

SYNTHESIS AND LUMINESCENT PROPERTIES OF MULTIPHASE GREEN PHOSPHOR BASED ON STRONTIUM THIOGALLATE

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Abstract

The detailed XRD analysis, EDS, Raman spectroscopy and PL study were achieved in order to enlarge the understanding of the radiative processes in multiphase green phosphors, based on strontium thiogallate. These phosphors were synthesized by solid state reaction at 900–1000°C with carbon as a reduction atmosphere. The crystal field splitting, Stokes shift, Red shift, and centroidal shift were estimated and they are in a good agreement with mathematical calculations. Our study confirms that proposed multiphase green phosphor based on strontium thiogallate is a good candidate for solid state lighting and display devices with higher intensity and better chromaticity coordinates in comparison with known commercial phosphors.

1. Introduction

For the purpose of developing energy-efficient white light sources, we need to produce highly efficient yellow, green, and red phosphors, which can absorb excitation energy from blue LEDs and generate emissions. Many efforts have focused on improving the performance of thiogallate luminescent materials. Luminescent properties of Barium, Strontium, and Calcium thiogallates doped with Europium activator have been investigated since 1970 [1-7]. Recently a new wave of intensive study of these materials has begun because they are very attractive photoluminescent, electroluminescent, and cathodoluminescent materials for the visible spectral range [8-15]. Since the absorption of the $4f \rightarrow 5d$ transitions of the doping ions extends to the visible spectrum, they are appropriate phosphors for excitation by near UV or blue emitting diodes for solid state lighting (SSL) applications [16]. While these practical applications have been successfully achieved, there are still several aspects regarding the general ways to provide advanced light-emitting materials with improved properties. Among them there are the searching of novel chemical composition and improving of the existing phosphors including the chemical synthesis. An atmosphere of synthesis plays an important role. Peters and Baglio synthesized thiogallate phosphors under H_2S stream by $CaCO_3$, Ga_2O_3 , and Eu_2O_3 [1]. In other works of preparing thiogallates this gas was also used [10, 11]. Since H_2S is very toxic to human organism, some interesting results were achieved recently without toxic gas using a reduction atmosphere of 5% of H_2 and 95% of N_2 [12]. Some other attempts were launched to prepare thiogallates without H_2S . For example, F. Aidaev made the synthesis at low temperature from NH_4CNS , but this process has long reaction times and it is complicated [13]. Nevertheless, the development of synthesis methods to improve the luminescent properties of thiogallate materials remains actual.

In this paper the luminescence of the thiogallate phosphors is revisited. The results of producing a new green multiphase thiogallate phosphor $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ with improved luminescence properties are presented in this contribution. However, to our knowledge, only the transition metal ion –doped magnesium gallate spinels were investigated. To date, Eu^{2+} –doped magnesium gallate spinels were not reported. A systematic investigation at the same preparation and investigation conditions of single and multiphase gallates has been performed in this study using carbon as a reduction atmosphere. The radiative mechanisms of thiogallates are not completely understood and their fundamental knowledge needs to be enlarged. In this paper, excitation and emission photoluminescence spectra with Raman spectroscopy and X-ray diffraction patterns were analyzed to estimate the nephelauxetic effect, crystal field splitting, and Stokes shift in dependence on activator surrounding in the different host lattices. These data will be useful to evaluate the quality of the powders prepared for different electronic devices.

2. Samples and experimental procedure

2.1. Synthesis

Polycrystalline single phase $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor and multiphase $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ samples were synthesized by solid-state reaction. For SrGa_2S_4 starting sulfide powders SrS and Ga_2S_3 mixed in stoichiometric composition and annealed at 900 -1000°C with a carbon reduction atmosphere for 4 h. For multiphase samples we used the same raw materials with addition amounts of MgS and $\text{Mg}(\text{NO}_3)_2$ at the same synthesis conditions. The doping ions in both cases were introduced in the form of EuS . This preparation method is a little different from that reported by Peters et al. [1] as well as above-mentioned [11-13], because we did not use the toxic H_2S stream in synthesis process. The method presented here provides powder samples with good crystalline properties as shown by X-ray diffraction measurements. Powder samples with 6 mol % Eu^{2+} concentration were prepared and studied. The thiogallate single and multiphase samples exhibit a deep green colors. Phosphor samples were characterized by crystalline structure and luminescence properties.

2.2. Sample characterization

2.2.1. X-ray diffraction measurement – The crystal structures of the prepared samples were determined by X-ray diffraction measurement using goniometer (PANalytical, X'Pert pro MPD with $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. The scan speed was 3 seconds per step (0.02° step – 2θ) and covered the range between 10° and 90° .

2.2.2. EDS (Energy Dispersive Spectroscopy) and EPMA (Electron probe micro analysis) – Qualitative and Quantitative non-destructive elemental analysis was performed with EPMA machine, model SX-100 (the electron acceleration was 20 kV, beam current 10 nA, and the diameter of electronic beam was 50 μm , DT:0.3 S). It is the most precise and accurate micro-analysis technique available and all elements from Beryllium to Uranium can be analyzed.

2.2.3. Raman spectroscopy - Raman scattering spectra of SrGa_2S_4 , and multiphase prepared phosphors were measured by a Renishaw 3000 spectrometer with a He-Ne laser (excitation wavelength of $\lambda = 633 \text{ nm}$ and $\lambda = 785 \text{ nm}$) and a photomultiplier counter at room temperature in back scattering configuration. The spectral resolution of spectrometer is about 4 cm^{-1} at 633 nm and 1 cm^{-1} at 785 nm.

2.2.4. Photoluminescence (PL) measurement – Optical spectroscopy and PL characteristics were estimated on the basis of emission and excitation spectra registered at room tempera-

ture (Xe 500 W lamp) with DARSA PRO 5100 PL System (Professional Scientific Instrument Co, Korea). Excitation spectra were corrected for the energy distribution of the Xe-lamp. The excitation was performed with a 460 nm radiation, which is usually used in blue LED.

2.2.5. *Morphology and size measurement* – Particle sizes and morphologies of the investigated phosphors were determined by scanning electron microscope (SEM) Hitachi-S-3000N. To control the particle size and to find the size distribution the Laser diffraction was carried out using HELOS particle size analysis system.

3. Results and discussion

3.1. XRD

Figure 1 shows the X-ray diffraction patterns of the multiphase phosphor on the basis of Strontium thiogallate powder fired at 1000°C (1). Their positions are in a good agreement with fitting (2) and ICSD (ICSD: Inorganic Crystallographic Structure Database) data (3-6).

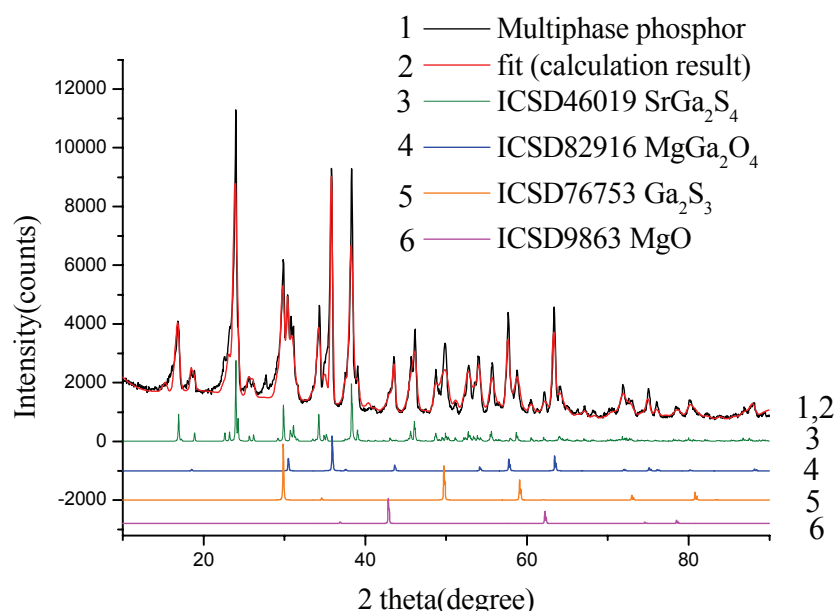


Fig. 1. The X-ray diffraction patterns of multiphase phosphor on the basis of Strontium thiogallate and its fitting in comparison with reference ICSD data.

Solid black curve (1) in Fig. 1 is the measured data and red curve (2) means the calculation result of Rietveld analysis which was developed by H. M. Rietveld in 1967 for structure profile refinement of X-ray powder diffraction data [17]. The Rietveld calculation uses the least squares method to get all these crystallographic information by comparing model profile and X-ray or neutron curves. The peak positions of X-ray diffraction curve are related to the unit cell lattice constants of the crystal structure and the peak intensities are affected by atomic position, atom species, atomic occupancy, and thermal parameters. The absence of peaks explains the crystallographic symmetry. In addition, crystalline size and strain induce peak broadening in XRD pattern. All these important information could be obtained from Rietveld analysis and, therefore, we applied this analysis for X-ray pattern. In case of multiphase structures, quantitative phase analysis is available by using Rietveld method. The detailed crystallographic information from Rietveld analysis is listed in Tables 1-3.

Table 1. Crystallographic data for single phase SrGa₂S₄ and multiphase phosphor.

Sample	Phase	Wt. %	Structure	Reference	Calculated structure		
					a (Å)	b(Å)	c(Å)
SrGa ₂ S ₄	SrGa ₂ S ₄	100	orthorhombic	ICSD46019	20.855	20.511	12.231
Multiphase phosphor	SrGa ₂ S ₄	62.2	orthorhombic	ICSD46019	20.860	20.488	12.219
	MgGa ₂ O ₄	27.8	Cubic Fd-3m	ICSD82916	8.301		
	Ga ₂ S ₃	6.9	Cubic F4-3m	ICSD76753	5.195		
	MgO	2.3	Cubic Fm-3m	ICSD9863	4.211		

First of all, we did Rietveld refinement to check the crystallographic structure of the samples. Figure 1 shows that the structure of our synthesized samples is similar to the structure of SrGa₂S₄ orthorhombic phase ICSD-46019 pattern (3). Thereby, we could confirm that in realized synthesis conditions we obtained not only one single phase of SrGa₂S₄, but also some other different phases. The most important of them is MgGa₂O₄, because when we introduce an activator Eu²⁺, it substitutes Sr and Mg in these two phases. The unit cell parameters of ICSD-46019 (SrGa₂S₄) are a=20.932Å, b=20.549Å, c=12.227Å and they are very similar to our sample as it is seen from Table 1. A slight difference in a cell parameter can be explained by a slight difference in atomic positions. The positions of Sr atoms were the same to the reference, but the positions of Ga atoms and S atoms were a little different. The different atomic positions affected the unit cell parameter and the distance of Sr atoms and S atoms. Crystallographic data for synthesized SrGa₂S₄ and multiphase {SrGa₂S₄ + MgGa₂O₄} sample are given in Tables 2-4.

Table 2. Crystallographic data for different ion positions in synthesized SrGa₂S₄.

wRp=0.12	orthorhombic		x	y	z	F	Multiple factor
Rp=0.095	a=20.8558(19)	Sr1	0.125	0.125	0.125	1	8
R(F ²)=0.174	b=20.5115(22)	Sr2	0.125	0.125	0.625	1	8
ICSD-46019	c=12.2138(12)	Sr3	0.8726	0.125	0.125	1	16
SrGa ₂ S ₄ Single phase		Ga1	-0.0033(8)	0.8040(4)	0.1633(7)	1.05(2)	32
	α=90	Ga2	-0.0052(8)	0.2370(4)	0.3752(8)	1.16(2)	32
	β=90	S1	0.1672(10)	0.2472(13)	0.997(2)	1.15(4)	32
	γ=90	S2	0.1725(14)	0.5078(17)	0.262(3)	0.83(4)	32
	F d d d	S3	0.999(2)	0.3438(8)	0.0089(15)	1.00(4)	32
		S4	-0.006(3)	0.4204(10)	0.2701(16)	1.00(3)	32

From the occupation factor F one can see that when $F=1$ or nearby, it means the site is occupied by an atom. When $F<1$ (S2 position in synthesized phosphor) the site could be substituted by a lighter atoms, in our case it maybe oxygen, for example.

The thiogallate compounds of the type SrGa₂S₄ belong to the orthorhombic crystal class with the space group D_{2h}^{24} ($Fddd$) [18] and MgGa₂O₄ to cubic structure with the space group $O_h^7 Fd3m$. There are 32 formula-mass units per unit cell ($z = 32$) and, therefore, 56 atoms in a primitive cell: 8 Sr, 16 Ga, 32 S. According to B. Eisenmann et al. [18], the Sr atoms occupy square anti-prismatic sites formed by eight sulfur (symmetry group D_{4d}) forming Sr(S)₈ units with C₂ and D₂ symmetry. In the SrGa₂S₄:Eu²⁺ compound, the cation ions are substituted by the Eu²⁺ ions. From XRD data (Table 2) they are situated in three slightly dif-

ferent sites: 8a, 8b, and 16c, whose multiplicity is not equal and exhibits a 1:1:2 relative ratio dictated by symmetry. Gallium atoms are tetrahedrally coordinated to four sulfur atoms forming $\text{Ga}(\text{S})_4$ units (symmetry group T_d) and the sulfur atoms are at the centre of deformed Sr_2Ga_2 tetrahedrons forming $(\text{S})\text{Sr}_2\text{Ga}_2$ units. The assembly of the $\text{Sr}(\text{S})_8$ anti-prismatic units with common edges forms chains parallel to the a axis of the unit cell. Each chain is linked to four chains by corner sharing. Gallium atoms are located between two consecutive chains. The unit cell consists of four layers along the c axis. Figures in Table 3 and Fig. 2 illustrate the symmetry of the S and Sr environments in orthorhombic and cubic crystals. The MgGa_2O_4 crystal has a spinel structure with a partially inverted nature, having a unit cell belonging to the cubic space group $Fd3m$. In this compound, the population of Mg^{2+} ions in tetrahedral and octahedral sites is 0.16 and 0.84, respectively. The site symmetry of each atom can be obtained from the correlation Tables [19].

Table 3. Crystal structure of strontium surrounding in SrGa_2S_4 and short distance Sr-S in comparison with reference data.

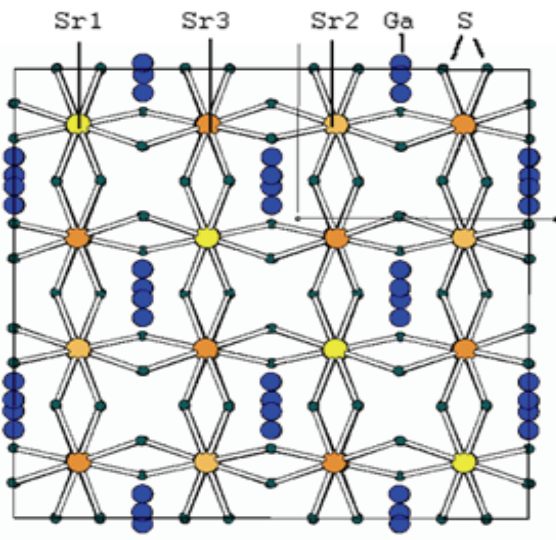
 Crystal structure of SrGa_2S_4	Short Distance	SrGa_2S_4 (Å)	ICSD _{ref} (Å)
	Sr(1)-S(6)	3.082	3.105
	Sr(1)-S(9)	2.944	3.134
	Sr(2)-S(7)	3.092	3.110
	Sr(2)-S(8)	3.126	3.122
	Sr(3)-S(6)	3.155	3.153
	Sr(3)-S(7)	3.195	3.117
	Sr(3)-S(8)	3.119	3.098
	Sr(3)-S(9)	3.201	3.102

Table 4. Crystallographic data for different ion positions in synthesized multiphase phosphor (MgGa_2O_4 phase) and short distance Mg-O in comparison with reference data.

atoms	Atomic position MgGa_2O_4			Short distance	MgGa_2O_4 (Å)	ICSD _{ref} (Å)
	a	b	c			
Mg1	0.125	0.25	0.125	Mg(1)-O	1.832	1.829
Ga1	0.125	0.125	0.125			
Ga2	0.5	0.5	0.5			
Mg2	0.5	0.5	0.5	Mg(2)-O	2.055	2.052
O	0.2573	0.2573	0.2573			

According to our data from Table 3, the shortest distance between Sr and S can be estimated as 3.20 Å, which is in a good agreement with reference ICSD data. (The measurements were made for all lengths less than 5 Å). For MgGa_2O_4 this length Mg-O is shorter and it was found as 1.94 Å (Table 4).

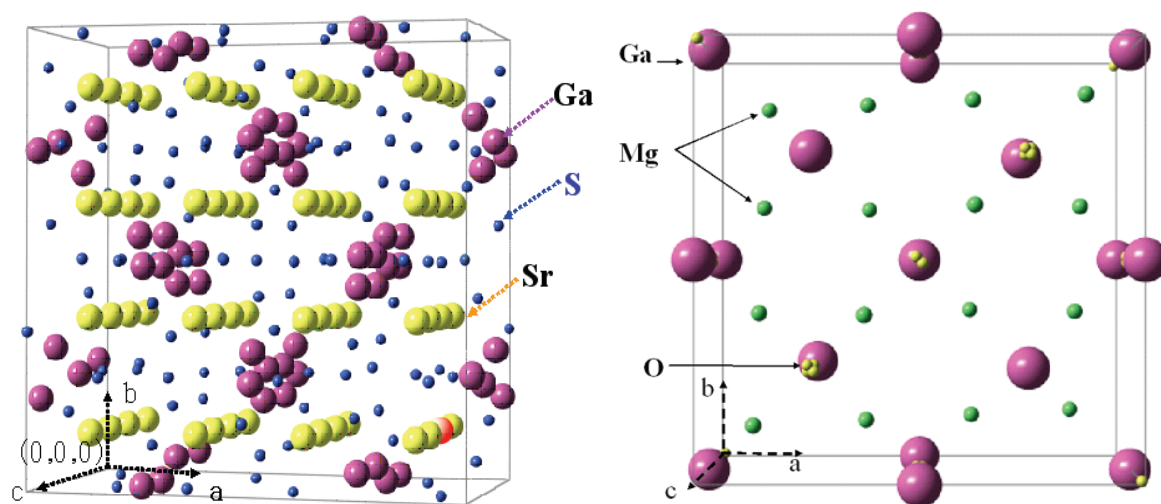


Fig. 2. Crystal structure of SrGa_2S_4 (left) and MgGa_2O_4 (right) and different ion positions in these unit cells.

3.3. EDS and EPMA

We carried out compositional analysis by energy dispersive X-ray spectrometry (EDS) by means a JEOL 2010 CX electron microscope. Energy dispersive spectra from one single phase SrGa_2S_4 phosphor and multiphase $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$ sample are shown in Fig. 3.

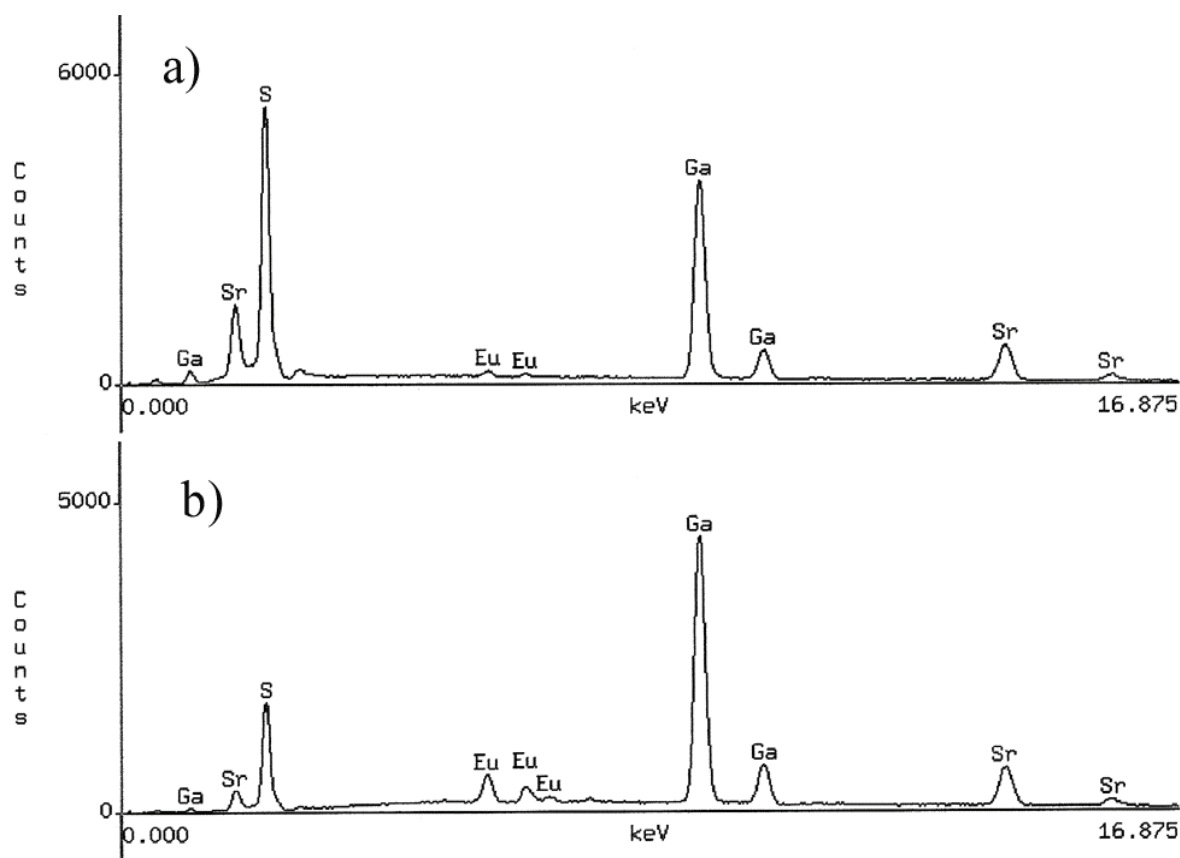


Fig. 3. EDS patterns corresponding to SrGa_2S_4 (a) and multiphase $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$ sample (b).

The distribution of elements could be analyzed from Table 5.

Table 5. Compositional EDS analysis.

Element	Atomic %		Weight %		Wt. % Error	
	Single (a)	Multi (b)	Single (a)	Multi (b)	Single (a)	Multi (b)
Sr - La	6.79	2.29	9.89	2.95	0.16	0.10
S - K	29.85	11.96	15.90	5.64	0.11	0.07
Eu La	0.59	2.89	1.50	6.45	0.17	0.22
Ga - K	62.76	82.86	72.71	84.96	0.59	0.65
Total	100.00	100.00	100.00	100.00		

It is clearly seen from Fig. 3 and Table 5 that at the initial 6 mol % Eu^{2+} concentration in both samples the activator incorporation degree in two samples differs about 4 times. This parameter is very important because instead of initial activator concentration the activator incorporation degree is responsible for luminescence properties [20]. Unfortunately, EDS analysis could not detect the light elements like magnesium and oxygen, therefore, the compositions of the samples were also examined by electron probe microanalysis.

The EPMA technique allowed us to use WDS (wavelength dispersive spectroscopy) and the sample composition can be easily identified. Magnesium and oxygen analyzed by electron probe microanalyses were detected in the multiphase phosphor and shown in Fig. 4. The quantitative data were found in a good agreement with EDS and XRD data.

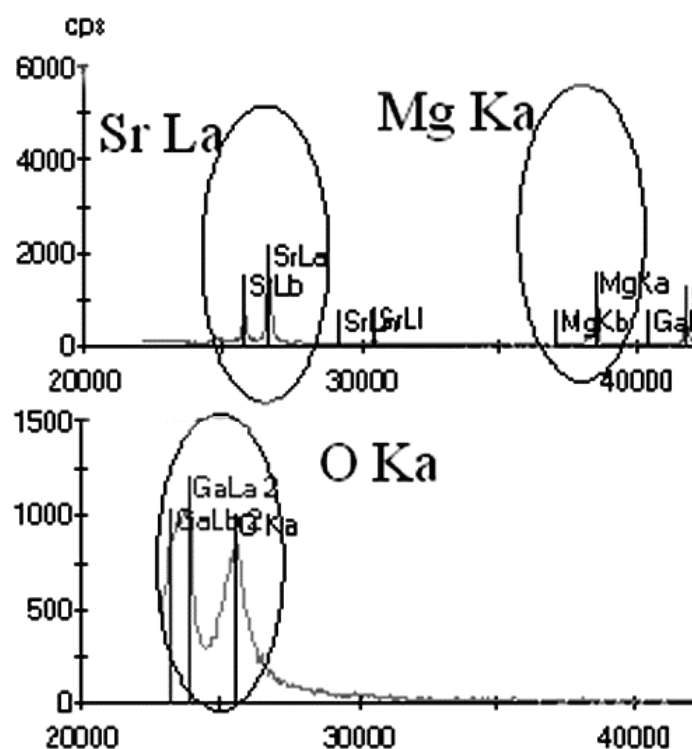


Fig. 4. Fragment of EPMA analysis of light elements in $\{\text{SrGa}_2\text{S}_4+\text{MgGa}_2\text{O}_4\}$.

3.2. Raman spectroscopy

The Stokes spectra of the polycrystalline SrGa_2S_4 and $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$ are given from 50 cm^{-1} to 500 cm^{-1} in Fig. 5.

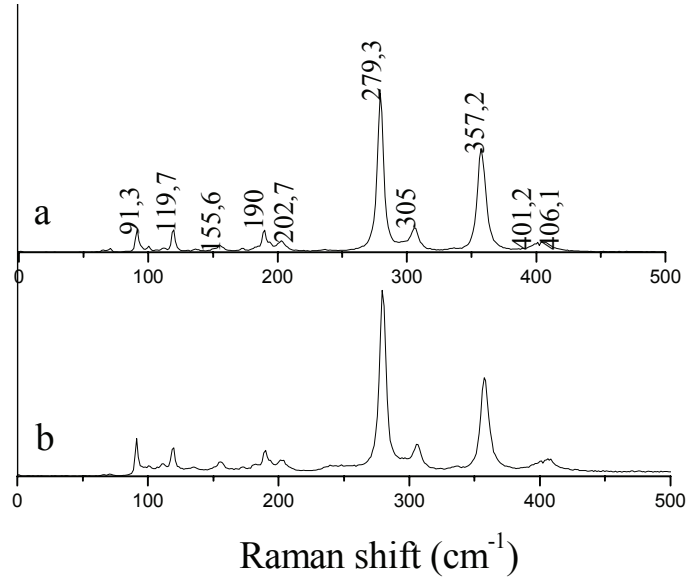


Fig. 5. Raman spectra of SrGa_2S_4 (a) and $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$ (b), excited with the 785 nm laser line.

Stokes spectra for both samples are very similar and consist of 19 vibration lines positioned between 68 cm^{-1} and 408 cm^{-1} . The factor-group method predicts that the total number of Raman-active phonons is 84 for this structure [21]. The reduced numbers of modes in the Raman spectra are in favour of a molecular model to describe the vibrations of these compounds [22, 23]. Two dominant peaks at 279 cm^{-1} (34.5 meV) and at 357 cm^{-1} (44.2 meV) for SrGa_2S_4 and $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$ are registered. One can see only one distinction from our data and Fig. 5. The ratio of these peaks is 1.88 for SrGa_2S_4 and 1.5 for $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$. All other peak intensities and peak positions coincide very well. These Raman spectra are in a good agreement with those reported in the literature for SrGa_2S_4 [24, 25] and could be used for the fitting of emission bands.

3.4. Excitation and emission spectra

The emission and excitation spectra of investigated compounds doped with 6 mol % of Eu^{2+} at 300 K are presented in Fig. 6. For both samples the emission spectra under excitation at 460 nm consist of a broad band in the visible range. The maximum wavelength of the band for multiphase phosphor (2) is shifted to 539 nm in comparison with 535 nm for SrGa_2S_4 (1). Full Widths at Half Maximum (FWHM) are equal, correspondingly, to 44 nm (2) and 49 nm (1). No additional bands due to the emission of Eu^{2+} in investigated samples are observed.

The emission is ascribed to the dipole-allowed transition from the lower $4f^6(^7F)5d$ state to the $4f^7(^8S_{7/2})$ fundamental state of the Eu^{2+} ions [1]. The single configuration coordinate model was used to fit the emission band of considered phosphors.

In first approximation, it is supposed that only the fundamental vibration level ($m=0$) of the excited electronic state is occupied. Using this hypothesis, the intensity of the vibronic transition from the fundamental vibration level of the emitting electronic state to the n vibration level of the ground electronic state, i.e., the $m=0 \rightarrow n$ transition, is proportional to the expression [26]

$$I \sim \exp(-S) \cdot S^n / n!$$

where S is the Huang-Rhys parameter and measures the interaction between the luminescent centre and the vibrating lattice. The energy gap between two vibronic peaks is equal to the

quantity $h\nu_g$, the mean lattice phonon energy for the $4f^7(^8S_{7/2})$ ground electronic state. The best fits of the emission band for $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ were obtained with $S=4$ and $h\nu_g=34.5$ meV (Fig. 7).

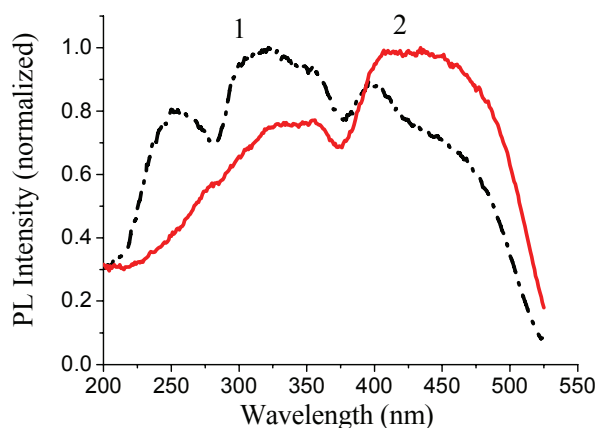


Fig. 6a. Excitation spectra of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (1) and $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ (2).

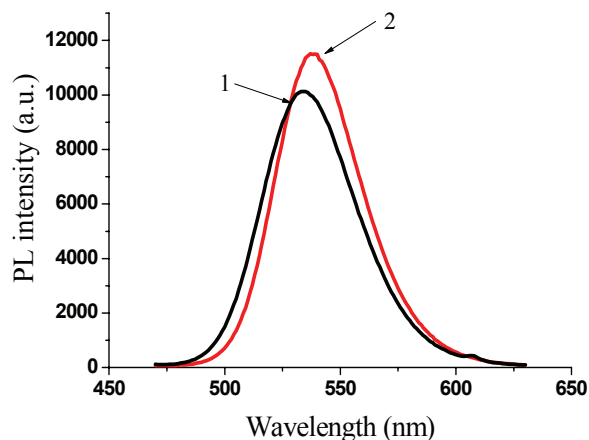


Fig. 6b. Emission spectra of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (1) and $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ (2) excited by 460 nm.

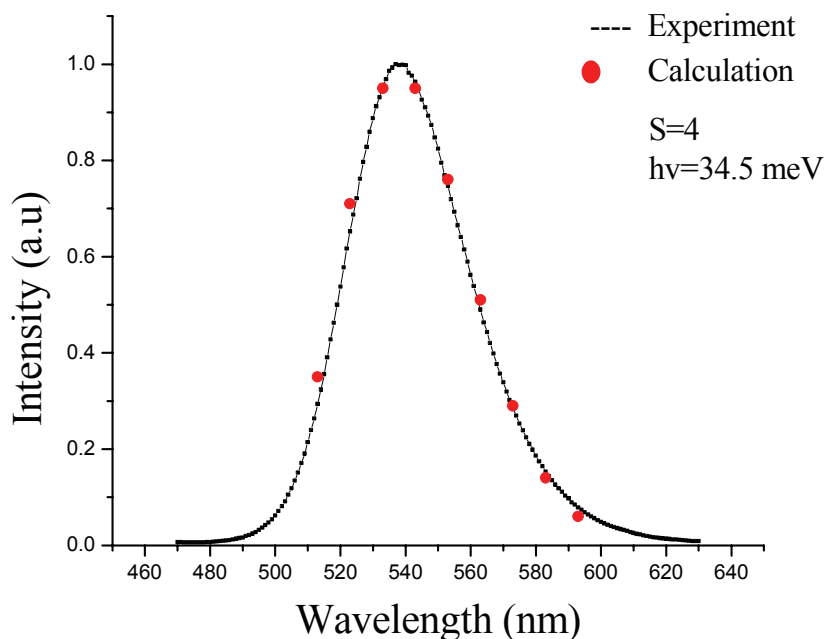


Fig. 7. Experimental (broken curve) and calculated (circles) emission spectrum of the $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ (6 mol %) at 300 K under excitation at 460 nm.

The values of Huang-Rhys parameter correspond to a strong electron-phonon coupling and can be linked to the high symmetry of the emission bands for both samples. These values are in a good agreement with those presented in literature for strontium thiogallates [11].

By supposing that the ground state parabola of the configuration coordinate model presents the same curvature as the excited state parabola, i.e., the phonon energy is the same for the $4f^7(^8S_{7/2})$ ground state as for the $4f^6(^7F)5d$ excited state ($h\nu_g = h\nu_e = h\nu$), we can determinate the Stokes shift (ΔS). ΔS is related to the offset of the parabolas in the configuration coordinate diagram and ΔS is equal to $(2S-1)h\nu$. Calculated Stokes shift for multiphase $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$ powder is $\Delta S=0.24$ eV (1935 cm^{-1}) and these data are similar to single phase SrGa_2S_4 .

The excitation and emission spectra of multiphase phosphor $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$, as well as its detailed analysis for 539 nm wavelength, are presented in Fig. 8.

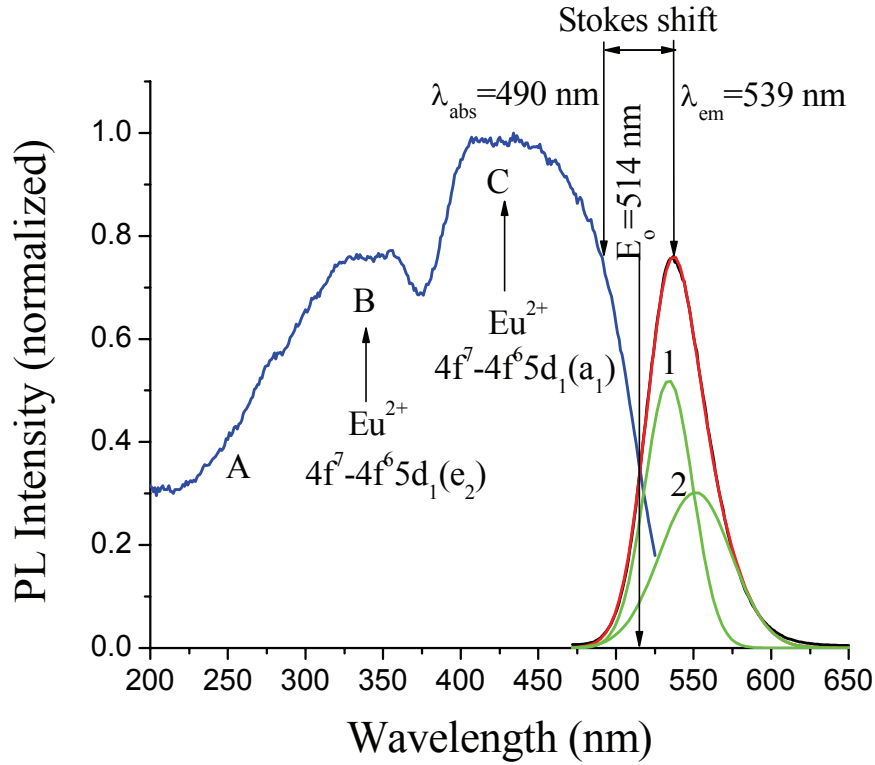


Fig. 8. Excitation and emission spectra of multiphase phosphor $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ at 300 K.

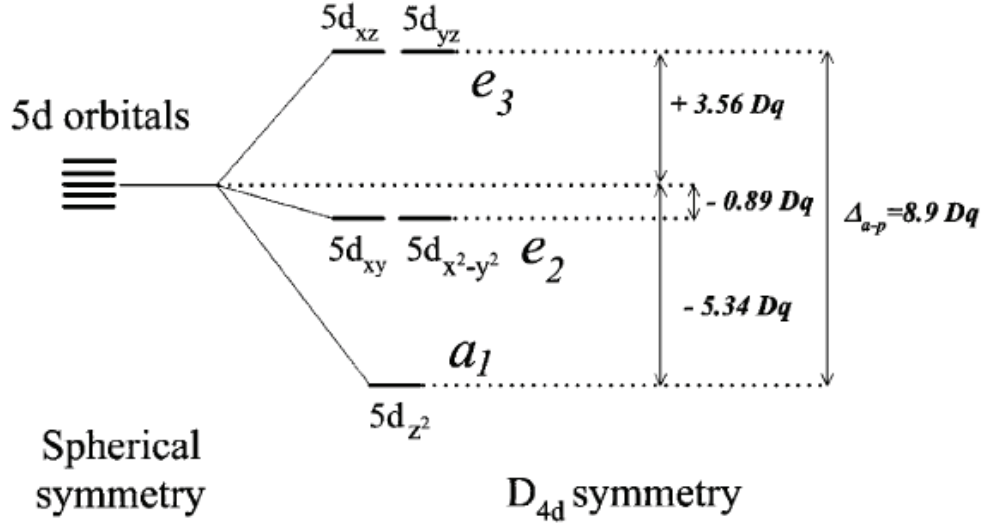


Fig. 9. Splitting of the five 5d orbitals in a square antiprismatic (D_{4d}) symmetry.

Figure 8 shows that the excitation spectrum is composed of three large bands in the UV–visible range:

Feebly marked at room temperature excitation band (A) is ascribed to the transitions between the valence band and the conduction band of the host matrix.

The two excitation bands (B) and (C) are ascribed to the $4f^7(^8S_{7/2})-4f^6(^7F)5d$ transitions in Eu^{2+} electronic levels.

This excitation spectrum is similar to spectrum of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ described by C. Chartier et al. [11]. It is not surprising because the emission spectrum can be fitted in a good approximation by two Gaussian curves (1 and 2) indicating dominant $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ emission peaking at 535 nm and $\text{MgGa}_2\text{O}_4:\text{Eu}^{2+}$ emission at 553 nm in Fig. 8. The observed emission band (Fig. 8, on the right) can be the superposition of these bands. In our multi phase compound, the Sr^{2+} ions, as well as Mg^{2+} are substituted by the Eu^{2+} ions. They occupy three different sites with C_2 and D_2 symmetry [5]. Since their shapes have minor differences, the emission bands of Eu^{2+} in the three available sites are expected to lie near each other. In first approximation, they are located at the centre of square anti-prisms formed by the 8 S^{2-} anions (Tables 2 and 3). In this D_{4d} symmetry, the 5d orbitals are split in three levels [11] as illustrated in Fig. 9.

The band (C) is ascribed to the $4f^7 (^8S_{7/2}) \rightarrow 4f^6 (^7F)5d (a_1)$ transitions and the band (B) to the $4f^7 (^8S_{7/2}) \rightarrow 4f^6 (^7F)5d (e_2)$ transitions. By evaluating the energy gap between the (B) and (C) bands to 8000 cm^{-1} (1 eV), the crystal field strength, $\Delta_{a-p}=8.9Dq$, can be estimated at about $16,000 \text{ cm}^{-1}$ (2 eV).

An almost mirror-image relationship seems to hold between the emission and the excitation spectra in the energy region between the two maxima (Fig. 8). This relation is characteristic of a phonon-broadened emission and confirms the hypothesis we have made previously; it suggests that the mean phonon energy $h\nu$ is the same for the $4f^7 (^8S_{7/2})$ ground state as for the $4f^6 (^7F)5d (a_1)$ excited state. We can determine the energy of the zero-phonon line E_0 at the intersection of the emission and excitation spectra. From Fig. 8, we found $E_0 = 2.41 \text{ eV}$, which corresponds to a wavelength of 514 nm (comparable with that given by Eichenauer et al. [27] and Chartier et al. [11]). Unfortunately, at room temperature we cannot distinguish the fine structure due to the spin-orbit coupling in the $4f^6$ configuration leading to the splitting of the ^7F levels in seven levels: ^7F_J with $J = 0-6$. The energy E_{abs} of the $f \rightarrow d$ transition from the ground state to the lowest level of the $4f^6 5d (a_1)$, corresponds to the $^7F_0$ level. Since this level is not resolved, we can only give an estimation of E_{abs} . By using the mirror-image relationship between the emission and the excitation spectra, we have found $E_{\text{abs}} = 2.53 \text{ eV}$ (490 nm). The energy of the transition from the $4f^7 (^8S_{7/2})$ ground state to the $4f^6 (^7F_0)5d$ excited state is lowered from the free ion value when the Eu^{2+} ion is brought into a crystal environment. The energy of the $f \rightarrow d$ absorption and of the $d \rightarrow f$ emission can be written according to the formalism of P.Dorenbos [28]

$$E_{\text{abs}} = E_{\text{free}} - D \text{ and } E_{\text{em}} = E_{\text{free}} - D - \Delta S,$$

where E_{free} is the energy difference between the lowest $4f^7$ level and the $4f^6 (^7F_0)5d$ level for the free or gaseous ion, D is the energy lowering also called redshift and ΔS the Stokes shift. The redshift energy depends on the crystal environment and can be represented by a term, called the centroid shift or nephelauxetic (covalence) effect, concerning the shift of the average of the five 5d levels relative to the free ion value, and a second term associated to the crystal field splitting. For Eu^{2+} , E_{free} is 4.19 eV [29]. The emission and excitation spectra provide the values of absorption and emission energies, $E_{\text{abs}} = 2.53 \text{ eV}$ and $E_{\text{em}} = 2.30 \text{ eV}$. The Stokes shift is then $\Delta S = E_{\text{abs}} - E_{\text{em}} = 0.23 \text{ eV}$ (1900 cm^{-1}) and the redshift $D = E_{\text{free}} - E_{\text{abs}} = 1.66 \text{ eV}$ ($13\,400 \text{ cm}^{-1}$). The value of the Stokes shift is comparable with this previously obtained by fitting the band emission (Fig. 7) 0.24 eV (1935 cm^{-1}).

The lower redshift in $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ ($D=13000 \text{ cm}^{-1}$) compared with $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$, (13400 cm^{-1}) is mainly explained by the lower nephelauxetic effect or centroid shift. This shift ϵ_c is calculated and schematically shown in Fig. 10.

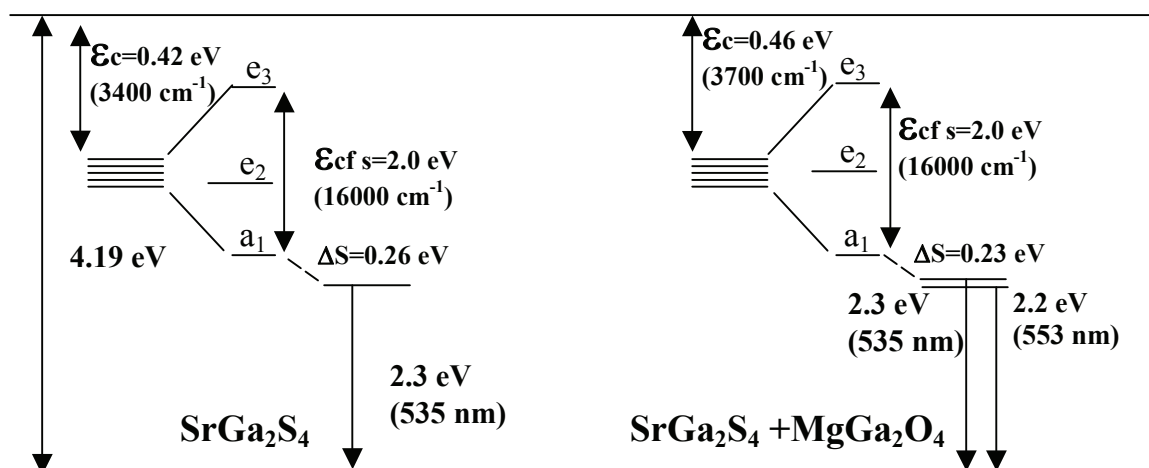


Fig. 10. Nephelauxetic effect in polycrystalline single phase $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor and multiphase $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ sample.

The Sr element is less electronegative than the Mg element and the cation-anion lengths Sr-S in strontium thiogallate are larger (3.21 Å) than Mg-O in magnesium digallium oxide (2.05 Å). The Sr-S bonds are then less covalent than the Mg-O ones and the nephelauxetic effect is weaker in SrGa_2S_4 than in MgGa_2O_4 . Stronger nephelauxetic effect (or centroid shift) replaces the peak wavelength from 535 nm to 539 nm that is very important for improvement the color rendering index.

Considering the proposed mechanism of Eu^{2+} luminescence from multiphase phosphor (superposition of two bands from $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ and $\text{MgGa}_2\text{O}_4:\text{Eu}^{2+}$), there are two near situated lines with energies 2.32 eV (535 nm) and 2.24 eV (553 nm), corresponding to different Eu sites in the two different phases (Fig. 10).

One of the important problems for practical application of thiogallates in LED, displays, and other devices is radiant efficiency and stability. Usually these materials are very bright and have very high efficiency, but sometimes their stability toward hydrolysis and temperature is not sufficient. Therefore, we propose to use the multiphase ternary compounds with oxide phase because they are much more stable than ternary sulfides.

Summarized luminescence and crystallographic data for investigated thiogallates, doped with 6 mol % Eu^{2+} concentration are given in Table 7.

Table 7. Luminescence data for SrGa_2S_4 and $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$ doped with 6 mol % Eu^{2+} .

Formula	$\lambda(\text{abs})$ nm/ (eV)	E_0 nm/ (eV)	$\lambda(\text{em})$ nm/ (eV)	FWHM (nm)	S	h ν (meV)	ΔS cm ⁻¹ / (eV)	D cm ⁻¹ / (eV)	$\epsilon(\text{cfs})$ cm ⁻¹ / (eV)	$\epsilon(\text{centr})$ cm ⁻¹ / (eV)
SrGa_2S_4	482 2.57	508 2.44	535 2.31	49	4	34.5	2000 0.26	13000 1.62	16000 2.0	3400 0.42
$\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}$	490 2.53	514 2.41	539 2.30	44	4	35.5	1900 0.23	13400 1.66	16000 2.00	3700 0.46

4. Conclusions

A new green multiphase phosphor $\{\text{SrGa}_2\text{S}_4 + \text{MgGa}_2\text{O}_4\}:\text{Eu}^{2+}$ with improved luminescence properties was synthesized.

Our experiments and detailed analysis show that the luminescence intensity in a new compound increases and it is about 15% higher than in the best commercial strontium thiogallate. The FWHM is narrower and general luminescence is shifted from 535 nm to 539 nm.

The luminescence and crystallographic data are summarized and listed in Tables 1 and 7. These data will be useful to evaluate the quality of the powders prepared for different electronic devices. Our study confirms that proposed multiphase green phosphor based on strontium thiogallate is a good candidate for solid state lighting, LED, and display devices.

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