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Synthesis, crystal structure and high-temperature heat capacity of substituted apatites $\text{Pb}_9R(\text{GeO}_4)_3(\text{VO}_4)_3$ ($R = \text{Tb, Dy, Ho}$)

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$\text{Pb}_9R(\text{GeO}_4)_3(\text{VO}_4)_3$ ($R = \text{Tb, Dy, Ho}$) apatites were obtained by solid-phase synthesis from the initial oxides of PbO , Tb_2O_3 (Dy_2O_3 , Ho_2O_3), GeO_2 and V_2O_5 by sequential annealing (at a temperature of 773–1073 K) in an air atmosphere. Their crystal structure has been determined by X-ray diffraction analysis. The high-temperature heat capacity was measured by differential scanning calorimetry. Based on the experimental dependence of the heat capacity on the temperature, the thermodynamic properties are calculated. Keywords: apatites, solid-phase synthesis, crystal structure, heat capacity, thermodynamic properties.

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1. Introduction

An important problem in the contemporary material science is the making of new oxide compounds and materials with preset physical and chemical properties on their basis. Complex oxide compounds with an apatite-like structure (space group $P6_3/m$) can be used as the latter. The interest in such compounds is conditioned by the unique properties which are of applied value; they can be used as biomaterials, phosphors, sensors, laser and fluorescent materials, organic synthesis catalysts [1–7], in acousto-optic devices, in medicine, power industry, oil refining, environment protection [8], for radioactive waste disposal [9]. A distinctive feature of compounds with the apatite structure is the possibility of substitution of certain structural units by others without a considerable change of the structure [3,10–15]. Such a substitution allows both for changing the properties of the already known compounds with the apatite structure and for making new materials [16,17]. Thus, for instance, partial substitution of lead in apatite $\text{Pb}_5(\text{GeO}_4)(\text{VO}_4)_2$ (or $\text{Pb}_{10}(\text{GeO}_4)_2(\text{VO}_4)_4$) by rare earth elements (REE) provides compounds with the general formula $\text{Pb}_{10-x}R_x(\text{GeO}_4)_{2+x}(\text{VO}_4)_{4-x}$ (R — rare earth element, x takes on values from 0 to 3) [13,18–25], and by bismuth — $\text{Pb}_{10-x}\text{Bi}_x(\text{GeO}_4)_{2+x}(\text{VO}_4)_{4-x}$ [26]. It should be noted that the properties of apatites $\text{Pb}_{10-x}R_x(\text{GeO}_4)_{2+x}(\text{VO}_4)_{4-x}$ have been poorly studied, while the available data mainly pertains to epy studies of their crystal structure. We have obtained the heat capacity data only for the apatites of this class which contain La [19,20,22,25], Pr [23,25], Nd [21,25], Eu [24], Sm [25]. The available published data about

thermodynamic properties pertains to other compounds with the apatite structure (fluor-, chlor- and hydroxyapatites) [27,28].

The present paper aims at establishing the regularities of change of the crystal structure and heat capacity in case of lead substitution with rare earth elements in apatites $\text{Pb}_9R(\text{GeO}_4)_3(\text{VO}_4)_3$ ($R = \text{Tb, Dy, Ho}$) based on experimental results.

2. Experiment

Substituted apatites $\text{Pb}_{10-x}R_x(\text{GeO}_4)_{2+x}(\text{VO}_4)_{4-x}$ were obtained from initial oxides by the solid-state reaction method. To do so, the preliminarily baked oxides in stoichiometric amounts were blended in an agate mortar, pressed in tables without a binder and successively annealed in air atmosphere at 773, 873 and 973 K for 10 h each. The time of final annealing at 1073 K was selected experimentally. It increased from 100 h (for La [22]) to 200 h (Tb, Dy, Ho). This agrees with the data of paper [3] where it is noted that the solid-state reaction is hindered in calcium-containing silicate apatites upon a transition from La to Er. The authors assumed that the latter is due to a decreased reactivity in the given series of rare earth element compounds. The samples were crushed and pressed again after each 10 h of annealing in order to increase the completeness of solid-state reactions. The phase composition of the synthesized samples was monitored by X-ray diffraction analysis (Bruker D8 ADVANCE diffractometer, $\text{CuK}\alpha$ -radiation with a graphite monochromator in the region of angles $2\theta = 7.5$ – 120° , scanning step 0.016° ,

Table 1. Unit cell parameters for apatites $\text{Pb}_9\text{R}(\text{GeO}_4)_2(\text{VO}_4)_4$ ($R = \text{Tb}, \text{Dy}, \text{Ho}$): a, c — cell parameters, V — cell volume, Z — number of formula units in the cell

Parameters	Tb	Dy	Ho
$a, \text{\AA}$	10.09290(18)	10.09371(30)	10.0917(3)
$c, \text{\AA}$	7.38863(16)	7.37080(25)	7.372(2)
$V, \text{\AA}^3$	651.82(3)	650.350(44)	650.20(4)
Z	1	1	1

exposure time per each scanning step 2 s, the compounds' crystal structure was refined by the Rietveld method in the TOPAS 4.2 software [29]).

The STA 449 C Jupiter thermal analyzer (NETZSCH, Germany) was used to measure high-temperature heat capacity by the differential scanning calorimetry method. The experiment procedure has been already described [30]. The experiment error did not exceed 2%.

3. Results and discussion

As an example, Fig. 1 shows an X-ray pattern for apatite $\text{Pb}_9\text{Ho}(\text{GeO}_4)_3(\text{VO}_4)_3$. All reflections were indexed in a hexagonal cell ($P6_3/m$) with parameters close to $\text{Pb}_5(\text{GeO}_4)(\text{VO}_4)_2$ [31,32]. Therefore, this structure was taken as a starting model for refinement. The unit cell parameters of the synthesized apatites are given in Table 1.

It should be noted that the structure of lead-containing apatites contains two structurally non-equivalent cation sites $\text{Pb}1(4f)$ and $\text{Pb}2(6h)$ [11,31–34]. The authors of [34] showed that La atoms in the apatite $\text{Pb}_8\text{La}_2(\text{GeO}_4)_4(\text{VO}_4)_2$

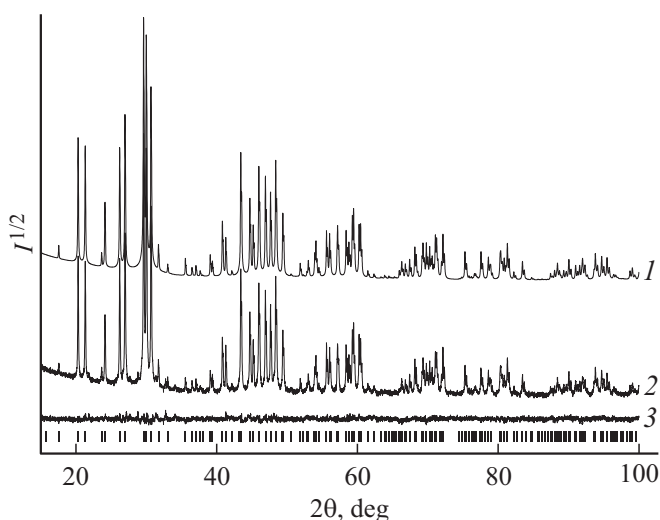


Figure 1. Experimental (1), calculated (2) and difference (3) profiles of the X-ray patterns of $\text{Pb}_9\text{Ho}(\text{GeO}_4)_3(\text{VO}_4)_3$ after refinement by minimization of the difference derivative; the dashes show the calculated positions of reflections.

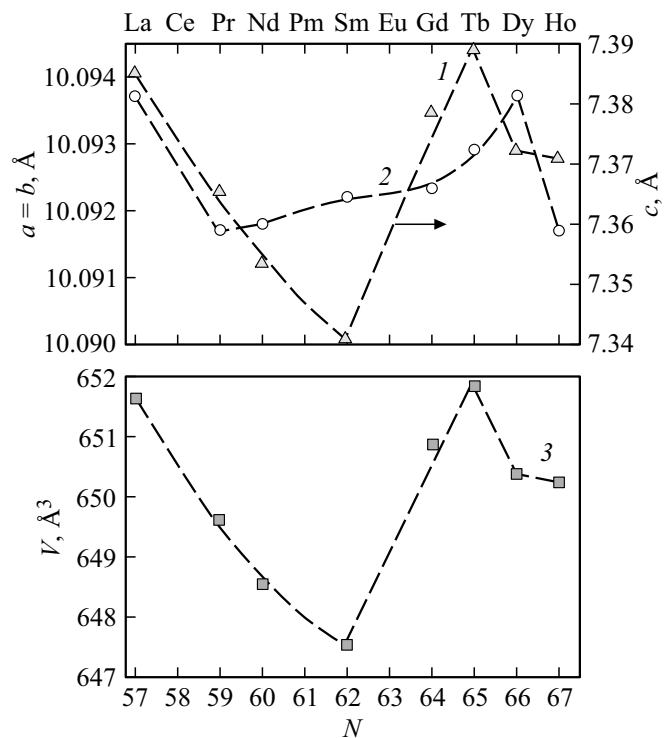


Figure 2. Dependences of unit cell parameters a (1), c (2) and V (3) of apatites $\text{Pb}_9\text{R}(\text{GeO}_4)_3(\text{VO}_4)_3$ on the ordinal number of rare earth elements.

after lead substitution by lanthanum are mainly located at site $\text{Pb}1$, despite the fact that the effective charge of La^{3+} is greater than the effective charge of Pb^{2+} . The same phenomenon was observed for $\text{Sr}_{10-x}\text{Eu}_x(\text{VO}_4)_6(\text{OH})_{2-x}\text{O}_x$ after strontium substitution by europium (Eu^{3+} predominantly occupies sites $\text{Sr}1$) [35]. Nevertheless, a substituting ion with a large effective charge in calcium hydroxyapatite occupies predominantly a smaller site $\text{Ca}2$ [36].

Fig. 2 shows the dependences of the unit cell parameters of apatites $\text{Pb}_9\text{R}(\text{GeO}_4)_3(\text{VO}_4)_3$ on the ordinal number of rare earth elements. It can be seen that a non-monotonic change of a , c and V takes place in the series from lanthanum to holmium. A similar phenomenon was also observed for other properties in the same series [37]. It is known that the formation of solid solutions is determined both by size factors and by electron shell structure [38]. Thereat, in case of a heterovalent substitution, an ion with a greater charge penetrates the crystal easier than an ion with a smaller charge (the Goldschmidt polarity rule) [38]. Taking into account the presence of lanthanoid compression, the obtained dependences (Fig. 2) can be related to the action of these two factors.

The influence of temperature on molar heat capacity of apatites $\text{Pb}_9\text{R}(\text{GeO}_4)_3(\text{VO}_4)_3$ ($R = \text{Tb}, \text{Dy}, \text{Ho}$) is shown in Fig. 3. The curves of $C_p = f(T)$ do not have various extreme values (the melting temperatures determined by us are equal to 1167, 1161 and 1157 K

Table 2. Thermodynamic properties of $Pb_9R(GeO_4)_2(VO_4)_4$ ($R = Tb, Dy, Ho$)

T, K	$C_p,$ $J K^{-1} mol^{-1}$	$H^\circ(T) - H^\circ(350 K),$ $kJ mol^{-1}$	$S^\circ(T) - S^\circ(350 K),$ $J K^{-1} mol^{-1}$	$-\Delta G/T^*,$ $J K^{-1} mol^{-1}$
$Pb_9Tb(GeO_4)_3(VO_4)_3$				
350	852.7	—	—	—
400	870.4	43.09	115.1	7.33
450	885.4	86.99	218.5	25.14
500	898.6	131.6	312.4	49.24
550	910.8	176.8	398.7	77.14
600	922.2	222.7	478.4	107.3
650	933.1	269.1	552.7	138.7
700	943.6	316.0	622.2	170.8
750	953.8	363.4	687.7	203.1
800	961.8	411.4	749.5	235.3
850	973.7	459.8	808.3	267.3
900	983.4	508.7	864.2	298.9
950	993.0	558.1	917.6	330.1
1000	1002	608.0	968.8	360.8
$Pb_9Dy(GeO_4)_3(VO_4)_3$				
350	912.4	—	—	—
400	926.3	45.97	122.7	7.82
450	939.1	92.61	232.6	26.80
500	951.2	139.9	332.2	52.44
550	962.9	187.7	423	82.07
600	974.3	236.2	507.7	114.1
650	985.4	285.1	586.1	147.4
700	996.4	334.7	659.5	181.4
750	1007	384.8	728.6	215.6
800	1018	435.4	794.0	249.7
850	1029	486.6	856.1	283.5
900	1039	538.3	915.2	317.0
950	1050	590.5	971.6	350.0
1000	1061	643.3	1026	382.5
$Pb_9Ho(GeO_4)_3(VO_4)_3$				
350	893.1	—	—	—
400	908.7	45.05	120.3	7.66
450	922.9	90.84	228.1	26.27
500	936.3	137.3	326.1	51.43
550	949.2	184.5	415.9	80.54
600	961.7	232.2	499.1	112.0
650	974.0	280.6	576.5	144.8
700	986.0	329.6	649.1	178.2
750	998.0	379.2	717.6	211.9
800	1010	429.4	782.4	245.6
850	1021	480.2	843.9	279.0
900	1033	531.6	902.7	312.0
950	1045	583.5	958.8	344.6
1000	1056	636.1	1013	376.7

Note. $-\Delta G/T^* = [H^\circ(T) - H^\circ(350 K)]/T - [S^\circ(T) - S^\circ(350 K)]$

respectively). The temperature dependences of molar heat capacity for $Pb_9Tb(GeO_4)_3(VO_4)_3$, $Pb_9Dy(GeO_4)_3(VO_4)_3$ and $Pb_9Ho(GeO_4)_3(VO_4)_3$ are described well by the classical Mayer–Kelly equation, which has the following form for

the studied apatites: for $Pb_9Tb(GeO_4)_3(VO_4)_3$

$$C_p = (826.6 \pm 1.9) + (180.1 \pm 2.0) \cdot 10^{-3}T - (45.41 \pm 1.98) \cdot 10^5 T^{-2}, \quad (1)$$

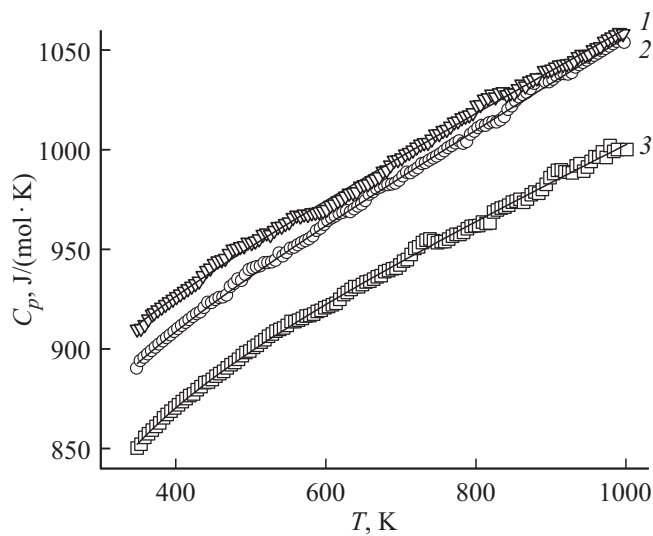


Figure 3. Influence of temperature on molar heat capacity of apatites $\text{Pb}_9\text{Dy}(\text{GeO}_4)_3(\text{VO}_4)_3$ (1), $\text{Pb}_9\text{Ho}(\text{GeO}_4)_3(\text{VO}_4)_3$ (2), $\text{Pb}_9\text{Tb}(\text{GeO}_4)_3(\text{VO}_4)_3$ (3).

for $\text{Pb}_9\text{Dy}(\text{GeO}_4)_3(\text{VO}_4)_3$

$$C_p = (854.7 \pm 2.5) + (207.0 \pm 2.7) \cdot 10^{-3}T - (18.51 \pm 2.67) \cdot 10^5 T^{-2}, \quad (2)$$

for $\text{Pb}_9\text{Ho}(\text{GeO}_4)_3(\text{VO}_4)_3$

$$C_p = (831.9 \pm 1.7) + (226.7 \pm 1.8) \cdot 10^{-3}T - (22.20 \pm 1.85) \cdot 10^5 T^{-2}, \quad (3)$$

where C_p is measured in $\text{J}/(\text{mol} \cdot \text{K})$, T — in K. The correlation coefficients for equations (1)–(3) are equal to 0.9993, 0.9986 and 0.9955, while the maximum deviations of the experimental points from the smoothing curves are 1.6, 2.3 and 1.5% respectively.

These equations were used for the studied apatites to calculate the temperature dependences of molar heat capacity C_p , changes of enthalpy $H^\circ(T) - H^\circ(350 \text{ K})$, entropy $S^\circ(T) - S^\circ(350 \text{ K})$ and Gibbs energy ΔG . These results are given in Table 2.

4. Conclusion

Apatites $\text{Pb}_9R(\text{GeO}_4)_3(\text{VO}_4)_3$ ($R = \text{Tb}, \text{Dy}, \text{Ho}$) were synthesized by the solid-phase method. Their crystal structure was determined. The influence of temperature (in the range of 320–1000 K) on molar heat capacity of these apatites was studied. It was found that the obtained experimental results are described well by the Mayer–Kelly equation. Thermodynamic functions were calculated using this data.

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Conflict of interest

The authors declare that they have no conflict of interest.

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