



Article

Sol-Gel Combustion Synthesis, Crystal Structure and Luminescence of Cr^{3+} and Mn^{4+} Ions in Nanocrystalline SrAl_4O_7

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Abstract: A series of strontium dialuminate SrAl_4O_7 nanopowders with the grossite-type structure doped with chromium and manganese ions were synthesized by the combined sol–gel solution combustion method with use of two different strontium salts. The Cr^{3+} and Mn^{4+} ions concentrations were varied from 0.05 to 5 at. %. Evolution of phase composition, crystal structure, and microstructural parameters of the nanocrystalline materials depending on the synthesis conditions, temperature of thermal treatment, and dopant content were investigated by the X-ray powder diffraction and the scanning electron microscopy techniques. Photoluminescent properties of SrAl_4O_7 nanophosphors activated with Cr^{3+} and Mn^{4+} ions were studied at room temperature. The samples exhibit typical photoluminescence in the deep-red spectral region, corresponding to $d-d$ transitions in Cr^{3+} or Mn^{4+} ions. The intensity of this deep-red emission is dependent on the dopant concentration and annealing temperature. Features of the formation of octahedral surroundings around Cr^{3+} or Mn^{4+} ions are discussed.

Keywords: strontium dialuminate; Cr- and Mn-doping; combustion synthesis; crystal structure; luminescence

1. Introduction

Aluminates (MAl_4O_7) and gallates (MGa_4O_7) of alkaline earth elements ($M = \text{Ca}, \text{Sr}, \text{Ba}$) with the monoclinic grossite-type structure are promising for applications in white light sources (WLEDs), fluorescent lamps, optical amplifiers, radiant displays, solid-state lasers, radiation dosimetry, sensors, and radiographs. Recently, a number of publications have appeared on the synthesis of MAl_4O_7 -based materials doped with rare-earth elements (Eu, Dy, Nd, Sm), bismuth, as well as some transition elements such as Cr, Mn, and Cu [1–15]. Phosphors activated with rare-earth (RE) ions have attracted great attention since they show high quantum efficiency, long persistence of phosphorescence, and suitable emitting color. On the other hand, phosphors doped with transition metal ions, particularly Mn^{4+} or Cr^{3+} , which have broadband excitation in the UV and visible regions of the spectrum and deep red radiation can be an alternative to phosphors activated by RE ions.

Recently, there has been a growing interest in such inexpensive phosphors (without RE ions) for the deep-red and near-IR emission range. Red light with a wavelength in the range of 650–800 nm can control the growth process of plants by regulating the ratio of

phytochrome [16]. Thus the aluminates of alkaline earth elements MA_4O_7 with the grossite structure, doped with suitable activators emitting in the red region of the spectrum, can find a potential application for the manufacturing of LEDs for greenhouses illumination.

Luminescent studies of MA_4O_7 and MGa_4O_7 -based materials doped with Cr^{3+} or Mn^{4+} indicate that these activators are in an octahedral surrounding, while the structure of the host materials does not have intrinsic octahedral sites [1,6]. The mechanism of octahedron formation around these activators in the grossite-type structures is not fully understood.

This work reports the results of precise structural investigations of Cr^{3+} and Mn^{4+} doped $SrAl_4O_7$ nanopowders synthesized by the sol–gel combustion route and the influence of the dopant concentrations and heat treatment temperature on their photoluminescent properties with the purpose to create new phosphors emitting in a deep red spectral region.

2. Results and Discussion

2.1. Evolution of Phase Composition, Crystal Structure, and Microstructural Parameters

Initially, the synthesis of $SrAl_4O_7:Cr^{3+}$ was performed by using $Sr(NO_3)_2 \cdot 4H_2O$ as a strontium source. X-ray diffraction (XRD) examination of the as-obtained foamy product after the auto-combustion process at 800 °C revealed the formation of X-ray amorphous material (Figure 1, top panel).

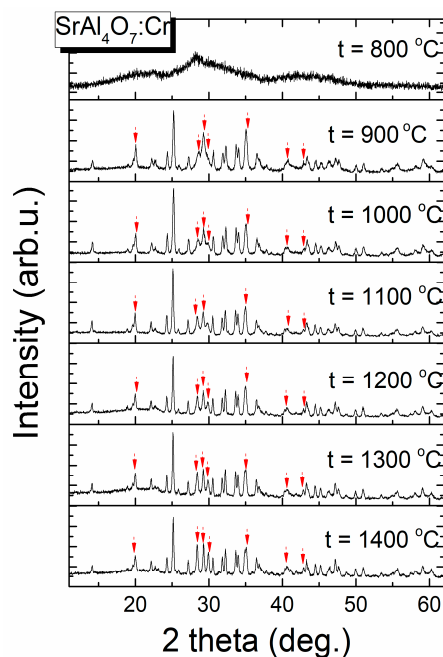


Figure 1. The evolution of XRD patterns of $SrAl_4O_7:Cr^{3+}$ powders, successively annealed at different temperatures. Arrows indicate extra peaks of the parasitic $SrAl_2O_4$ phase.

Crystallization of $SrAl_4O_7$ occurs after extra annealing at 900 °C for 4 h. However, besides the desired grossite-type phase, the parasitic $SrAl_2O_4$ phase with a monoclinic structure is formed (Figure 1). Further heat treatment of the powders at 1000, 1100, 1200, 1300, and 1400 °C does not improve the phase composition of the materials. In contrast, the amount of secondary $SrAl_2O_4$ phase increased from 35–37 wt.% up to 43% after final firing at 1400 °C, as it was estimated from experimental XRD patterns by full quantitative profile Rietveld refinement (see Figure 2 as an example). Evidently, appearing of parasitic $SrAl_2O_4$ phase with higher Sr/Al ratio as in $SrAl_4O_7$ could be explained by deviation of $Sr(NO_3)_2 \cdot 4H_2O$ tetrahydroxonitrate precursor used from a stoichiometric composition.

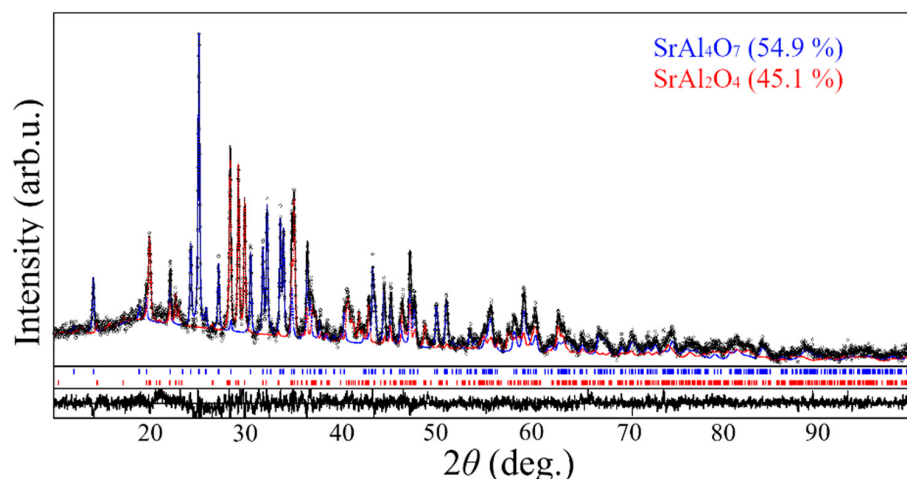


Figure 2. Graphical results of simultaneous two-phase Rietveld refinement illustrating coexistence of two monoclinic phases— SrAl_4O_7 (blue) and SrAl_2O_4 (red) in the $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ sample, annealed at 1400°C .

Indeed, further usage of extra pure grade SrCO_3 as a strontium source for the next synthesis of two series of chromium and manganese doped SrAl_4O_7 materials allow obtaining almost single-phase products with the grossite structure. Both series of $\text{SrAl}_4\text{O}_7:\text{xCr}$ ($x = 0.0005, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05$) and $\text{SrAl}_4\text{O}_7:\text{xMn}$ ($x = 0.0005, 0.005, 0.05$) powders were synthesized in order to study the effect of the concentration and type of activator ion on the luminescence properties of the phosphors. The chromium concentrations were chosen for easier comparison with the corresponding crystalline phosphors based on the isostructural strontium digallate $\text{SrGa}_4\text{O}_7:\text{xCr}$, recently described in [1]. XRD examination of new series of solution combustion synthesized $\text{SrAl}_4\text{O}_7:\text{xCr}$ and $\text{SrAl}_4\text{O}_7:\text{xMn}$ powders after their heat treatment at 1100°C for 4 h revealed almost pure grossite-type structure for all dopant concentrations; only traces of foreign phases could be detected on some patterns (Figure 3).

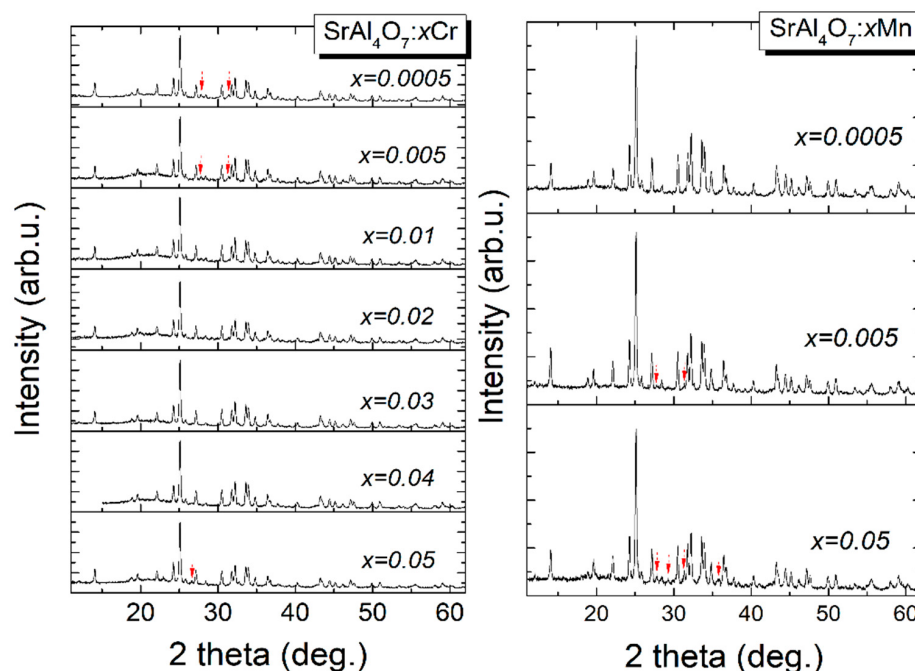


Figure 3. Experimental XRD patterns of $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ powders with different chromium and manganese content, annealed at 1100°C . Arrows indicate the traces of the foreign phase(s).

The number of parasitic phases increased after extra annealing of the $\text{SrAl}_4\text{O}_7:\text{xCr}^{3+}$ powders at 1200 °C. In the case of $\text{SrAl}_4\text{O}_7:\text{xMn}^{4+}$ series, this effect is much more pronounced and the amount of the extraneous phases rises 20–25%. This observation is not surprising, because SrAl_4O_7 becomes metastable when the temperature is raised beyond 1100 °C [17].

Morphology of $\text{SrAl}_4\text{O}_7:\text{xCr}$ powders, chemical composition, and the homogeneity of the element's distribution was selectively controlled by scanning electron microscopy (SEM) and local X-ray spectral analysis on an example of the sample with $x = 0.05$ synthesized through solution combustion route and heat-treated at 1200 °C (Figure 4). SEM micrographs revealed a fluffy platelet-like structure of cirrus morphology with non-uniform distribution of crystallites. Nominal chemical composition and homogeneous distribution of elements through the powder analyzed was confirmed (Figure 4).

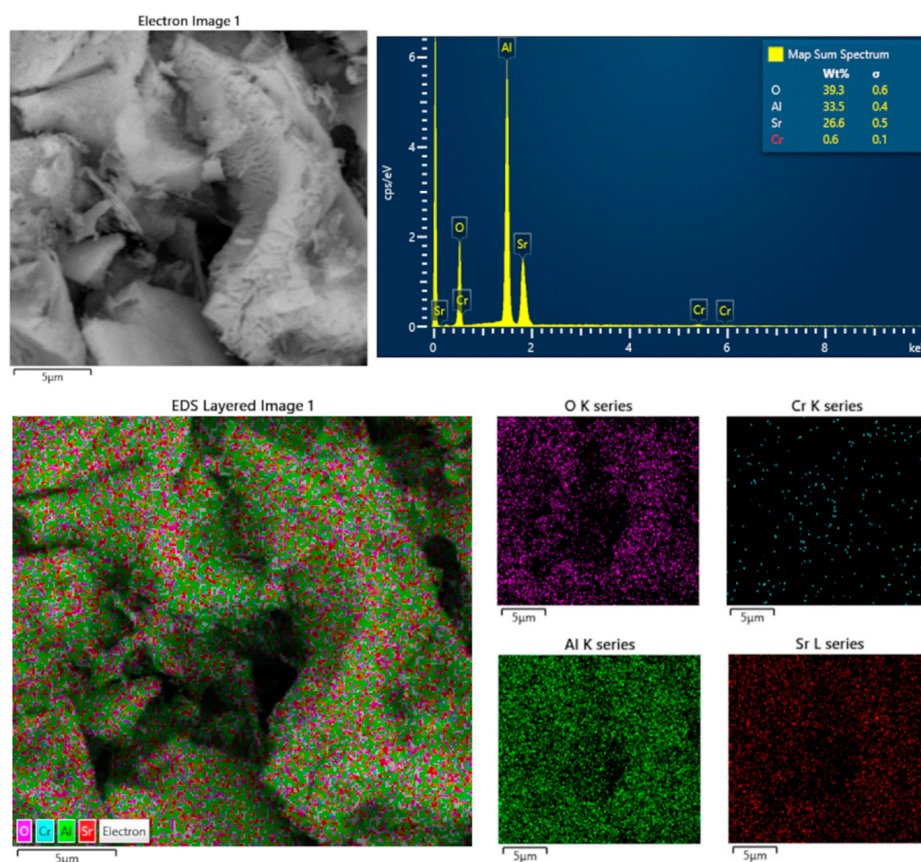


Figure 4. SEM images, results of local X-ray spectral analysis and elements distribution in the $\text{SrAl}_4\text{O}_7:0.05\text{Cr}$ powder heat-treated at 1200 °C.

Microstructural parameters of the $\text{SrAl}_4\text{O}_7:\text{xCr}$ powders, such as average crystallite size D_{ave} and microstrain values $\langle \epsilon \rangle$ were evaluated from XRD patterns by full profile Rietveld fitting. It was established that D_{ave} varies in the limits of 65–110 nm independent of the activator concentration and the temperature of heat treatment (Figure 5, upper part). Evaluated lattice strain values $\langle \epsilon \rangle$ show a minor tendency to a decreasing behavior with increasing x in $\text{SrAl}_4\text{O}_7:\text{xCr}$ series (Figure 5, bottom part). One could also observe that the increase in the heat treatment temperature from 1100 to 1200 °C led to a detectable decrease of the microstress values for all concentrations of dopant.

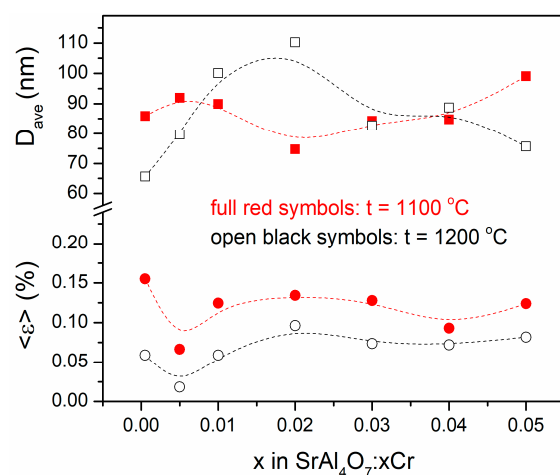


Figure 5. Average crystallite size D_{ave} and lattice strain values $\langle \epsilon \rangle$ of $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ powders, depending on the Cr^{3+} content and annealing temperature. The dashed B-Spline lines are a visual guide.

A full profile Rietveld refinement was also used for the evaluation of precise structural parameters of both $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ series. As the initial model for the refinement of the chromium- and manganese-doped SrAl_4O_7 -based structures, atomic coordinates in nominally pure SrAl_4O_7 ($\text{CaO} \cdot 2\text{Al}_2\text{O}_3$) compound, derived from single-crystal data in Ref. [18] were used. In the refinement procedure, the lattice parameters, coordinates, and displacement parameters of all atoms were refined together with profile parameters and corrections for absorption and instrumental sample shift. In all cases, an excellent agreement between the calculated and experimental diffraction profiles was reached. Exemplary results of the Rietveld refinement of $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ structures are presented in Figure 6.

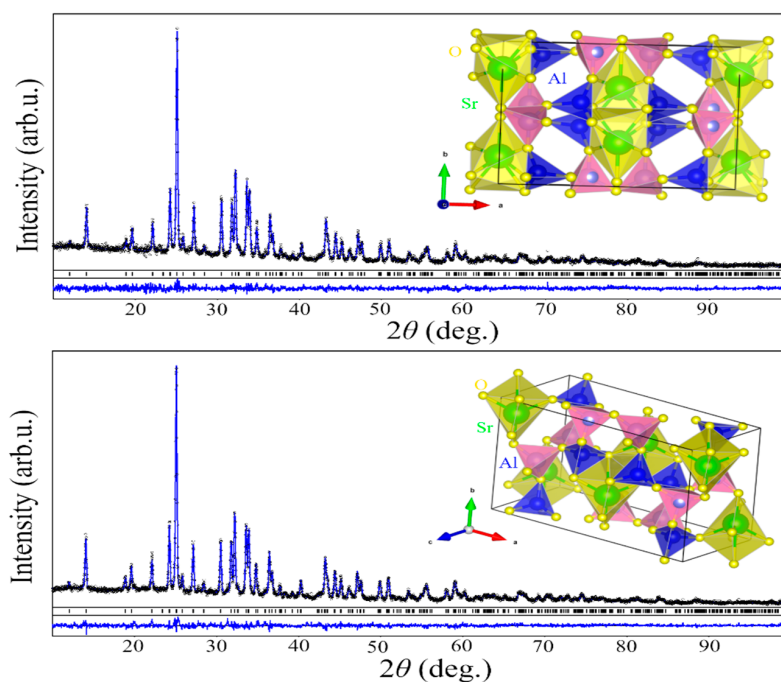


Figure 6. Graphical results of Rietveld refinement of $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ (top) and $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ (bottom) structures with $x = 0.005$. Experimental XRD patterns (black circles) are shown in comparison with calculated ones. Short vertical bars indicate positions of Bragg's maxima in grossite-type $C2/c$ structure. Insets show polyhedral views of SrAl_4O_7 structure in two different projections. The a , b , and c indicate corresponding crystallographic axes.

Obtained structural parameters for $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ powders, annealed at 1100 °C and corresponding interatomic distances calculated from these data are presented in Tables 1 and 2, respectively.

Table 1. Lattice parameters, coordinates, and displacement parameters of atoms in $\text{SrAl}_4\text{O}_7:\text{xCr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{xMn}^{4+}$ ($\text{x} = 0.005$) materials (SG C2/c, Z = 4) after heat treatment at 1100 °C.

Lattice Parameters, Residuals	Atom, Sites	x/a	y/b	z/c	$B_{\text{isoleq}}, \text{\AA}^2$
$\text{SrAl}_4\text{O}_7:\text{xCr}^{3+}$					
	Sr, 4e	0	0.8113(4)	1/4	1.00(6)
$a = 13.0462(9) \text{\AA}$	Al1, 8f	0.1663(6)	0.0857(8)	0.2940(15)	0.7(2)
$b = 9.0221(7) \text{\AA}$	Al2, 8f	0.1259(6)	0.0857(8)	0.2655(15)	0.6(2)
$c = 5.5439(4) \text{\AA}$	O1, 4e	0	0.516(2)	1/4	0.7(5)
$\beta = 106.209(2)^\circ$	O2, 8f	0.1252(9)	0.0376(12)	0.540(3)	1.6(4)
$V = 626.6(2) \text{\AA}^3$	O3, 8f	0.1281(8)	0.2554(13)	0.179(2)	0.7(3)
	O4, 8f	0.1936(11)	0.4433(11)	0.595(2)	1.5(4)
$R_I = 0.056; R_P = 0.190$					
$\text{SrAl}_4\text{O}_7:\text{xMn}^{4+}$					
	Sr, 4e	0	0.8115(4)	1/4	0.99(6)
$a = 13.0469(8) \text{\AA}$	Al1, 8f	0.1672(6)	0.0853(7)	0.2974(13)	0.9(2)
$b = 9.0227(6) \text{\AA}$	Al2, 8f	0.1246(6)	0.4390(8)	0.2660(13)	1.0(2)
$c = 5.5443(3) \text{\AA}$	O1, 4e	0	0.5218(15)	1/4	1.7(5)
$\beta = 106.197(2)^\circ$	O2, 8f	0.1243(8)	0.0374(11)	0.544(2)	1.2(3)
$V = 626.8(1) \text{\AA}^3$	O3, 8f	0.1260(7)	0.2567(12)	0.170(2)	0.8(3)
	O4, 8f	0.1904(9)	0.4434(10)	0.597(2)	1.3(4)
$R_I = 0.057; R_P = 0.172$					

Table 2. Selected interatomic distances in $\text{SrAl}_4\text{O}_7:\text{xCr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{xMn}^{4+}$ ($\text{x} = 0.005$) structures annealed at 1100 °C.

Atoms	Distances [$\text{\AA}$]	Atoms	Distances [$\text{\AA}$]	Atoms	Distances [$\text{\AA}$]
$\text{SrAl}_4\text{O}_7:\text{xCr}^{3+}$					
Sr-O3 $\times$ 2	2.570(11)	Al1-O2	1.659(14)	Al2-O3	1.731(14)
Sr-O2 $\times$ 2	2.634(12)	Al1-O3	1.679(13)	Al2-O1	1.763(10)
Sr-O1	2.660(15)	Al1-O2	1.755(14)	Al2-O4	1.794(14)
Sr-O2 $\times$ 2	2.821(12)	Al1-O4	1.78(2)	Al2-O4	1.805(15)
Sr-Al1 $\times$ 2	3.256(8)	Al1-Al2	3.109(11)	Al2-O1	2.899(8)
Sr-Al1 $\times$ 2	3.319(8)	Al1-Al2	3.114(12)	Al2-Al2 $\times$ 2	2.979(11)
Sr-Al2 $\times$ 2	3.656(8)	Al1-Sr	3.256(8)	Al2-Al1	3.109(11)
Sr-O4 $\times$ 2	3.688(13)	Al1-Sr	3.319(8)	Al2-Al1	3.114(12)
Sr-Al2 $\times$ 2	3.725(8)	Al1-O4	3.441(15)	Al2-O2	3.130(15)
$\text{SrAl}_4\text{O}_7:\text{xMn}^{4+}$					
Sr-O3 $\times$ 2	2.524(9)	Al1-O2	1.671(13)	Al2-O3	1.731(12)
Sr-O2 $\times$ 2	2.614(10)	Al1-O3	1.722(12)	Al2-O1	1.769(9)
Sr-O1	2.614(14)	Al1-O2	1.754(12)	Al2-O4	1.784(13)
Sr-O2 $\times$ 2	2.822(10)	Al1-O4	1.805(14)	Al2-O4	1.798(13)
Sr-Al1 $\times$ 2	3.257(7)	Al1-Al2	3.101(10)	Al2-O1	2.891(7)
Sr-Al1 $\times$ 2	3.338(7)	Al1-Al2	3.127(10)	Al2-Al2 $\times$ 2	2.983(10)
Sr-Al2 $\times$ 2	3.653(7)	Al1-Sr	3.257(7)	Al2-Al1	3.101(10)
Sr-O4 $\times$ 2	3.653(11)	Al1-Sr	3.338(7)	Al2-Al1	3.127(10)
Sr-Al2 $\times$ 2	3.724(8)	Al1-O4	3.486(13)	Al2-O2	3.157(13)

Detailed analysis of obtained structural parameters of the $\text{SrAl}_4\text{O}_7:\text{xCr}$ materials and their concentration-dependence on the chromium content revealed detectable deviations

from the monotonic behavior in both series of the powders heat-treated at 1100 and 1200 °C (Figure 7). The discontinuities in the $\text{SrAl}_4\text{O}_7\text{:xCr}$ series are manifested as detectable minima in all lattice parameters and a clear jump in the monoclinic angle at the value of the compositional parameter $x = 0.02$. As a result, clear minima in the unit cell volume of $\text{SrAl}_4\text{O}_7\text{:xCr}$ structure is observed. Up to now, we have no explanation of such deviations in structural parameters observed for $\text{SrAl}_4\text{O}_7\text{:0.02Cr}$ composition.

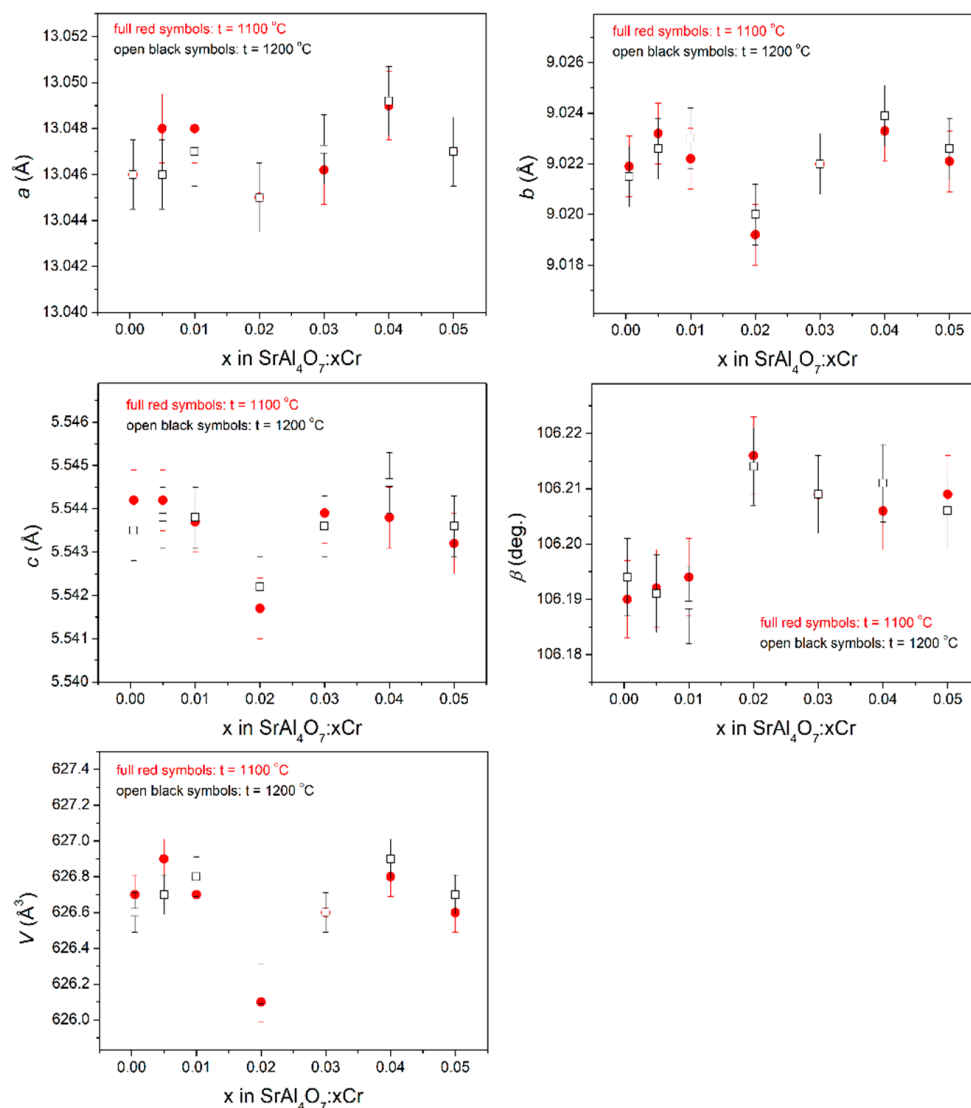


Figure 7. Dependencies of the lattice parameters and volume of the $\text{SrAl}_4\text{O}_7\text{:xCr}^{3+}$ unit cell on nominal content of chromium in samples.

The crystal structure of SrAl_4O_7 can be represented as a framework of edge-shared SrO_7 polyhedra, which are connected with two types of apex-shared AlO_4 tetrahedra (see Figure 8 and insets on Figure 6).

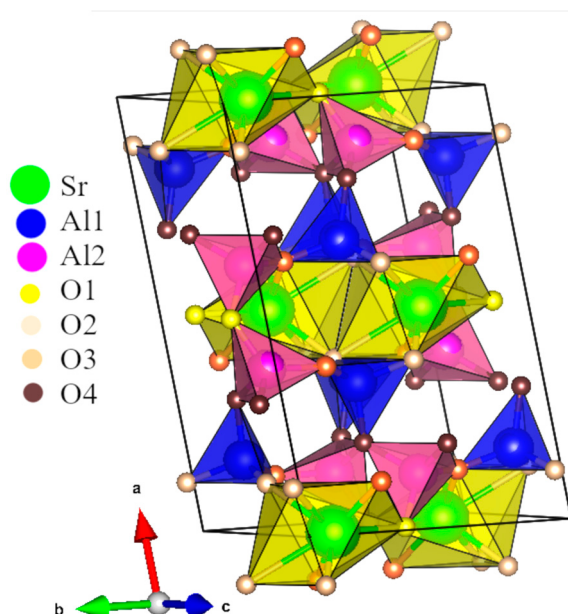


Figure 8. Polyhedral representation of SrAl_4O_7 structure. Two types of AlO_4 tetrahedra (blue Al1O_4 and pink Al2O_4 ones) and SrO_7 polyhedra (yellow) are shown. The a , b , and c indicate corresponding crystallographic axes.

In the SrAl_4O_7 structure, the Sr atoms are located in 4-fold positions (Table 1) and are surrounded by seven oxygen atoms located at the distances 2.53–2.83 Å (Table 2) and forming pentagonal bipyramids around the central atoms (see Figure 8). The next coordination sphere is formed with eight Al atoms and two oxygens located at the distances 3.26–3.76 Å (Table 2). Aluminum atoms in the SrAl_4O_7 structure are located in two non-equivalent 8-fold positions (Table 1), which are characterized by a tetrahedral environment (Figure 8) formed by four oxygen atoms located at the distances 1.66–1.80 Å and 1.73–1.80 Å from Al(1) and Al(2) atoms, respectively (Table 2). In spite of there being no octahedral positions in the SrAl_4O_7 structure, further investigations of luminescence characteristics of $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ series (see next section) revealed clear features of octahedrally coordinated Cr^{3+} and Mn^{4+} ions. Similar observation (luminescence of transition metal ions in octahedral positions) was recently reported for the phosphors based on SrAl_4O_7 and the related isostructural compounds CaAl_4O_7 and SrGa_4O_7 [1,6,7]. It is necessary to note that there is no consensus in the literature on the scenario of cation substitution in the strontium and calcium aluminates and gallates $(\text{Sr}/\text{Ca})(\text{Al}/\text{Ga})_4\text{O}_7$ with transition metal ions. The authors [6] reported that red luminescence of $\text{CaAl}_4\text{O}_7:\text{Mn}$ phosphors comes from distorted octahedral Mn^{4+} sites due to substitution for Ca sites in the CaAl_4O_7 structure. In contrast, Liu et al. [7] postulated that because the Mn^{4+} ionic radius is closely equal to that of Al^{3+} , it is expected that Mn^{4+} ions can readily replace Al^{3+} ions, and are unlikely substituted for larger Ca^{2+} ions in the CaAl_4O_7 compound. Similarly, Lai et al. [1] suggested that red emission in $\text{SrGa}_4\text{O}_7:\text{Cr}$ phosphors arises from Cr^{3+} ions in the distorted octahedra, which are generated by the transition from the GaO_4 tetrahedra to the octahedra, as Cr^{3+} ions replaced Ga^{3+} ions in SrGa_4O_7 structure.

Our analysis of the structural peculiarities of the grossite-type MAl_4O_7 and MGa_4O_7 host materials [19], as well as $\text{SrAl}_4\text{O}_7:\text{Cr}^{3+}$ and $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ series investigated (see, e.g., interatomic distances distribution around the Sr^{2+} and Al^{3+} cations in corresponding structures presented in Table 2) favor a first above-mentioned scenario of cation substitution, namely, replacing with transition metal ions for the Sr sites. Indeed, in the case of $\text{Cr}^{3+}/\text{Mn}^{4+}$ substitution for Sr^{2+} ions, which are surrounded with 7 oxygens located at the distances 2.53–2.83 Å (Figure 8, Table 2), the transition metal ions can easily coordinate around themselves six near oxygen atoms to form CrO_6 or MnO_6 octahedra. In contrast, it is difficult to imagine the entry of Cr^{3+} or Mn^{4+} ions into both tetrahedral positions of

Al^{3+} ions in the SrAl_4O_7 structure and their subsequent conversion into the octahedral ones, given the great distance to the next two oxygen atoms located at 3.44–3.38 Å from Al1 atoms and at 2.90 Å and 3.16 Å from Al2 atoms (see Table 2), which are required for octahedra formation. Unfortunately, very low concentrations of Cr^{3+} and Mn^{4+} ions in the materials studied do not allow refining their positions in SrAl_4O_7 structure from X-ray powder diffraction data. To shed light on the mechanism of transition of metal cation substitution in MAl_4O_7 and MGa_4O_7 materials, a precise investigation of local structures is required.

2.2. Luminescent Properties

Characteristic photoluminescence excitation and emission spectra of $\text{SrAl}_4\text{O}_7:0.0005\text{Cr}^{3+}$ annealed at 1300 °C are shown in Figure 9. The luminescence excitation spectra show excitation in the wavelength range from 250 to 650 nm, with three intense maxima at approximately 330, 420, and 560 nm. Two broad maxima in the visible spectral region corresponded to the intracenter $4\text{A}_2 \rightarrow 4\text{T}_1(^4\text{F})$ and $4\text{A}_2 \rightarrow 4\text{T}_2(^4\text{F})$ transitions in Cr^{3+} ions.

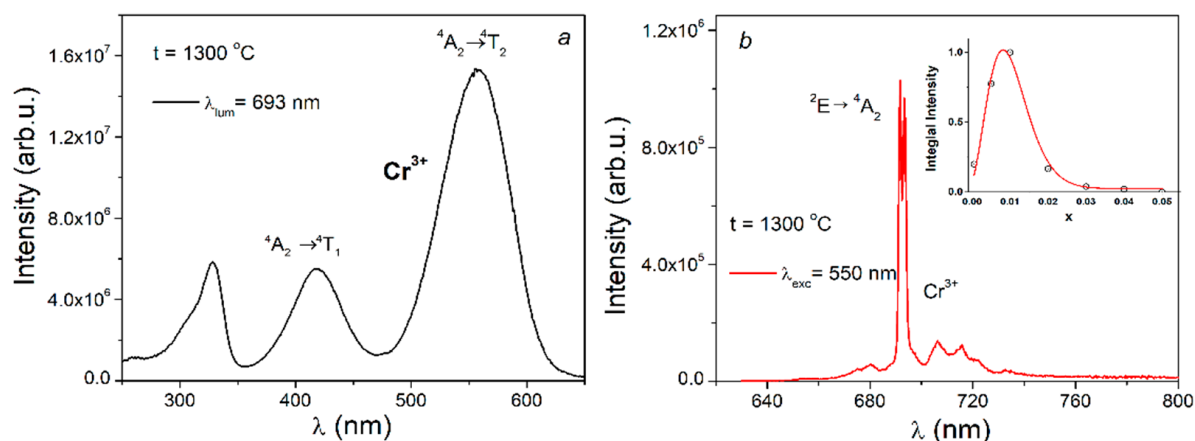


Figure 9. The luminescence excitation (a) and photoluminescence (b) spectra of Cr^{3+} ions in $\text{SrAl}_4\text{O}_7:0.0005\text{Cr}^{3+}$ powders. The inset of (b) presents the concentration dependence of Cr^{3+} integral photoluminescence.

The UV excitation band at about 330 nm (see Figure 9a) is most probably associated with a charge-transfer $\text{O}^{2-} \rightarrow \text{Cr}^{3+}$ or/and with $4\text{A}_2 \rightarrow 4\text{T}_1$ (^4P) transitions. The photoluminescence is observed in the spectral region of 640–760 nm at room temperature. The dominant narrow luminescence lines (R-lines) observed in $\text{SrAl}_4\text{O}_7:\text{Cr}$ at about 691.7 and 693.2 nm at room temperature corresponds to the transitions from the split (3.9 meV) metastable ^2E level to the $^4\text{A}_2$ ground state and are inherent for the Cr^{3+} ions in an octahedral environment. In the isostructural SrGa_4O_7 compound [1], similar luminescent features were also shown to arise from Cr^{3+} ions in the distorted octahedra. It should be noted that such excitation and emission bands are typical for Cr^{3+} ions in strong crystal field strength of the octahedral surrounding for different oxide materials (see [20–22], for instance).

The photoluminescence efficiency of phosphors can be improved by changing the annealing temperature and/or the concentration of the doping impurity. That is why these parameters are essential in determining the optimal conditions for obtaining suitable phosphors.

The concentration dependence of integral photoluminescence intensity of SrAl_4O_7 powders for different levels of Cr^{3+} doping in the range of $x = 0.0005$ – 0.05 after samples annealing at 1200 °C for 4 h are presented in the inset of Figure 9b. It was established that with the increasing of Cr^{3+} ions content, there were no significant changes in the shape of the luminescence spectra. However, the integral photoluminescence intensity increases until the concentration of Cr^{3+} ions reaches 0.01. Further, the intensity begins to sharply decrease with an increase in the Cr^{3+} concentration. Probably, this behavior is coupled with the above-mentioned discontinuities in concentration dependencies of structural parameters observed in the $\text{SrAl}_4\text{O}_7:x\text{Cr}$ series between $x = 0.01$ and 0.02 (see Figure 7).

The decrease in the photoluminescence intensity at a concentration of Cr^{3+} ions over 0.01 is due to concentration quenching, which is explained by the processes of cross-relaxation between neighboring Cr^{3+} ions, i.e., with increasing Cr^{3+} content, the distance between adjacent Cr^{3+} ions decreases. Therefore, there is a more effective non-radiative energy transfer, which leads to a decrease in the photoluminescence intensity with the Cr^{3+} dopant concentration increasing.

The integral photoluminescence intensity in the spectral region 640–800 nm depending on the annealing temperature during 4 h was investigated for $\text{SrAl}_4\text{O}_7:0.0005\text{Cr}^{3+}$ powder to establish the optimal annealing temperature of powders. The intensity of photoluminescence increases with increasing annealing temperature, in the range 1200–1400 °C. In particular, a change in calcination temperature of samples from 1200 to 1300 °C leads to a ~6 times increase in emission intensity. For the sample annealed at 1400 °C, the emission is more than an order higher than for the sample annealed at 1300 °C. We can assume that at higher temperatures, the intensity of photoluminescence increases significantly due to the improving crystallinity of SrAl_4O_7 and/or increase in the concentration of Cr^{3+} ions in a regular octahedral surrounding.

The $\text{SrAl}_4\text{O}_7:\text{Mn}^{4+}$ samples also show red photoluminescence, but it is slightly shifted towards higher energies relative to the luminescence of the Cr^{3+} activator (Figure 10). In the case of $\text{SrAl}_4\text{O}_7:0.0005\text{Mn}^{4+}$ under excitation with UV or blue lights, all the samples exhibit typical Mn^{4+} red photoluminescence (Figure 10a). The excitation spectrum of this luminescence consists of two broad peaks at 313 and 455 nm in the spectral range between 250 to 500 nm. The intensity of the blue peak is at about 20% of the UV peak intensity. The photoluminescence spectrum of Mn^{4+} (Figure 10b) extends from 600 to 750 nm with a sharp maximum at about 653 nm, attributed to ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transitions in Mn^{4+} ions. It should be noted that only Mn^{4+} in an octahedral surrounding can emit such a spectrum in the red spectral range. As was shown for the CaAl_4O_7 , when Mn^{4+} replaces $\text{Ca}(1)$, the local field is distorted due to increased Coulomb interaction, and it turns into a typical octahedral field eventually [6].

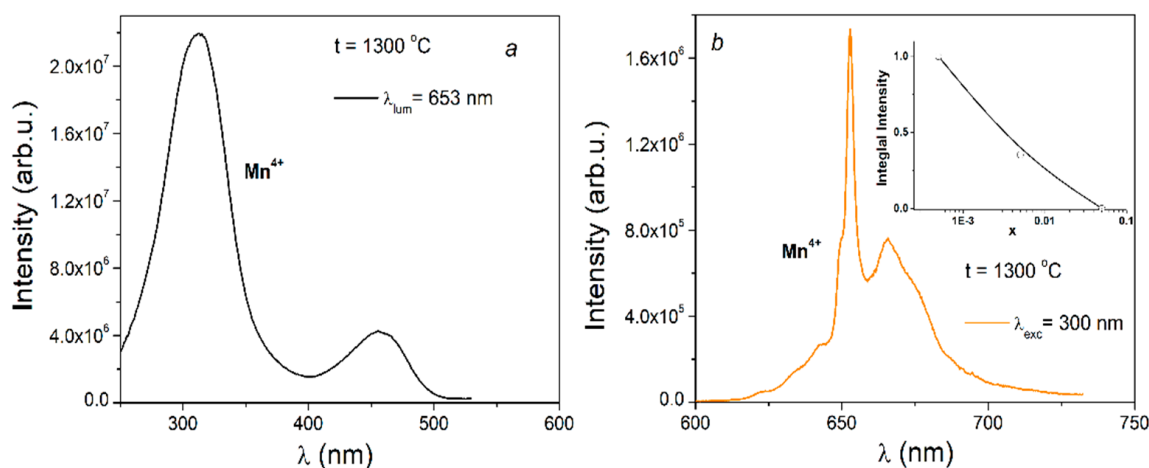


Figure 10. The luminescence excitation (a) and photoluminescence (b) spectra of Mn^{4+} ions in $\text{SrAl}_4\text{O}_7:0.0005\text{Mn}^{4+}$ powders. The inset of (b) presents the concentration dependence of Mn^{4+} integral photoluminescence.

It should be noted that Mn^{4+} ions, as well as Cr^{3+} ions, have an electronic configuration of $3d^3$. The emission bands on both sides of the narrow intense maximum at 653 nm correspond to the anti-Stokes and Stokes sidebands, which are caused by oscillations of $3d^3$ electrons when the activator ions are located in the octahedral positions of the structure.

3. Materials and Methods

3.1. Samples Preparation

A combined sol–gel solution combustion method was used to synthesize a series of nanocrystalline SrAl_4O_7 powders doped with Cr^{3+} and Mn^{4+} ions. In this method, the following substances were used: $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or SrCO_3 (Sfera Sim, Lviv, Ukraine), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, Haverhill, MA, USA), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, Haverhill, MA, USA), and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sfera Sim, Lviv, Ukraine) as metal sources, citric acid $\text{C}_6\text{H}_8\text{O}_7$ (CA) and ethylene glycol (EG) (Sfera Sim, Lviv, Ukraine) as a chelating agent and fuel. A 25% NH_4OH (Sfera Sim, Lviv, Ukraine) solution was used to achieve the desired pH of the solutions. All substances were analytical grade of purity. Molar ratio of sum of metal cations, CA and EG was kept as follow: $n(\Sigma(\text{Me}^{n+})) : n(\text{CA}) : n(\text{EG}) = 1:2:8$. The concentration of Cr or Mn dopant varied from 0.05 to 5.0 at.%. The amounts of reagents were calculated according to their nominal composition, considering the desired mass of final products (typically from 0.75 to 2.0 g) and mixed in ceramic vessels with a volume of up to 200 mL. Obtained mixtures of components with a minimal amount of distilled water were placed in a preheated to 80–90 °C oven for 30–60 min to ensure complete dissolution of the components, followed by neutralization of the resulting solutions to pH 7 in the case of Cr-doped series or by achieving pH 9.5 for Mn-doped samples. After correcting the pH, the solutions were placed again in an oven heated to 125–150 °C for 2–4 h to remove residual water and ensure completeness of the esterification process. Visually, the completion of the process was monitored by the appearance of the gel, which from transparent began to acquire a brownish-black color. After finishing of gelation process, the plates with the formed gel were cooled and placed in a muffle furnace, preheated to the temperature of 800 °C necessary to initiate the processes of components decomposition and spontaneous combustion of the mixture. Due to the rapid thermal decomposition and self-combustion of the components of the reaction mixture, the formation of a bulky foamy product (Figure 11, inset) was observed.

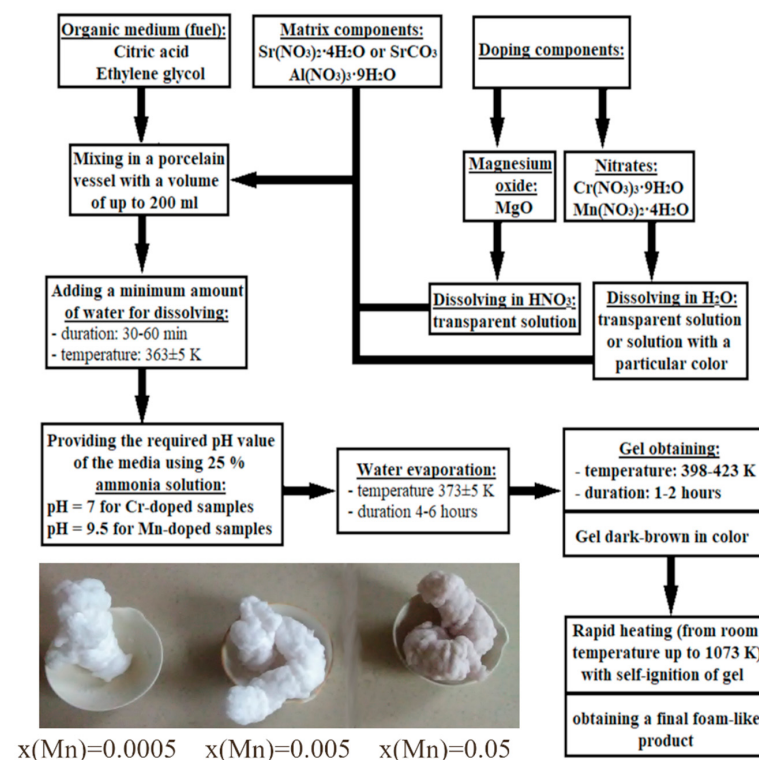


Figure 11. Technological scheme of sol–gel combustion synthesis of Cr^{3+} and Mn^{4+} doped SrAl_4O_7 . Inset shows self-combustion products of precursors for $\text{SrAl}_4\text{O}_7:\text{xMn}$ materials with $\text{x} = 0.0005$, 0.005 , and 0.05 .

After furnace cooling, the obtained foamy products were ground in a porcelain mortar and subsequently annealed at the temperatures from 900 to 1400 °C to study the effect of heat treatment temperature on the phase composition, crystal structure, morphology, and luminescent characteristics of the materials prepared.

3.2. Physical–Chemical Characterization

The evolution of phase composition, crystal structure, and microstructural parameters of nanophosphors within the synthesis process and further thermal treatment was investigated by X-ray powder diffraction using a modified DRON-3M powder diffractometer (Burevesnik, Leningrad, former USSR). XRD patterns were collected by using Cu K α -radiation ($\lambda = 1.54456$ Å) in the 2θ range of 10–110° with the step of 0.02°. Crystal structure parameters of SrAl₄O₇:Cr³⁺ and SrAl₄O₇:Mn⁴⁺ materials were derived from experimental XRD data by full profile Rietveld refinement by using WinCSD program package [23]. The same method was used for the evaluation of average crystallite sizes and microstrain values from an analysis of angular dependence of Bragg's diffraction maxima. For a correction on instrumental peak broadening LaB₆ external standard was used. Scanning electron microscopy (Tescan Vega 3 LMU, Brno, Czech Republic) and X-ray spectral analysis (Aztec ONE with X-MaxN 20 detector, Oxford Instruments, Abingdon, UK) were used for spot-check examination of the morphology of the powders, chemical composition, and homogeneity of cation distribution in the materials synthesized.

Photoluminescence and photoluminescence excitation spectra were measured using a Horiba/Jobin-Yvon Fluorolog-3 spectrofluorometer (HORIBA Instruments, Edison, NJ, USA) with a 450 W continuous spectrum xenon lamp for excitation and optical detection with a Hamamatsu R928P photomultiplier operating in the photon counting mode. The measured photoluminescence excitation spectra were corrected with the xenon lamp emission spectrum. The photoluminescence spectra were corrected for the spectral response of the spectrometer system used.

4. Conclusions

Series of Cr³⁺ and Mn⁴⁺ doped strontium dialuminate SrAl₄O₇ nanophosphors with an average crystallite size of 65–115 nm were synthesized for the first time by the combined sol–gel solution combustion method. Precise structural characterization of the SrAl₄O₇:Cr³⁺ and SrAl₄O₇:Mn⁴⁺ materials with different dopant concentrations heat-treated at 1100 °C and 1200 °C revealed monoclinic grossite-type structure.

After visible and UV excitations, SrAl₄O₇ phosphors exhibit an intense deep-red and NIR emission. This strong red emission is peaked at about 695 nm in Cr³⁺ and at about 653 nm in Mn⁴⁺ doped phosphors is due to ²E→⁴A₂ transitions. This luminescence occurs from distorted octahedral Cr³⁺/Mn⁴⁺ sites, which arise due to substitution for Sr sites in the strontium aluminate. The latter suggestion was made based on an analysis of peculiarities of the interatomic distances distribution in the host SrAl₄O₇ material and the related MAl₄O₇ and MGa₄O₇ compounds.

It was found that the optimal concentration of impurities Cr³⁺ and Mn⁴⁺ is close to 0.01 and 0.0005, respectively. Despite the fact that the crystallinity of the structure is formed after annealing of samples at 1000 °C, the maximum of manganese and chromium ions photoluminescence intensity is observed only after annealing at 1400 °C, which may indicate the easier formation of octahedra around these transition ions at higher temperatures.

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