Functional Materials 14, No.3 (2007)

Isomorphic substitution of samarium for strontium in the $Sr_5(VO_4)_3OH$ structure

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Received April 24, 2007

Using the X-ray phase analysis and IR spectroscopy, the isomorphic substitution of samarium for strontium according to the $Sr^{2+}+OH^- \rightarrow Sm^{3+}+ O^{2-}$ has been studied in a synthetic hydroxyapatite corresponding to the system composition $Sr_{5-x}Sm_x(VO_4)_3(OH)_{1-x}O_x$ ($0 \le x \le 0.40$). The solid solutions on the basis of strontium hydroxyapatites (synthesized at 800°C from solutions) have been established to be formed within limits $0 < x < 0.12$. The crystal structure of the solid solutions obtained has been refined by the Rietveld method.

Методами рентгенофазового анализа и ИК-спектроскопии изучено изоморфное замещение ионов стронция ионами самария в соответствии со схемой $Sr^{2+}+OH^- \rightarrow Sm^{3+}+ O^{2-}$ в синтетическом гидроксиапатите, что отвечает составу системы $Sr_{5-x}Sm_x(VO_4)_3(OH)_{1-x}O_x$ ($0 \le x \le 0{,}40$). Установлено, что твердые растворы на основе гидроксиапатита стронция, синтезированные при температуре 800°C из растворов, образуются в области $x = 0 \div 0{,}12$. Проведено уточнение кристаллической структуры полученных твердых растворов методом Ритвельда.

Last years, much attention is paid to development of new materials with pre-specified necessary physical and chemical characteristics. The modification of existing compounds with various impurities is of paramount importance when designing novel materials with controlled useful properties. The study of formation of solid solutions with apatite structure and their crystallografic peculiarities will allow to extend the usage field of the apatite structure compounds (phosphors, catalysts, different sensors, etc. [1–3]), and also will be promote to further development of isomorphic substitution theory. This work is aimed at investigation of isomorphic substitutions of samarium for strontium ($Sr^{2+}+OH^- \rightarrow Sm^{3+}+ O^{2-}$) in strontium hydroxovanadate.

The title system was studied using samples with $x = 0$; 0.02; 0.04; 0.06; 0.08; 0.10; 0.12; 0.14; 0.16; 0.20; 0.25; 0.30; 0.35; 0.40. The test samples were prepared by solution thermolysis. The starting chemicals used were $Sr(NO_3)_2$ (analytical purity grade), Sm_2O_3 (SmO–I grade) and NH_4VO_3 (chemical purity grade). The solutions for synthesis were prepared by dissolving $Sr(NO_3)_2$ in water, Sm_2O_3 was dissolved in minimal amount of nitric acid, and NH_4VO_3 was dissolved in water with hydrogen peroxide added. The dry residues after concentrating the solutions were ground in an agate mortar and calcined at temperature increasing from 600 to 800°C with intermittent grindings.

The samples obtained were studied by X-ray powder diffraction, IR-spectroscopy, the crystal structure was refined by Rietveld method. The powder X-ray diffraction experiments were carried out using a DRON-2 diffractometer in the continuous mode using CuKα radiation. The scanning rate was 1–2 grad/min for phase analysis and 0.25 grad/min for interplanar spacing measurements. The unit cell parameters were calculated using the least square tech-

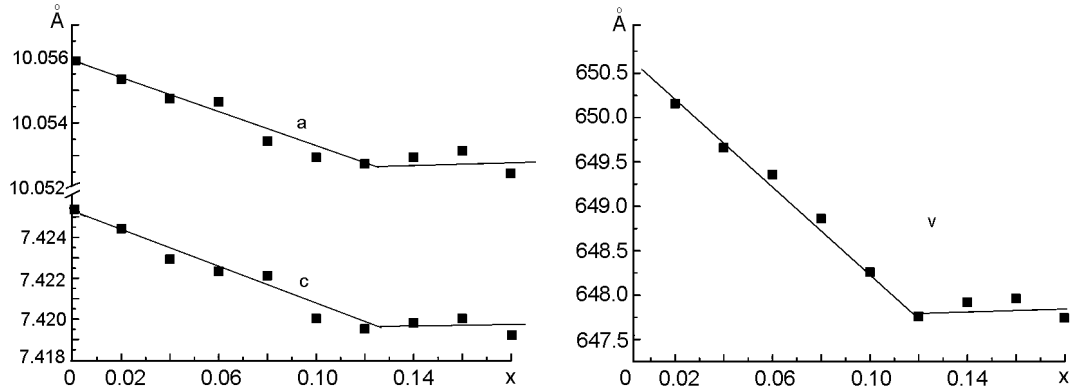

Fig. 1. Dependences of unit cell parameters a and c and volume V in $Sr_{5-x}Sm_x(VO_4)_3(OH)_{1-x}O_x$ vs. composition.

nique. The crystal structure was refined using the Rietveld method. The measurements were carried out in the step scan mode in the range of $15.00 \le 2\Theta \le 140.00$. The step size was 0.05 grad 2Θ, the exposure time per point was 10 s. The FULLPROF.2k program package, version 2.80 was used in the calculations. The IR-spectra were recorded as KBr pellets in the wavenumber range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum BX spectrometer.

According to the XPA data, the $Sr_{5-x}Sm_x(VO_4)_3(OH)_{1-x}O_x$ system samples calcined at 800°C are single-phase ones within the range $0<x<0.12$ having the strontium hydroxovanadate structure. At higher x, values, the phases with $Sr_3(VO_4)_2$ and Sm_2O_3 structure are formed along with the apatite phase. The calcination of samples at a temperature exceeding 800°C does not result in expansion of homogeneous region of the studied system, but favors the decomposition of the apatite structure phase into $Sr_3(VO_4)_2$ and SrO [4].

The a and c lattice parameters and the apatite phase hexagonal unit cell volume decrease gradually in the homogeneous region (Fig. 1). This dependence indicates that the single-phase solid solutions are formed. This fact is due to a larger ionic radius of Sr^{2+} (1.35 Å) as compared to Sm^{3+} (1.16 Å) [5]. In spite of the fact that the samarium ion is substantially less than the strontium one, the variations in the unit cell parameters are small due to the small substitution limits.

The homogeneous region has been also determined by the "disappearing phase" method. The dependence of the strontium orthovanadate line hkl 015 reflection intensity on the solid solution composition was plotted. This is illustrated in Fig. 2. The obtained line cuts the abscissa axis at

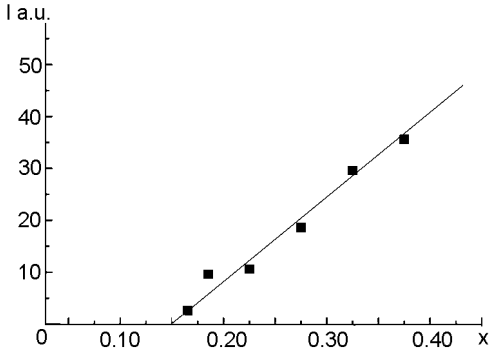

Fig. 2. Dependence of the strontium orthovanadate line hkl 015 reflection intensity vs. composition.

$x \approx 0.12$, which confirms the cell parameters variations.

IR-spectra were measured for samples with compositions lying within the homogeneous region. The hydroxyl group presence in hydroxovanadate was determined from the IR spectra corresponding to torsional (560 cm^{-1}) and stretching (3567 cm^{-1}) modes of OH- groups [6, 7]. The spectra have shown the absorption bands ascribed to VO_4^{3-} ion vibrations. This fact confirms the phase analysis results showing formation of a phase with apatite structure (Fig. 3). The increasing x practically does not affect either the intensity or the position of the VO_4^{3-} ion fundamental vibrations. However, the torsional bands and stretching bands of the hydroxide ion change their intensities, which corresponds to the suggested substitution scheme $Sr^{2+}+OH^- \rightarrow Sm^{3+}+O^{2-}$.

The refinement of the crystal structure was carried out for the starting $Sr_5(VO_4)_3OH$ and for a sample with $x = 0.12$. As the starting model, the data from [8] for calcium hydroxylapatite (the apatite structure type, space group $P6_3/m$) were used. The refinement was carried out for 966 lines to the following reliability factors: $R_F = 0.05$;

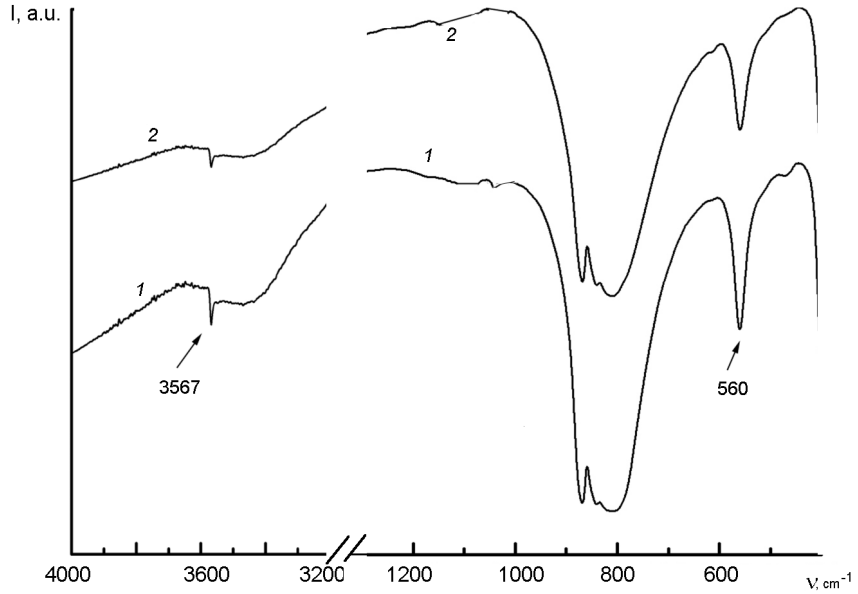

Fig. 3. IR spectra of the $Sr_{5-x}Sm_x(VO_4)_3(OH)_{1-x}O_x$ samples: $x = 0$ (*1*); $x = 0.12$ (*2*).

$R_{Bragg} = 0.07$; $R_p = 0.07$; $R_{WP} = 0.08$ and $\chi^2 = 1.39$. This is typical values differentiating in the last sign by 1–2 units for different samples. As it is obvious from the Table, a considerable decrease of average Sr(2)–OH(O) spacings from 2.620 to 2.593 Å and Sr(2)–Sr(2) from 4.381 to 4.339 Å in spite of small substitution limits ($x = 0.12$ corresponds to the 2.4 mol. % substitution of samarium for strontium atoms). This is due to the substitution of O^{2-} for OH^- in the structure channels and the induced increase in the electrostatic interactions with cations [9]. At the same time, a shortening of Sr(1)–O distances takes place. Basing on this fact as well as on information of previous researches [10, 11], it is possible to say that the substitution of samarium for strontium occur mainly at the Sr(1) position of nine-apical cells.

Table. Some interatomic distances in $Sr_{5-x}Sm_x(VO_4)_3(OH)_{1-x}O_x$.

Composition	$x = 0$	$x = 0.12$
V–O(1)	1.700(18)	1.680(30)
V–O(2)	1.719(18)	1.670(30)
V–O(3)×2	1.731(9)	1.743(13)
<V–O>	1.720	1.715
Sr(1)–O(1)×3	2.559(14)	2.591(13)
Sr(1)–O(2)×3	2.628(12)	2.565(18)
Sr(1)–O(3)×3	2.989(10)	2.889(11)
<Sr(1)–O(1.2.3)>	2.725	2.682
Sr(2)–O(1)	2.832(16)	2.820(30)
Sr(2)–O(2)	2.476(17)	2.570(30)
Sr(2)–O(3)×2	2.824(9)	2.728(14)
Sr(2)–O(3)×2	2.379(9)	2.461(13)
<Sr(2)–O(1.2.3)>	2.619	2.628
Sr(2)–OH	2.620(6)	2.593(9)
Sr(2)–Sr(2)	4.381(5)	4.339(5)

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Ізоморфне заміщення стронцію на самарій у структурі $Sr_5(VO_4)_3OH$

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Методами рентгенофазового аналізу та ІЧ-спектроскопії вивчено ізоморфне заміщення іонів стронцію на іони самарію згідно зі схемою $Sr^{2+}+OH^- \rightarrow Sm^{3+}+ O^{2-}$ у синтетичному гідроксіапатиті, що відповідає складу системи $Sr_{5-x}Sm_x(VO_4)_3(OH)_{1-x}O_x$ ($0 \le x \le 0{,}40$). Встановлено, що тверді розчини на основі гідроксіапатиту стронцію, які синтезовано при температурі 800°C з розчинів, утворюються у межах $x = 0 \div 0{,}12$. Проведено уточнення кристалічної структури отриманих твердих розчинів методом Рітвельда.