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Chemical and Phase Transformations during the Synthesis of Cs[$MgR_{0.5}P_{1.5}O_6$] (R = B, Al, Fe) Complex Oxides from Metal Nitrates

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Abstract—Cesium-containing complex oxides Cs[$MgR_{0.5}P_{1.5}O_6$], where R = B, Al, or Fe, were prepared from solutions containing H_3BO_3, metal nitrates, and H_3PO_4/$NH_4H_2PO_4$. The chemical and phase transformations occurring during the synthesis of these oxides were elucidated by differential thermal analysis (DTA) and X-ray powder diffraction (XRD. Optimal synthesis parameters were found. The boron compound was found to be formed at 800°C, and the aluminum and iron compounds, at 1200°C. All compounds have the pollucite structure (cubic system, space group $I4_132$). A comparative analysis of the synthesis of complex oxides under study from various precursors that differed from one another in metal and phosphorus chemical species was carried out.

Keywords: metal nitrates, synthesis, complex oxide, pollucite, differential thermal analysis, X-ray powder diffraction, phase and chemical transformations

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Structural analogues of natural minerals attract the attention of researchers involved in materials design for the consolidation of hazardous components of nuclear waste [1–4]. Materials having the pollucite or pyrochlore structure are of interest for the immobilization of cesium radionuclides from radioactive waste and the creation of high specific activity γ-sources [5, 6]. An important stage in the design of such materials is studies into the processes involved in synthesis, namely, the degradation of the starting compounds and the formation and conversions of intermediates leading to the formation of the desired product. This should ultimately determine the optimal routes for the implementation of technologies under study. Those studies should pay a great deal of attention to the selection of precursors and their combinations.

We choose this approach to the development of optimal conditions preparing for crystalline cesium-containing complex oxides Cs[$MgR_{0.5}P_{1.5}O_6$], where R = B, Al, or Fe (the pollucite structural type) from metal chlorides. We have studied the formation of these compounds and the intermediates, their formation conditions and behavior (phase and chemical transformations) at various stages of the synthesis of desired phases. The precursors were mixtures of chemicals. For precursor I, metal chlorides were used (for the boron-containing oxide, H_3BO_3) and H_3PO_4; precursor II differed from precursor I in that $NH_4H_2PO_4$ was used instead of H_3PO_4.

In the course of the synthesis of studied compounds from metal chlorides, CsCl exists in the systems up to rather high temperatures (600°C), so it can be transferred to the gas phase, as typical of alkali metal chlorides. The vaporized chloride fraction is insignificant and almost does not influence the stoichiometry of the compounds formed of it, but for the chloride comprising cesium radionuclides this process can give rise to an environmentally undesirable effect, namely, to the radioactive contamination of the equipment and environment.

It is expedient to replace chlorides in precursors, in particular, cesium chloride, by other chemical species. These chemical species can be thermally degradable nitrates, carbonates, and organometal compounds. Their use can help to reduce synthesis process parameters (T and τ) due to their comparatively low thermal decomposition temperatures.

In this study, we prepared the above-described complex oxides using metal nitrates (for the boron-containing oxide, H_3BO_3) and H_3PO_4 (precursor III); precursor IV was obtained by replacing H_3PO_4 by $NH_4H_2PO_4$.

Our goals in this study were to elucidate the processes underlying the synthesis of Cs[$MgR_{0.5}P_{1.5}O_6$] (R = B, Al, or Fe) oxides from precursors III and IV;

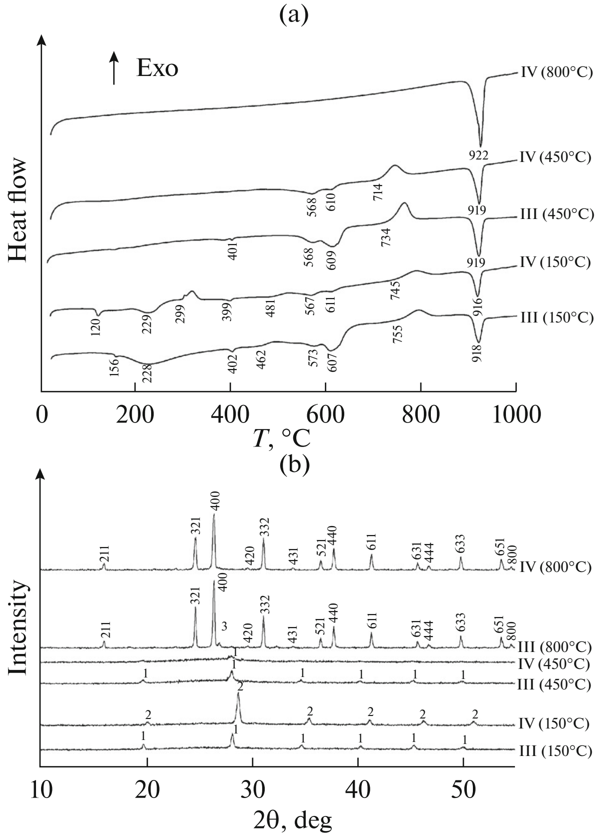

Fig. 1. (a) DTA data and (b) (b) XRD data for precursors III and IV in the course of $Cs[MgB_{0.5}P_{1.5}O_6]$ preparation: (1) $CsNO_3$ (No. 01-0779), (2) $CsNO_2$ (No. 26-0394), (3) $CsMgPO_4$ (No. 45-0275), and (*hkl*) $Cs[MgB_{0.5}P_{1.5}O_6]$.

to determine optimal synthetic parameters, namely, temperature, the number and length of heat-treatment stages; and to perform a comparative analysis of these parameters for systems with precursors I and II (metal chloride systems).

EXPERIMENTAL

Synthesis

$Cs[MgR_{0.5}P_{1.5}O_6]$ oxides where R = B, Al, or Fe were prepared by sol–gel technology from two batches: batch III contained metal nitrates (for the boron-containing oxide, H_3BO_3) and H_3PO_4; batch IV contained $NH_4H_2PO_4$ instead of H_3PO_4.

The chemicals used to prepare the precursor mixtures were 0.5 M H_3BO_3 solution, 1 M metal nitrate solutions, 1.5 M H_3PO_4, or 1 M $NH_4H_2PO_4$ solution.

The as-prepared batches were heated at 80°C under stirring for 5–20 min on a magnetic stirrer; afterwards they were thermostated at 90°C until gels were formed and then at 120–150°C until dry residues were formed. Batch III yielded precursor III, and batch IV yielded precursor IV. The precursors were placed into porcelain or alundum crucibles and subjected to multistage heating at temperatures from 300 to 1200°C in 100–150°C steps. The exposure time to each temperature was 10–20 h. Heat-treatment stages were alternated with 5-min dispersions with an agate mortar and a pestle.

Methods and Instruments

A sample after every heat-treatment stage was characterized by differential thermal analysis (DTA) and X-ray powder diffraction (XRD).

DTA experiments were carried out on a Setaram LABSYS differential scanning calorimeter. A polycrystalline fine-powder sample weighing ~100 mg was heated in a 100-μL crucible made of high-purity Al_2O_3 at 10 K/min. The DTA experiments were carried out under an argon atmosphere. The program suite SetSoft 2000 V 1.2 was used to process DTA curves. Thermal events were assigned with reference to relevant reference literature [7–10].

The reaction character was elucidated by the correspondence between the measured and reported values of reaction temperatures and phase-transition temperatures in the initial, intermediate, and final products.

X-ray diffraction patterns were recorded on a Shimadzu LabX XRD-6000 diffractometer (filtered CuK_α radiation, $\lambda = 1.54178$ Å) at 30 kV and 30 mA over the range of angles from 10° to 55° 2θ at 4 deg/min. The patterns were indexed with reference to JCPDS-ICDD PDF-2 Release 2004.

RESULTS AND DISCUSSION

DTA and XRD data on the phase and chemical transformations experienced by the $Cs[MgR_{0.5}P_{1.5}O_6]$ systems where R = B, Al, or Fe in the course of synthesis from precursors III and IV are compiled in Tables 1–3; some of them are shown in Figs. 1–3 as DTA curves and X-ray diffraction patterns.

$Cs[MgB_{0.5}P_{1.5}O_6]$

The DTA and XRD studies of precursors III and IV after they were heat-treated at temperatures in the range 150–450°C identified in them the initial $CsNO_3$ (polymorphic transition at 154°C and melting at 409°C), intermediates NH_4NO_3 and CsH_2PO_4 (polymorphic transitions at 125 and 230°C, respectively), and γ-HBO_2 (melting at 236°C); the intermediates were formed by the following reactions [2]:

$$NH_4H_2PO_4 + CsNO_3 \rightarrow CsH_2PO_4 + NH_4NO_3, \quad (1)$$

$$H_3BO_3 \xrightarrow{107.5°C} \gamma\text{-}HBO_2 + H_2. \quad (2)$$

The exotherm at 299°C is due to NH_4NO_3 decomposition by the reaction [2]

Table 1. Phase and chemical transformations during $Cs[MgB_{0.5}P_{1.5}O_6]$ preparation

T, °C*	Precursor III				Precursor IV			
	DTA data			XRD data	DTA data			XRD data
	T, °C		thermal feature		*T*, °C		thermal feature	
	observed	reported			observed	reported		
150	156	154	$CsNO_3$, cII → cI	$CsNO_3$	120	125.5	NH_4NO_3, cII → cI	$CsNO_2$
	228	230	CsH_2PO_4, cII → cI		229	230	CsH_2PO_4, cII → cI	
		236	γ-HBO_2, c → l			236	γ-HBO_2, c → l	
	402	398	$CsNO_2$, c → l		299	>270	*Reaction (3)	
		409	$CsNO_3$, cI → l		306	302	Cs_3PO_4, cIII → cII	
	573	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII		399	398	$CsNO_2$, c → l	
						409	$CsNO_3$, cI → l	
					481	495	Cs_2O, c → l	
		571	P_4O_{10}, cII → g		567	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII	
	607	596	$Cs_2O \cdot 9B_2O_3$, c → l			571	P_4O_{10}, cII → g	
	710	–	Synthesis reaction**		611	596	$Cs_2O \cdot 9B_2O_3$, c → l	
					745	–	Synthesis reaction**	
	918	–	Desired product, c → l		916	–	Desired product, c → l	
300	157	154	$CsNO_3$, cII → cI	$CsNO_3$	155	154	$CsNO_3$, cII → cI	$CsNO_3$
	400	398	$CsNO_2$, c → l		398	398	$CsNO_2$, c → l	
		409	$CsNO_3$, cI → l			409	$CsNO_3$, cI → l	
	572	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII		490	495	Cs_2O, c → l	
		571	P_4O_{10}, cII → g		570	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII	
	610	596	$Cs_2O \cdot 9B_2O_3$, c → l			571	P_4O_{10}, cII → g	
					610	596	$Cs_2O \cdot 9B_2O_3$, c → l	
	715	–	Synthesis reaction**		720	–	Synthesis reaction**	
	920	–	Desired product, c → l		916	–	Desired product, c → l	
450	156	154	$CsNO_3$, cII → cI	$CsNO_3$	154	154	$CsNO_3$, cII → cI	$CsNO_3$ (on the background of an amorphous phase)
	202	206	Cs_3PO_4, cIV → cIII					
	401	398	$CsNO_2$, c → l		568	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII	
		409	$CsNO_3$, c → l					
	568	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII			571	P_4O_{10}, cII → g	
		571	P_4O_{10}, cII → g		610	596	$Cs_2O \cdot 9B_2O_3$, c → l	
	609	596	$Cs_2O \cdot 9B_2O_3$, c → l		714	–	Synthesis reaction**	
	690	–	Synthesis reaction**					
	919	–	Desired product, c → l		919	–	Desired product, c → l	
600	558	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII	Desired product, $CsMgPO_4$	559	570	$Cs_2O \cdot 5B_2O_3$, cIII → cII	$CsMgPO_4$
	663	–	Synthesis reaction**		669	–	Synthesis reaction**	
	924	–	Desired product, c → l		919	–	Desired product, c → l	
800	914	–	Desired product, c → l	Desired product, $CsMgPO_4$	922	–	Desired product, c → l	Desired product

* The temperature of precursor heat-treatment steps; "c" denotes a crystalline phase, "l" denotes a liquid phase, "g" denotes a gas phase, and "cI –cVI" denote polymorphs of the crystalline phase;

** An exothermic reaction.

Table 2. Phase and chemical transformations during $Cs[MgAl_{0.5}P_{1.5}O_6]$ preparation

T, °C*	Precursor III				Precursor IV			
	DTA data			XRD data	DTA data			XRD data
	T, °C		thermal feature		T, °C		thermal feature	
	observed	reported			observed	reported		
150	156	154	$CsNO_3$, cII → cI	$CsNO_3$, $AlPO_4$	122	126	NH_4NO_3, cII → cI	$CsNO_2$, $AlPO_4$
	220	230	CsH_2PO_4, cII → cI		173	170	NH_4NO_3, cI → l	
	399	406	$CsNO_2$, c → l		235	200–270	Reaction** (8)	
	436	426	$Mg(NO_3)_2$, c → l		303	>270	Reaction** (3)	
	528	518	$Cs_5P_3O_{10}$, c → l + cI		397	398	$CsNO_2$, c → l	
					419	426	$Mg(NO_3)_2$, c → l	
	665	672	Cs, l → g		521	518	$Cs_5P_3O_{10}$, c → l + cI	
300	154	154	$CsNO_3$, cII → cI	$CsNO_3$, $AlPO_4$	152	154	$CsNO_3$, cII → cI	$CsNO_3$, $AlPO_4$
	400	406	$CsNO_2$, c → l		398	398	$CsNO_2$, c → l	
	462	465	Cs_3PO_4, cII → cI		421	426	$Mg(NO_3)_2$, c → l	
	529	518	$Cs_5P_3O_{10}$, c → l + cI		528	518	$Cs_5P_3O_{10}$, c → l + cI	
	670	672	Cs, l → g		632	–	Unidentified	
450	152	154	$CsNO_3$, cII → cI	$CsMgPO_4$, $CsNO_3$, $AlPO_4$	151	154	$CsNO_3$, cII → cI	$CsMgPO_4$, $CsNO_3$, $AlPO_4$
	392	406	$CsNO_2$, c → l		196	186	$Cs_2Mg(NO_3)_4$, c → l	
	563	580	$AlPO_4$, cVI → cV		389	398	$CsNO_2$, c → l	
	654	–	Unidentified		550	557	CsO_2, c → l	
600	Unobserved			$CsMgPO_4$, $AlPO_4$	Unobserved			$CsMgPO_4$, $AlPO_4$
800				$CsMgPO_4$, $AlPO_4$				$CsMgPO_4$, $AlPO_4$, desired product
1000				$CsMgPO_4$, desired product, $AlPO_4$				$CsMgPO_4$, desired product, $AlPO_4$
1200				Desired product				Desired product

* The temperature of precursor heat-treatment steps; "c" denotes a crystalline phase, "l" denotes a liquid phase, "g" denotes a gas phase, and "cI –cVI" denote polymorphs of the crystalline phase;

** An exothermic reaction.

$$2NH_4NO_3 \xrightarrow{<270°C} 2N_2 + O_2 + 4H_2O. \qquad (3)$$

The initial cesium nitrate decomposes to $CsNO_2$ (melting at 398°C) and Cs_2O (melting at 490°C) by the reactions

$$2CsNO_3 \xrightarrow{<300°C} 2CsNO_2 + O_2, \qquad (4)$$

$$4CsNO_3 \xrightarrow{700°C} 2Cs_2O + 2N_2 + 5O_2. \qquad (5)$$

The exotherm at T = 706°C characterizes the desired product synthesis reaction, and the endotherm at 916°C is due to its melting.

Subsequent heating to 450°C reduced the contents of $CsNO_3$ and its decomposition products in the systems with simultaneous detection of cesium and boron double oxides on DTA curves. XRD identified only $CsNO_3$.

Table 3. Phase and chemical transformations during $Cs[MgFe_{0.5}P_{1.5}O_6]$ preparation

T, °C*	Precursor III				Precursor IV			
	DTA data			XRD data	DTA data			XRD data
	T, °C		thermal feature		T, °C		thermal feature	
	observed	reported			observed	reported		
150	230	230	CsH_2PO_4, cII → cI	$CsMgPO_4$ (on the background of an amorphous phase)	124	126	NH_4NO_3, cII → cI	$CsNO_2$
	394	398	$CsNO_2$, cI → l		190	186	$Cs_2Mg(NO_3)_4$, c → l	
	568	557	CsO_2, c → l			190	$NH_4H_2PO_4$, c → l	
		571	P_4O_{10}, cII → g		255	200–270	*Reaction (7)	
	594	594	Cs_2O_2, c → l		290	>270	*Reaction (3)	
	707	700	$Cs_2Fe_2P_2O_7$, cII → cI		417	409	$CsNO_3$, cI → l	
		715	$Cs_3Fe_2(PO_4)_3$, cII → cI		547	557	CsO_2, c → l	
	814	815	$CsMg(PO_3)_3$, c → l		890	889	$FePO_4$, cII → cI	
300	163	154	$CsNO_3$, cII → cI	$CsMgPO_4$ (on the background of an amorphous phase)	154	154	$CsNO_3$, cII → cI	$CsNO_3$ (on the background of an amorphous phase)
	414	409	$CsNO_3$, cI → l		416	409	$CsNO_3$, cI → l	
	567	571	P_4O_{10}, cII → g		547	557	CsO_2, c → l	
	717	715	$Cs_3Fe_2(PO_4)_3$, cII → cI		818	815	$CsMg(PO_3)_3$, c → l	
	747	746	$Cs_6Fe_2(P_2O_7)_3$, c → l		853	856	$Cs_2Fe_2P_2O_7$, cI → l	
	824	815	$CsMg(PO_3)_3$, c → l		887	889	$FePO_4$, cII → cI	
450	577	571	P_4O_{10}, cII → g	$CsMgPO_4$ (on the background of an amorphous phase)	570	571	P_4O_{10}, cII → g	$CsMgPO_4$, $CsNO_3$
	700	700	$Cs_2Fe_2P_2O_9$, cII → cI		682	–	Synthesis reaction**	
	728	715	$Cs_3Fe_2(PO_4)_3$, cII → cI		854	856	$Cs_2Fe_2P_2O_7$, cI → l	
	841	842	$Cs_3Fe_2(PO_4)_3$, cI → l		891	889	$FePO_4$, cII → cI	
	944	940	$Fe(PO_3)_3$, cII → cI					
600	543	557	CsO_2, c → l	$CsMgPO_4$, desired product	687	–	Synthesis reaction**	$CsMgPO_4$, desired product
	817	815	$CsMg(PO_3)_3$, c → l					
	848	842	$Cs_3Fe_2(PO_4)_3$, cI → l		778	784	$FePO_4$, cIII → cII	
	877	865	$Fe_4(P_2O_7)_3$, cII → cI		856	856	$Cs_2Fe_2P_2O_7$, cI → l	
		889	$FePO_4$, cII → cI		891	889	$FePO_4$, cII → cI	
	932	940	$Fe(PO_3)_3$, cII → cI		946	940	$Fe(PO_3)_3$, cII → cI	
800	318	302	Cs_3PO_4, cIII → cII	Desired product, $CsMgPO_4$	857	856	$Cs_2Fe_2P_2O_7$, cI → l	Desired product, $CsMgPO_4$
	857	856	$Cs_2Fe_2P_2O_7$, cI → l					
	893	889	$FePO_4$, cII → cI		894	889	$FePO_4$, cII → cI	
1000	Unobserved			Desired product, $CsMgPO_4$	Unobserved			Desired product, $CsMgPO_4$
1200				Desired product, $CsMgPO_4$				Desired product

* The temperature of precursor heat-treatment steps; “c” denotes a crystalline phase, “l” denotes a liquid phase, “g” denotes a gas phase, and “cI –cVI” denote polymorphs of the crystalline phase;

** An exothermic reaction.

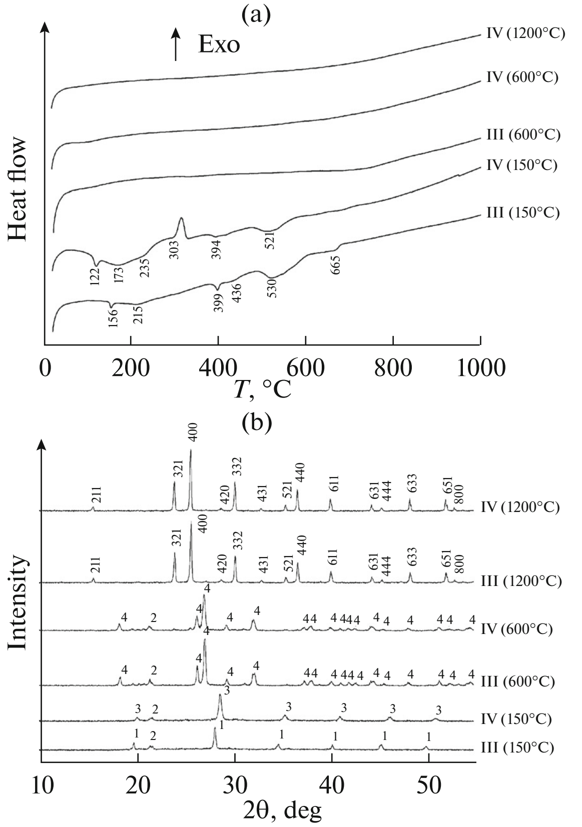

Fig. 2. (a) DTA data and (b) (b) XRD data for precursors III and IV in the course of $Cs[MgAl_{0.5}P_{1.5}O_6]$ preparation: (1) $CsNO_3$ (No. 01-0779), (2) $AlPO_4$ (No. 87-1127), (3) $CsNO_2$ (No. 26-0394), (4) $CsMgPO_4$ (No. 45-0275), and (*hkl*) $Cs[MgAl_{0.5}P_{1.5}O_6]$.

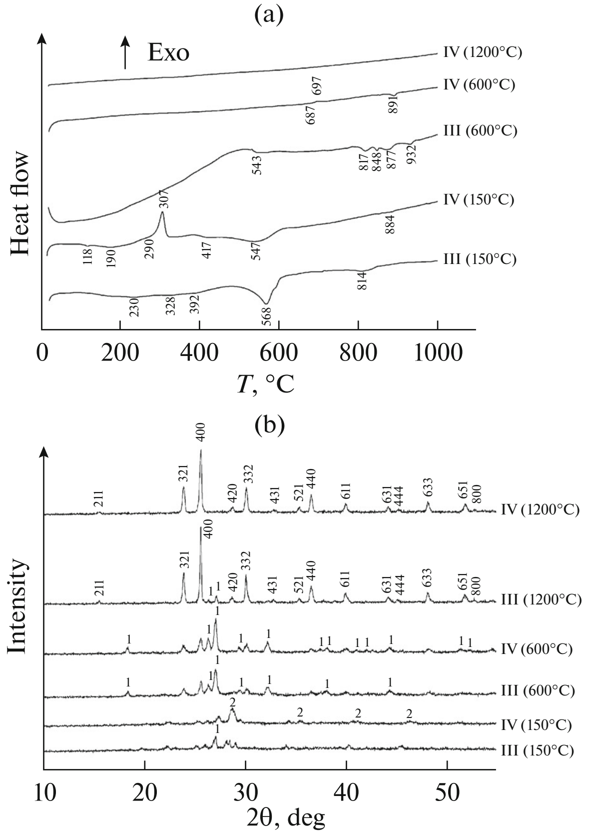

Fig. 3. (a) DTA data and (b) (b) XRD data for precursors III and IV in the course of $Cs[MgFe_{0.5}P_{1.5}O_6]$ preparation: (1) $CsMgPO_4$ (No. 45-0275), (2) $CsNO_2$ (No. 26-0394), and (*hkl*) $Cs[MgFe_{0.5}P_{1.5}O_6]$.

The exothermic reaction of desired product synthesis and its melting endotherm appear on DTA curves for all thermal exposure stages in the range 150–600°C.

After precursors were exposed at 600°C, they contained, as found by DTA, the desired product and a $Cs_2O \cdot 5B_2O_3$ admixture, and as found by XRD, the desired product and $CsMgPO_4$. The heat treatment of the precursors at 800°C yielded, as found by DTA and XRD, the desired product with a $CsMgPO_4$ minor phase.

The overall reactions for synthesis of the boron-containing desired product from precursors III and IV are given below:

$$\begin{aligned} &\text{III: } 2CsNO_3 + 2Mg(NO_3)_2 + H_3BO_3 \\ &+ 3H_3PO_4 \rightarrow 2Cs[MgB_{0.5}P_{1.5}O_6] \\ &+ 3NO_2 + 3NO + 9O_2 + 6H_2O, \end{aligned} \tag{6}$$

$$\begin{aligned} &\text{IV: } 4CsNO_3 + 4Mg(NO_3)_2 + 2H_3BO_3 \\ &+ 6NH_4H_2PO_4 \rightarrow 4Cs[MgB_{0.5}P_{1.5}O_6] \\ &+ 7NO_2 + 7NO + 2N_2 + 21H_2O. \end{aligned} \tag{7}$$

$Cs[MgAl_{0.5}P_{1.5}O_6]$

The DTA and XRD studies of precursors III and IV after they were heat-treated at temperatures in the range 150–450°C show the initial cesium and magnesium nitrates, thermal degradation products of cesium nitrate (cesium nitrite and cesium peroxide), and intermediates: ammonium nitrate, cesium and aluminum phosphates, and cesium magnesium double nitrate.

The exotherms at 235 and 300°C correspond to NH_4NO_3 decomposition by reactions (3) and (8) [2]:

$$NH_4NO_3 \xrightarrow{200-270°C} N_2O + 2H_2O. \tag{8}$$

After heating in the range 600–1200°C, the DTA curves of the systems are featureless.

X-ray powder diffraction patterns show that the heat treatment of the precursors at 800°C produced a two-phase system comprised of $CsMgPO_4$ and $Cs[MgAl_{0.5}P_{1.5}O_6]$, the latter increasing as the exposure temperature elevated to 1100°C. An individual phase of the desired product was formed after the precursors were heat treated at 1200°C.

The overall reactions for the synthesis of $Cs[MgAl_{0.5}P_{1.5}O_6]$ from precursors III and IV are the following:

$$\begin{aligned}\text{III: } & 4CsNO_3 + 4Mg(NO_3)_2 + 2Al(NO_3)_3 \\ & + 6H_3PO_4 \rightarrow 4Cs[MgAl_{0.5}P_{1.5}O_6] + 9NO_2 \\ & + 9NO + 9O_2 + 9H_2O,\end{aligned} \quad (9)$$

$$\begin{aligned}\text{IV: } & 2CsNO_3 + 2Mg(NO_3)_2 + Al(NO_3)_3 \\ & + 3NH_4H_2PO_4 \rightarrow 2Cs[MgAl_{0.5}P_{1.5}O_6] \\ & + 6NO_2 + 6NO + 9H_2O.\end{aligned} \quad (10)$$

$Cs[MgFe_{0.5}P_{1.5}O_6]$

After precursors III and IV were heat-treated at temperatures in the range 150–450°C, their DTA curves show the initial products (ammonium dihydrogenphosphate and cesium nitrate) and intermediates (cesium nitrite, cesium oxides, metal phosphates, cesium magnesium and cesium iron double phosphates). At higher temperatures, iron and magnesium phosphates are detected, as well as cesium magnesium and cesium iron double phosphates.

In the precursors heat-treated at 150 and 300°C, XRD shows that $CsNO_2$ and $CsNO_3$ phases can be distinguished on the background of an amorphous phase; after heating at 450°C, P_4O_{10} and $CsMgPO_4$ phases appear. Exposure of the precursors at 600°C gives rise to the formation of a two-phase system comprised of $CsMgPO_4$ (the major phase) and $Cs[MgFe_{0.5}P_{1.5}O_6]$ (the minor phase). As in the case of the aluminum-containing compound, the desired product fraction increases as temperature rises from 800 to 1200°C. Heat treatment at 1200°C makes it possible to prepare $Cs[MgFe_{0.5}P_{1.5}O_6]$ as an individual phase.

The intermediates formed in the course of $Cs[MgFe_{0.5}P_{1.5}O_6]$ synthesis are iron phosphates and pyrophosphates, double cesium phosphates and pyrophosphates of iron and magnesium.

A desired product phase starts to form at 600°C, as evidenced by the appearance of its reflections on the background of the major phase $CsMgPO_4$. When temperature rises to 1000°C, the major phase becomes the desired product and the minor phase is $CsMgPO_4$, the latter disappearing at 1200°C.

The overall reactions for the synthesis of $Cs[MgFe_{0.5}P_{1.5}O_6]$ from precursors III and IV are shown below:

$$\begin{aligned}\text{III: } & 4CsNO_3 + 4Mg(NO_3)_2 + 2Fe(NO_3)_3 \\ & + 6H_3PO_4 \rightarrow 4Cs[MgFe_{0.5}P_{1.5}O_6] \\ & + 9NO_2 + 9NO + 9O_2 + 9H_2O,\end{aligned} \quad (11)$$

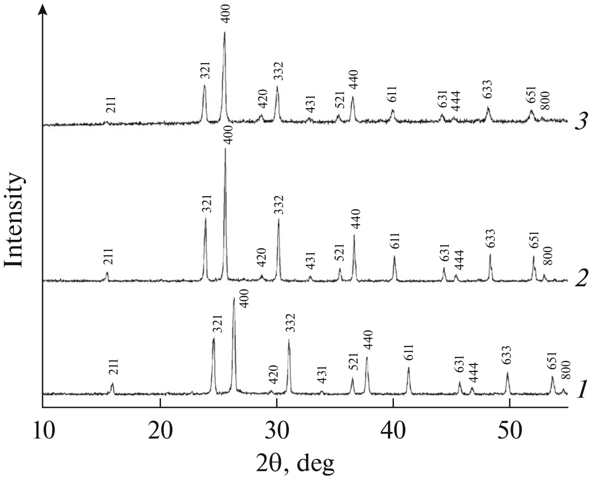

Fig. 4. XRD data: (*1*) $Cs[MgB_{0.5}P_{1.5}O_6]$, T = 800°C; (*2*) $Cs[MgAl_{0.5}P_{1.5}O_6]$, T = 1200°C; and (*3*) $Cs[MgFe_{0.5}P_{1.5}O_6]$, T = 1200°C. Analogue: $Cs_2Co_2Al(PO_4)_3$ [10].

$$\begin{aligned}\text{IV: } & 2CsNO_3 + 2Mg(NO_3)_2 + Fe(NO_3)_3 \\ & + 3NH_4H_2PO_4 \rightarrow 2Cs[MgFe_{0.5}P_{1.5}O_6] \\ & + 6NO_2 + 6NO + 9H_2O.\end{aligned} \quad (12)$$

Based on the data obtained, we may recommend one to include the following steps into the synthesis of $Cs[MgR_{0.5}P_{1.5}O_6]$ compounds where R = B, Al, or Fe: drying of the batch at 150°C; heat treatment at 600°C for 20 h; and final heat treatment for 20 h at 800°C for $Cs[MgB_{0.5}P_{1.5}O_6]$ and at 1200°C for $Cs[MgAl_{0.5}P_{1.5}O_6]$ and $Cs[MgFe_{0.5}P_{1.5}O_6]$ (Fig. 4).

All prepared compounds crystallize in the pollucite structural type, cubic crystal system, space group $I4_132$ (an analogue of $Cs_2Co_2Al(PO_4)_3$ [4]). The unit cells parameter a in the $Cs[MgR_{0.5}P_{1.5}O_6]$ (R = B, Al, or Fe) series is 13.433, 13.814, and 13.866 Å, respectively (the increase in unit cell parameter value correlates with the increase in the ionic radii of tervalent cations B^{3+}, Al^{3+}, and Fe^{3+}).

From a comparative analysis of the synthetic protocols for preparing cesium-containing complex oxides from various precursors that differ from one another by chemical species of the metals (chlorides or nitrates) and phosphorus (H_3PO_4 or $NH_4H_2PO_4$), it flows that the lowest synthesis temperature (800°C) is typical of all precursors (I–IV) of the boron-containing complex oxide. The iron-containing oxide is formed at 800°C from precursor I, at 1000°C from precursor II, and at 1200°C from precursor IV. The highest synthesis temperature is observed for the aluminum-containing compound: 1100°C from precursor I or precursor II and 1200°C from precursor III or IV.

CONCLUSIONS

Apart from the thermal decomposition of boric acid, phosphoric acid, and ammonium dihydrogenphosphate observed in chloride systems, $Cs[MgR_{0.5}P_{1.5}O_6]$ (R = B, Al, or Fe) synthesis from metal nitrates involves the thermal decomposition of the nitrates. The following intermediates are formed: cesium dihydrogenphosphate and cesium nitrate, ammonium nitrate, metal phosphates, cesium and phosphorus oxides, cesium and boron double oxides, and double cesium nitrates and phosphates of magnesium and iron.

The formation reactions of intermediates and the overall reactions of the synthesis of desired products have been described. The synthesis temperature of the studied complex oxides is independent of whether precursor III or IV is used, being 800°C for the oxide where R = B and 1200°C for the oxides where R = Al or Fe. The prepared compounds have the pollucite structure (cubic space group $I4_132$).

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