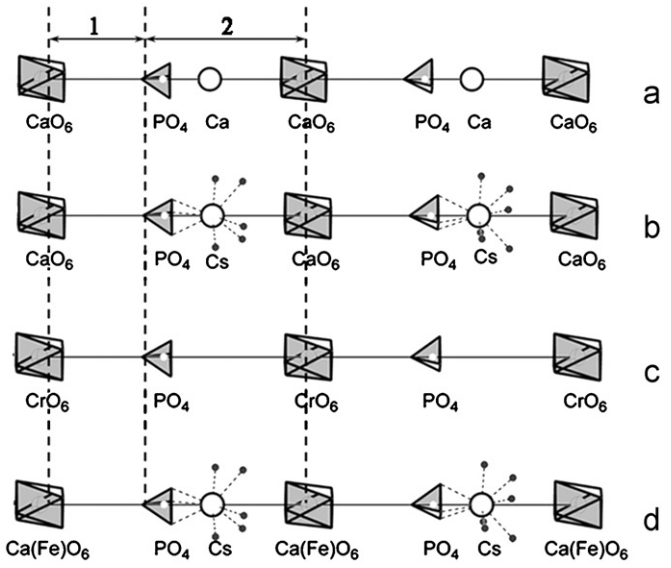

Fig. 1. The positions of calcium atoms on three-fold axis those are liable to substitution of calcium by heterovalent metals in β-$Ca_3(PO_4)_2$ framework: (a) β-$Ca_3(PO_4)_2$ (1–7.163 Å, 2–11.539 Å [24]); (b) $CsCa_{10}(PO_4)_7$ (1–7.083 Å, 2–11.531 Å); (c) $Ca_9Cr(PO_4)_7$ (1–7.053 Å, 2–11.513 Å [23]); (d) $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ (1–7.089 Å, 2–11.531 Å).

framework (Fig. 1(b)). The crystallization of compounds with general formula $Ca_9M^{III}(PO_4)_7$ results in complete substitution of Ca by iron or chromium in octahedral coordinated sites on three-fold axis and the Ca position in cavity remains unoccupied [24] (Fig. 1(c)). In $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ the cavity position is occupied by caesium only (occ. 0.626), and octahedral sites are partially occupied by Ca and Fe (Table 2, Fig. 1(d)). By this reason we can conclude that the whitlockite-related compounds consists of a rigid anion-like framework $[Ca_{10}(PO_4)_7]^-$ and cations in the cavities to compensate charge of the framework. When the cavities are filled by potassium or caesium their oxygen environment consist of nine O atoms (three groups each containing three equidistant O atoms). In $KCa_{10}(PO_4)_7$ K–O contacts are in the range of 2.64–3.25 Å [28]. In reported compounds they are in the range of 2.75–3.26 Å (Table 3). Thus increasing the ionic radius of alkaline metal insignificantly influences the lengths of its oxygen contacts.

It should be noted, that dependence of the variation of cell parameters are different for different kinds of aliovalent substitutions in whitlockite-related structures. In compounds with general composition $Ca_9M^{III}(PO_4)_7$ [29–32] decreasing a and c parameters occurs with decreasing three valent metal's ionic radii. From Li to Cs sequence simultaneously increasing of a and decreasing c is observed in $M^ICa_{10}(PO_4)_7$ phosphates. That accompanied with increasing of the cell volume. Those facts can be

Table 2
The atomic coordinates and their equivalent isotropic thermal parameters for $CsCa_{10}(PO_4)_7$ (I) and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ (II).

Atom		Site	Occ.	x	y	z	U_{eq}/U^*_{iso}(Å^2)
Ca1	I	6a	1	0.3333	0.6667	0.15339(5)	0.0097(3)
	II		0.627(4)	0.3333	0.6667	0.15355(3)	0.01715(18)
Fe1	II	6a	0.373(3)	0.3333	0.6667	0.15355(3)	0.01715(18)
Ca2	I	18b	1	0.46462(14)	0.52328(14)	0.08485(2)	0.00571(18)
	II		1	0.46500(7)	0.52334(7)	0.085039(16)	0.01024(11)
Ca3	I	18b	1	0.27656(13)	0.15336(14)	0.05409(3)	0.0074(2)
	II		1	0.27849(7)	0.15380(7)	0.053783(17)	0.01090(12)
Ca4	I	18b	1	0.40522(12)	0.19261(13)	0.14605(3)	0.0091(2)
	II		1	0.40352(8)	0.19152(7)	0.146111(17)	0.01573(13)
Cs1	I	6a	1	0	0	0.16622(2)	0.02631(19)
	II		0.626(3)	0	0	0.166396(19)	0.01998(19)
P1	I	6a	1	0.6667	0.3333	0.08925(6)	0.0043(4)
	II		1	0.6667	0.3333	0.08864(4)	0.0096(2)
P2	I	18b	1	0.15348(16)	0.34487(16)	0.01936(3)	0.0044(3)
	II		1	0.15361(9)	0.34491(9)	0.01929(2)	0.00852(14)
P3	I	18b	1	0.14346(18)	0.32168(16)	0.12119(3)	0.0060(3)
	II		1	0.14208(10)	0.31939(10)	0.12121(2)	0.01070(16)
O1	I	6a	1	0.6667	0.3333	0.1298(2)	0.0165(15)
	II		1	0.6667	0.3333	0.12985(11)	0.0152(8)
O2	I	18b	1	0.5211(4)	0.3192(5)	0.07595(11)	0.0102(8)
	II		1	0.5209(2)	0.3201(3)	0.07569(7)	0.0165(5)
O3	I	18b	1	0.0784(5)	0.1816(4)	0.02987(11)	0.0085(7)
	II		1	0.0786(3)	0.1810(3)	0.02950(7)	0.0136(4)
O4	I	18b	1	0.0546(5)	0.4054(5)	0.03189(10)	0.0083(8)
	II		1	0.0536(3)	0.4039(3)	0.03191(6)	0.0141(4)
O5	I	18b	1	0.1719(5)	0.3665(5)	−0.02137(8)	0.0067(7)
	II		1	0.1732(3)	0.3683(3)	−0.02134(6)	0.0142(4)
O6	I	18b	1	0.3066(4)	0.4229(5)	0.03632(10)	0.0120(9)
	II		1	0.3062(3)	0.4216(3)	0.03660(6)	0.0178(5)
O7	I	18b	1	−0.0049(4)	0.2715(5)	0.10217(10)	0.0085(8)
	II		1	−0.0053(3)	0.2713(3)	0.10161(6)	0.0137(4)
O8	I	18b	1	0.2397(5)	0.4854(4)	0.11100(11)	0.0132(8)
	II		1	0.2396(3)	0.4842(3)	0.11180(8)	0.0196(5)
O9	I	18b	1	0.2233(5)	0.2416(5)	0.10907(11)	0.0120(9)
	II		1	0.2233(3)	0.2408(3)	0.10847(7)	0.0182(5)
O10	I	18b	1	0.1115(6)	0.3026(6)	0.16136(10)	0.0226(12)
	II		1	0.1086(4)	0.2983(5)	0.16135(7)	0.0349(9)

Table 3
Selected bond distances (Å) for $CsCa_{10}(PO_4)_7$ and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$.

$CsCa_{10}(PO_4)_7$				$Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$			
Ca(Fe)O$_x$ polyhedra							
Ca(1)–O(8)^{i}	2.288(4) × 3	Ca(1)–O(3)^{iii}	2.313(4) × 3	Ca(1)|Fe(1)–O(8)^{i}	2.276(3) × 3	Ca(1)|Fe(1)–O(3)^{iii}	2.292(3) × 3
Ca(2)–O(6)	2.324(4)	Ca(2)–O(8)^{ii}	2.426(5)	Ca(2)–O(6)	2.325(2)	Ca(2)–O(8)^{ii}	2.436(3)
Ca(2)–O(4)^{ii}	2.390(4)	Ca(2)–O(2)	2.528(4)	Ca(2)–O(4)^{ii}	2.398(2)	Ca(2)–O(2)	2.510(3)
Ca(2)–O(5)^{v}	2.402(3)	Ca(2)–O(7)^{ii}	2.599(5)	Ca(2)–O(5)^{v}	2.401(2)	Ca(2)–O(7)^{ii}	2.582(3)
Ca(2)–O(8)	2.406(5)	Ca(2)–O(9)	2.927(5)	Ca(2)–O(8)	2.411(3)	Ca(2)–O(9)	2.917(3)
Ca(3)–O(10)^{vi}	2.366(4)	Ca(3)–O(9)	2.428(4)	Ca(3)–O(7)^{vi}	2.363(2)	Ca(3)–O(9)	2.420(3)
Ca(3)–O(7)^{vii}	2.378(4)	Ca(3)–O(3)	2.429(4)	Ca(3)–O(10)^{vii}	2.364(3)	Ca(3)–O(3)	2.434(2)
Ca(3)–O(3)^{vii}	2.381(4)	Ca(3)–O(6)	2.780(5)	Ca(3)–O(3)^{vi}	2.388(3)	Ca(3)–O(6)	2.760(3)
Ca(3)–O(2)	2.422(4)	Ca(3)–O(4)^{vii}	2.799(4)	Ca(3)–O(2)	2.402(2)	Ca(3)–O(4)^{vi}	2.765(3)
Ca(4)–O(7)^{vii}	2.397(4)	Ca(4)–O(5)^{v}	2.588(4)	Ca(4)–O(7)^{vi}	2.398(2)	Ca(4)–O(5)^{v}	2.582(3)
Ca(4)–O(4)^{v}	2.405(4)	Ca(4)–O(9)	2.616(4)	Ca(4)–O(4)^{v}	2.409(2)	Ca(4)–O(9)	2.611(3)
Ca(4)–O(1)	2.467(2)	Ca(4)–O(2)	2.908(4)	Ca(4)–O(1)	2.475(13)	Ca(4)–O(10)^{vi}	2.873(4)
Ca(4)–O(6)^{viii}	2.530(4)	Ca(4)–O(10)^{vii}	2.912(5)	Ca(4)–O(6)^{viii}	2.540(3)	Ca(4)–O(2)	2.926(3)
Ca(4)–O(5)^{viii}	2.586(4)			Ca(4)–O(5)^{viii}	2.570(3)		
CsO$_x$ polyhedra							
Cs(1)–O(10)^{ix}	2.803(6) × 3	Cs(1)–O(9)^{vii}	3.251(5) × 3	Cs(1)–O(10)^{ix}	2.758(4) × 3	Cs(1)–O(2)^{iii}	3.187(3) × 3
Cs(1)–O(2)^{iii}	3.200(4) × 3			Cs(1)–O(9)^{vi}	3.262(3) × 3		
PO$_4$ tetrahedra							
P(1)–O(1)	1.510(8)	P(1)–O(2)^{xi}	1.549(4) × 3	P(1)–O(1)	1.535(4)	P(1)–O(2)^{xi}	1.546(2) × 3
O(1)–P(1)–O(2)^{xi}	108.65(17)	O(1)–P(1)–O(2)^{xii}	108.65(17)	O(1)–P(1)–O(2)^{xi}	108.17(11)	O(1)–P(1)–O(2)	108.17(11)
O(2)^{xi}–P(1)–O(2)^{xii}	110.28(16)	O(1)–P(1)–O(2)	108.65(17)	O(1)–P(1)–O(2)^{xii}	108.17(11)	O(2)^{xi}–P(1)–O(2)	110.74(10)
O(2)^{xi}–P(1)–O(2)	110.28(16)	O(2)^{xii}–P(1)–O(2)	110.28(16)	O(2)^{xi}–P(1)–O(2)^{xii}	110.74(10)	O(2)^{xii}–P(1)–O(2)	110.74(10)
P(2)–O(5)	1.531(3)	P(2)–O(4)	1.543(4)	P(2)–O(5)	1.530(2)	P(2)–O(4)	1.539(3)
P(2)–O(6)	1.536(4)	P(2)–O(3)	1.544(4)	P(2)–O(6)	1.532(3)	P(2)–O(3)	1.543(3)
O(5)–P(2)–O(6)	107.8(2)	O(6)–P(2)–O(4)	113.7(3)	O(5)–P(2)–O(6)	108.04(15)	O(5)–P(2)–O(3)	112.08(15)
O(5)–P(2)–O(4)	107.4(2)	O(6)–P(2)–O(3)	108.0(3)	O(5)–P(2)–O(4)	107.57(14)	O(6)–P(2)–O(3)	107.49(15)
O(5)–P(2)–O(3)	111.9(2)	O(4)–P(2)–O(3)	108.0(2)	O(6)–P(2)–O(4)	113.98(15)	O(4)–P(2)–O(3)	107.78(14)
P(3)–O(10)	1.524(4)	P(3)–O(7)	1.551(4)	P(3)–O(10)	1.526(3)	P(3)–O(8)	1.551(3)
P(3)–O(9)	1.529(4)	P(3)–O(8)	1.551(4)	P(3)–O(9)	1.531(3)	P(3)–O(7)	1.553(3)
O(10)–P(3)–O(9)	111.3(3)	O(10)–P(3)–O(8)	111.5(3)	O(10)–P(3)–O(9)	112.06(17)	O(10)–P(3)–O(7)	107.02(18)
O(10)–P(3)–O(7)	106.5(3)	O(9)–P(3)–O(8)	108.0(3)	O(10)–P(3)–O(8)	111.1(2)	O(9)–P(3)–O(7)	114.51(15)
O(9)–P(3)–O(7)	114.7(2)	O(7)–P(3)–O(8)	104.8(3)	O(9)–P(3)–O(8)	107.36(17)	O(8)–P(3)–O(7)	104.62(15)
Symmetry codes							
(i) $-x+y$, $1-x$, z; (ii) $1-y$, $1+x-y$, z; (iii) 0, 0, 0; (iv) 0, 0, 0; (v) 0, 0, 0; (vi) 0, 0,0; (vii) $-x+y$, $-x$, z; (viii) 0, 0, 0; (ix) $-y$, $x-y$, z; (x) 0, 0, 0; (xi) $1-y$, $x-y$, z; (xii) $1-x+y$, $1-x$, z; (xiii) 0, 0, 0; (xiv) 0, 0, 0.				(i) $-x+y$, $1-x$, z; (ii) $1-y$, $1+x-y$, z; (iii) 0, 0, 0; (iv) 0, 0, 0; (v) 0, 0, 0; (vi) $-x+y$, $-x$, z; (vii) 0, 0, 0; (viii) 0, 0, 0; (ix) $-y$, $x-y$, z; (x) 0, 0, 0; (xi) $1-y$, $x-y$, z; (xii) $1-x+y$, $1-x$, z; (xiii) 0, 0, 0; (xiv) 0, 0, 0.			

explained by the analyses of the changes in local geometry of the building blocks. Moving from Li to Cs (for compounds with fully occupied cavity position—$M^{I}Ca_{10}(PO_4)_7$) with corresponding growing the ionic radii strongly influents on the distance between [CaO_6] and [PO_4] which lies on the same threefold axis. They become a little bit closer to each other which results in compressing the cell along axis *c*. At the same time, compressing the cell along axis *c* can be observed as a deformation of [CaO_6] octahedra. They are compressed along threefold axis which is accompanied by elongation of Ca–O contacts.

The facts denoted above give us complete explanation about the nature of obtained compounds in the investigated systems. Thus, in the Al-containing system only one kind of whitlockite-related compound can be synthesized—$CsCa_{10}(PO_4)_7$. The formation of $Ca_9Al(PO_4)_7$ or its solid solutions with $CsCa_{10}(PO_4)_7$ is impossible for a reason of a great difference between ionic radii of Al and Ca (0.535 and 1.0 Å, respectively). In phosphates $Ca_9M^{III}(PO_4)_7$ (M^{III}—Fe, Cr) M^{III}–O bonds ([$M^{III}O_6$] octahedra) are in range of 1.95–2.16 Å [24,30,31]. These compounds grow in the melts with comparatively small amount of caesium (Cs/P=1). Further increasing Cs/P ratio should promote the crystallization of Cs-containing whitlockite-related solid solutions with general composition $Cs_xCa_{9+x}M^{III}_{1-x}(PO_4)_7$ (x=0–1). Formation of $Cs_xCa_{9+x}Fe_{1-x}(PO_4)_7$ (x=0–0.63) was observed in Fe-containing system. As it was shown above, the inclusion of alkaline metal ions into whitlockite framework increases the Ca–O bond lengths in [CaO_6] octahedra (in $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ the distance Ca(Fe)–O is 2.27–2.29 Å). Such long bond lengths are unusual for contacts Cr–O. So inclusion of Cs cations into whitlockite framework prevents formation of the solid solutions like $Cs_xCa_{9+x}Cr_{1-x}(PO_4)_7$ which was observed in Cr-containing system. For alkaline metals with smaller ionic radii the limits of the formation of this solid solutions should be expanded which can be confirmed by the existence of $Na_{1.5}Ca_9Fe_{0.5}(PO_4)_7$ (PDF2-88-0792) [33] and $Na_2Ca_{19}Fe_{0.667}(PO_4)_{14}$ (PDF2-47-0895). Finally, the analyses of collected data indicates that formation of solid solutions like $M^{I}_xCa_{9+x}M^{III}_{1-x}(PO_4)_7$ depends on the properties of aliovalent substituted pair M^{I}+M^{III}.

3.3. FTIR-spectra

Initial identification of obtained compounds was performed by analyses of condensation degree of phosphate tetrahedra. For this purpose FTIR spectroscopy was used. The spectrum of $CsCaP_3O_9$ (Fig. 2(a)) indicates the presence of cyclic polyphosphate anion. It is clearly understood by the appearance of three intense absorption bands in the range of 1320–1270 cm^{-1} which belong to asymmetric vibrations ν_{as}(OPO) and two at 1175 and 1110 cm^{-1}—symmetric vibrations ν_s(OPO) in the six-member phosphate cycle $[P_3O_9]^{3-}$. The absorptions at 1007 and 773 cm^{-1} belong to ν_{as}(POP) and ν_s(POP). The bands at 650–400 cm^{-1} belong to deformation vibrations of cyclopolyphosphate anion. Similar combination of vibration modes is observed for $Ca_3(P_3O_9)_2 \cdot 10H_2O$ [34].

For $Cs_3CaFe(P_2O_7)_2$ and $Cs_2CaP_2O_7$ (Fig. 2(b)) absorption bands at 690–770 and 890–970 cm^{-1} are observed which correspond to

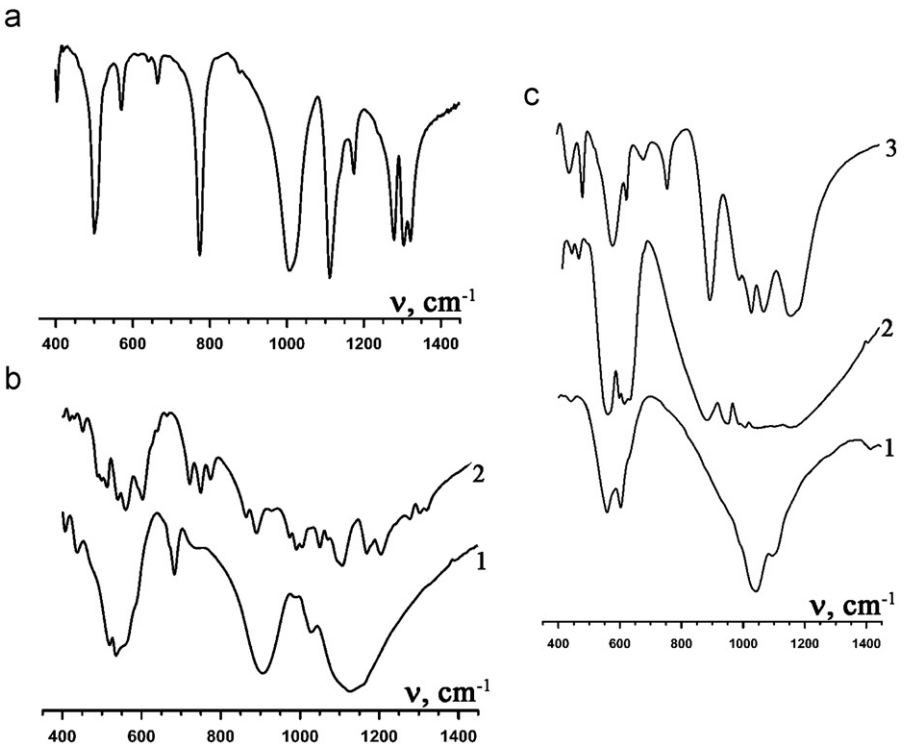

Fig. 2. FTIR-spectra:(a) cyclotriphosphate $CsCaP_3O_9$; (b) diphosphates: 1–$Cs_2CaP_2O_7$, 2–$Cs_3CaFe(P_2O_7)_2$; (c) orthophosphates: 1–$CsCa_{10}(PO_4)_7$, 2–$Ca_9Fe(PO_4)_7$, 3–$Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$.

ν_s(POP) and ν_{as}(POP) in diphosphate anion. ν_s and ν_{as} vibrations in PO_3 group are observed in a region of 1250–1040 cm^{-1}.

Composite character of the bands splitting at 720–1320 cm^{-1} in $Cs_3CaFe(P_2O_7)_2$ spectrum can be explained by the presence of four types of P atoms, and respectively two types of P_2O_7 groups with different geometric values (P–O bond lengths, P–O–P angle, etc.).

For $CsCa_{10}(PO_4)_7$ a combination of absorption bands is similar to those in β-$Ca_3(PO_4)_2$ spectrum with the positions shift less than 20 cm^{-1} (Fig. 2(c)). Consequently, the substitution of Ca by Cs in the initial crystal structure of β-$Ca_3(PO_4)_2$ do not change significantly the character of bands splitting in the investigated region. At the same time, the substitution of Ca by Cs (in cavity position) and Fe (in octahedral sites of the framework) lead to broadening of the bands which belong to PO_4 group (800–1200 cm^{-1}) in $Ca_9Fe(PO_4)_7$ and $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$. This results in splitting of ν_s and ν_{as} vibrations belonging three kinds of PO_4^{3-} anions. Such a splitting can be explained by differences of force constants which are induced by different type of atom (Ca or Fe) which is connected to different PO_4 group.

4. Conclusions

The principles of formation of complex phosphates in the melts of Cs_2O–P_2O_5–CaO–$M^{III}_2O_3$ (M^{III}—Al, Fe, Cr) systems with Cs/P=0.7–1.3 at fixed ratios Ca/P=0.2 and Ca/M^{III}=1.0 were determined. A group of complex phosphates were synthesized in mentioned regions of crystallization from the melts. Among them whitlockite-related orthophosphates $CsCa_{10}(PO_4)_7$, $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$, $Ca_9M^{III}(PO_4)_7$ (M^{III}—Fe, Cr), triple diphosphate $Cs_3CaFe(P_2O_7)_2$, diphosphates $Cs_2CaP_2O_7$ and β-$Ca_2P_2O_7$, cyclotriphosphate $CsCaP_3O_9$ were obtained. The composition and structure of the synthesized compounds depend on the nature of threevalent metal and condensation degree of the phosphate anions that can be set by initial ratio of Cs/P in the melts.

The new compounds were investigated by single crystal X-ray diffraction. IR-spectra of the phosphates were interpreted taking into account the structure. The analyses of the structures of $CsCa_{10}(PO_4)_7$, $Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO_4)_7$ and previously reported isotypic compounds results in conclusion of possibility of existence of solid solutions with a general composition $M^{I}_xCa_{9+x}M^{III}_{1-x}(PO_4)_7$ which belongs to whitlockite family. The occurrence of such kind of compounds depends on the nature of aliovalent substituted pair M^{I} and M^{III}.

References

[1] O.V. Yakubovich, M.A. Simonov, O.K. Mel'nikov, Z. Kristallogr. 35 (1990) 42–46.
[2] P.F. Henry, E.M. Hughes, M.T. Weller, J. Chem. Soc. Dalton Trans. (2000) 555–558.
[3] D. Blum, A. Durif, M.T. Averbuch-Pouchot, Ferroelectrics 69 (1986) 283–292.
[4] A.R. Zaripov, E.A. Asabina, V.I. Petkov, V.S. Kurazhkovskaya, S.Yu. Stefanovich, S.I. Rovny, Russ. J. Inorg. Chem. 53 (2008) 861–866.
[5] L. Campayo, F. Audubert, D. Bernache-Assollant, Solid State Ionics 176 (2005) 2663–2669.
[6] Y.P. Wang, J.J. Chen, Acta Crystallogr. C45 (1989) 1210–1211.
[7] D.R. Nandini, K. Vidyasagar, J. Chem. Soc. Dalton Trans. (2000) 1605–1608.
[8] J. Lesage, A. Guesdon, B. Raveau, J. Solid State Chem. 178 (2005) 1212–1220.
[9] E.V. Murashova, N.N. Chudinova, Russ. J. Inorg. Chem. 44 (1999) 1966–1969.
[10] I. Grunze, K.K. Palkina, N.N. Chudinova, L.S. Guzeeva, M.A. Avaliani, S.I. Maksimova, Izv. Akad. Nauk SSSR, Neorg. Mater 23 (1987) 610–615.
[11] A.V. Lavrov, V.P. Nikolaev, G.G. Sadikov, M.J. Vojtenkov, Dokl. Akad. Nauk SSSR 259 (1981) 103–106.
[12] N.N. Chudinova, E.V. Murashova, A.B. Ilyukhin, Inorg. Mater. (Transl. Neorg. Mater) 39 (2003) 1499–1503.
[13] E.V. Murashova, N.N. Chudinova, Crystallogr. Rep. 41 (1996) 236–238.
[14] I.A. Tokman, G.A. Bukhalova, Russ. J. Inorg. Chem. 17 (1972) 544–547.
[15] I.A. Tokman, G.A. Bukhalova, Inorg. Mater. (Transl. Neorg. Mater) 11 (1975) 1654–1656.
[16] I.V. Ogorodnyk, V.N. Baumer, I.V. Zatovsky, N.S. Slobodyanik, O.V. Shishkin, K.V. Domasevitc, Acta Crystallogr. B63 (2007) 819–827.
[17] I.V. Zatovsky, V.N. Baumer, N.Yu. Strutynska, N.S. Slobodyanik, O.V. Shishkin, Acta Crystallogr. C66 (2010) i71–i74.
[18] G.M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997.
[19] G.M. Sheldrick, SHELXL-97: Program for crystal structure refinement, University of Göttingen, Germany, 1997.

[20] I.V. Zatovsky, N. Yu., N.S. Strutynska, N.S. Slobodyanik, V.N. Baumer, O.V. Shishkin, Cryst. Res. Technol. 43 (2008) 362–368.
[21] N.Yu. Strutynska, I.V. Zatovsky, N.S. Slobodyanik, Dokl. Akad. Nauk Ukraine 6 (2008) 138–142.
[22] N.Yu. Strutynska, V.N. Baumer, I.V. Zatovsky, A.A. Babaryk, N.S. Slobodyanik, Acta Crystallogr. C66 (2010) i39–i41.
[23] I.V. Zatovsky, N.Yu. Strutynska, V.N. Baumer, N.S. Slobodyanik, O.V. Shishkin, Acta Crystallogr. E62 (2006) i263–i265.
[24] I.V. Zatovsky, N.Yu. Strutynska, V.N. Baumer, O.V. Shishkin, N.S. Slobodyanik, Acta Crystallogr. E63 (2007) i180–i181.
[25] M. Yashima, A. Sakai, T. Kamiyama, A. Hoshikawa, R. Gopal, J. Solid State Chem. 175 (2003) 272–277.
[26] C. Calvo, R. Gopal, Am. Mineral. 60 (1975) 120–133.
[27] V.A. Morozov, A.A. Belik, R.N. Kotov, I.A. Presnyakov, S.S. Khasanov, B.I. Lazoryak, Crystallogr. Rep. 45 (2000) 13–20.
[28] M.H. Sandström, D. Boström, Acta Crystallogr. E62 (2006) i253–i255.
[29] B.I. Lazoryak, V.A. Morozov, A.A. Belik, S.Yu. Stefanovich, V.V. Grebenev, I.A. Leonidov, E.B. Mitberg, S.A. Davydov, O.I. Lebedev, G.V. Tendeloo, Solid State Sci. 6 (2004) 185–195.
[30] B.I. Lazoryak, V.A. Morozov, A.A. Belik, S.S. Khasanov, V.Sh. Shekhtman, J. Solid State Chem. 122 (1996) 15–21.
[31] V.A. Morozov, A.A. Belik, S.Yu. Stefanovich, V.V. Grebenev, O.I. Lebedev, G.V. Tendeloo, B.I. Lazoryak, J. Solid State Chem. 165 (2002) 278–288.
[32] A.I. Orlova, M.P. Orlova, E.M. Solov'eva, E.E. Loginova, V.T. Demarin, G.N. Kazantsev, S.G. Samoilov, S.V. Stefanovskii, Radiokhimiya 48 (2006) 561–568.
[33] T.V. Strunenkova, V.A. Morozov, S.S. Khasanov, K.V. Pokholok, A.N. Zhdanova, B.I. Lazoryak, Crystallogr. Rep. 42 (1997) 55–60.
[34] N. El-Horr, A. Durif, C.R. Acad., Sci. 296 (1983) 1185–1187.