



June 2007

Volume 2 Issue 2

# Inorganic CHEMISTRY

*An Indian Journal*

Trade Science Inc.

Full Paper

ICAIJ, 2(2), 2007 [81-87]

## Hydrothermal Synthesis And Luminescent Properties Of $\text{SrMgF}_4:\text{RE}$ (RE=Eu, Tb)



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Received: 21<sup>st</sup> March, 2007

Accepted: 26<sup>th</sup> March, 2007

Web Publication Date : 27<sup>th</sup> May, 2007



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### ABSTRACT

The  $\text{SrMgF}_4$  powder has been hydrothermally synthesized from the double system. The effects of factors such as the ratio of initial reaction, pH value, reaction temperature and time were investigated. Moreover, the  $\text{SrMgF}_4:\text{RE}$  (RE=Eu, Tb) phosphors were prepared by the hydrothermal method. Further, they were characterized by means of inductively coupled plasma atomic emission spectrometer, X-ray powder diffraction, scanning electron microscopy, thermogravimetric analysis, and infrared spectroscopy. The luminescent properties were investigated by the luminescence spectrometer. The results show that the molar ratio and pH in the initial reaction mixture associated with the reaction temperature dominate the crystallization of the products. The products are air stable.  $\text{SrMgF}_4:\text{RE}$  obtained was pure phase of  $\text{SrMgF}_4$ . It indicates that doping a low concentration of  $\text{RE}^{3+}$  ions couldn't change the structure. In the co-doped  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  system,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Eu}^{2+}$  are observed in one matrix. These phenomena can be explained using an electron transfer theory. These RE ions occupy the sites of  $\text{Sr}^{2+}$  in  $\text{SrMgF}_4$ .

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### KEYWORDS

Fluorides;  
Rare earth;  
Hydrothermal synthesis;  
Luminescent properties.

### INTRODUCTION

Complex fluorides, which show various interesting structures, have been extensively studied due to

their particular physical properties, especially as photoluminescence host material<sup>[1,2]</sup>. Different isomorphous replacements in the framework of complex fluorides lead to many controllable properties<sup>[3]</sup>. It is

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well known that complex fluorides can be prepared by a conventional solid-state reaction. In the way, a calcinations step is required at high temperature for enhancing the diffusivity between raw solid materials. During calcinations, solid-state diffusion results in the particle coarsening and agglomeration. And, this synthetic apparatus requires a complicated set-up because of its corrosive nature of fluoride. For improving the drawbacks of the solid-state reaction, various kinds of solution processes (or so called soft-chemical processes) have been investigated. Among the solution processing routes, the hydrothermal process has been proposed to be an effective method for synthesizing complex fluorides. In general, the hydrothermal process progresses in a closed system at a high autogenous pressure. By the benefit of the closed system with a high pressure, the required temperature for preparing complex fluorides can be greatly reduced because the reactivity of reactive species can be enhanced. Recently, mild hydrothermal and solvothermal synthesis of complex fluorides at 120–240°C have been reported<sup>[4,5]</sup>. In this manuscript we report the synthesis of SrMgF<sub>4</sub> and SrMgF<sub>4</sub>:RE (RE=Eu, Tb) by hydrothermal method and examined the effects of the reaction temperature and time, solution pH value, ratio of initial composition on the products and investigate their luminescent properties.

## EXPERIMENTAL

A series of complex fluorides SrMgF<sub>4</sub> which doped Eu or/and Tb were prepared by hydrothermal method, using SrF<sub>2</sub> (A.R.) and MgF<sub>2</sub> (A.R.) as raw materials. The total mass of the starting materials was 1.5g, precise ratio and reaction conditions were listed in TABLE 1 and TABLE 2. A reaction mixture was obtained by mix SrF<sub>2</sub>, MgF<sub>2</sub>, Eu<sub>2</sub>O<sub>3</sub> (99.99%) or/and Tb<sub>4</sub>O<sub>7</sub> (99.99%) in 9mL deionized water, then NH<sub>4</sub>HF<sub>2</sub> (A.R.) was added drop wise to the mixture under magnetic stirring. The reaction mixture was transferred into a teflon-lined autoclave of 20mL capacity, and the autoclave was filled with water up to 75-80% of the total volume. The autoclave was sealed into a stainless-steel tank and heated in an oven under autogenous pressure. After cooling to room temperature, the resultant precipitate was centrifuged and washed with deionized water for several times to pH ca. 7 and air-dried at room temperature. Excess ions were removed during washing.

All products were characterized by X-ray powder diffraction (XRD) on rigaku D/max-IIB diffractometer with a rotating target with Ni-filtered Cu-K $\alpha$  radiation at room temperature. The XRD data for indexing and cell-parameter calculation were collected by a scanning mode with a step length of 0.02° in the 2 $\theta$  range from 10 to 60° and a scanning rate of 0.2°min<sup>-1</sup>. Silicon was used as an internal standard.

TABLE 1: Hydrothermal synthesis conditions for SrMgF<sub>4</sub>

Starting materials			a:b:c (mole ratio)	pH	Reacture temperature/°C	Reaction time/h	Phase in product
a	b	c					
SrF <sub>2</sub>	MgF <sub>2</sub>	-	1:1	6	240	72	SrMgF <sub>4</sub>
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	1:1:1	7	160	144	SrMgF <sub>4</sub>
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	1:1:1	4	240	72	SrMgF <sub>4</sub>
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	1:1:1	10	240	72	SrMgF <sub>4</sub> +SrF <sub>2</sub>
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	1:1:1	7	240	72	SrMgF <sub>4</sub>
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	2:1:1	7	240	72	SrMgF <sub>4</sub> +SrF <sub>2</sub>

TABLE 2: Hydrothermal synthesis condition of SrMg<sub>4</sub>:Eu, Tb

Starting materials				Mole ratio		Phase in product
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	Eu <sub>2</sub> O <sub>3</sub>	-	0.98:1:1:0.02	SrMgF <sub>4</sub> :Eu
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	-	Tb <sub>4</sub> O <sub>7</sub>	0.98:1:1:0.02	SrMgF <sub>4</sub> :Tb
SrF <sub>2</sub>	MgF <sub>2</sub>	NH <sub>4</sub> HF <sub>2</sub>	Eu <sub>2</sub> O <sub>3</sub>	Tb <sub>4</sub> O <sub>7</sub>	0.96:1:1:0.02:0.02	SrMgF <sub>4</sub> :Eu, Tb

Particle-size and morphology were observed on a philips XL-30-EDAX scanning electron microscope (SEM). Powder samples were suspended in absolute ethanol by ultrasound for 10min in an ultrasonic bath, then a few drops of the suspension were deposited onto a glass slice, dried, and sputter coated with gold. Thermal gravimetric analysis (TGA) was performed using a seiko instrument DG/DTA320 thermogravimetric system in air from ambient temperature to 800°C at a heating rate of 5°C min<sup>-1</sup>. Infrared spectra (IR) were obtained with a nicolet 550-II spectrometer in the range 4000-400cm<sup>-1</sup>. The samples were pressed KBr pellets for the spectra measurements. The contents of Sr and Mg in the samples were analyzed by thermo jarrell ash POEMS-II inductively coupled plasma atomic emission spectrometer (ICP-AES). Optical measurements were performed at room temperature using a perkin elmer LS 55 luminescence spectrometer.

## RESULTS AND DISCUSSION

### Synthesis

TABLE 1 lists the various reaction conditions for the synthesis of SrMgF<sub>4</sub>. It seems that pure SrMgF<sub>4</sub> samples can be obtained, which the critical factor for obtaining the single-phase product are the ratio of initial composition, pH of the reaction system, reaction temperature and time.

#### 1. Effect of the ratio of initial composition

The ratio of Sr/Mg is a dominating factor for synthesis of SrMgF<sub>4</sub>. When the Sr/Mg ratio was 1, the powder formed was pure. However, when Sr/Mg=2, impurity phases SrF<sub>2</sub> appeared.

It is known that F<sup>-</sup> ion is an effective mineralizer in both aqueous and non-aqueous system<sup>6,7</sup>. In the synthesis of SrMgF<sub>4</sub>, F<sup>-</sup> ion was either a reactant or a mineralizer. Excess F<sup>-</sup> ions may lower remarkably the

temperature of crystallization. Thus SrMgF<sub>4</sub> can be crystallized even at 160°C when excess F<sup>-</sup> ions are added. Further more, when RE ions were doped in SrMgF<sub>4</sub>, F<sup>-</sup> ions play role as charge compensation. And it can be found that addition of a small excess of NH<sub>4</sub>HF<sub>2</sub> did not result in the formation of impurities. In fact, NH<sub>4</sub>HF<sub>2</sub> acts not only as a F<sup>-</sup> source but also eliminates the risk of possible air pollution<sup>8</sup>. Therefore, some NH<sub>4</sub>HF<sub>2</sub> was added to the reaction system, though the results show that the pure products can be prepared without NH<sub>4</sub>HF<sub>2</sub>.

#### 2. Effect of pH

The pH value of the reaction system considerably influences the crystallization of the complex fluorides. It can be found from TABLE 1. That single phase products were obtained as long as the pH is around 4~7. A high pH value (>7) often result in the presence of SrF<sub>2</sub>. Other hand, a pH value that is too low may cause HF gas pollution when the autoclave is opened. We note that NH<sub>4</sub>HF<sub>2</sub> is a good system because it play role as the buffer agent to retain the pH during the reaction. So the suitable pH for the formation of the well-crystallized SrMgF<sub>4</sub> powder is around 4~6.

#### 3. Effect of reaction temperature and time

To investigate the crystallization behavior of the precursor, the hydrothermal reaction was conducted at various temperatures for different times. Single phase SrMgF<sub>4</sub> can be prepared after the mixture heated at 240°C for 72h. It obvious that SrMgF<sub>4</sub> can be crystallized below 240°C, but prolonged reaction time is required, e.g. well-crystallized SrMgF<sub>4</sub> powders are obtained at 160°C for 144h. However, the pure phase SrMgF<sub>4</sub> cannot be obtained below 160°C for 144h. Although the SrMgF<sub>4</sub> phase begin to form at 160°C, a temperature higher than 200°C is necessary for preparation of the well-crystallized powder because the crystallinity increase with increasing tem-

TABLE 3: The ICP-AES data of SrMgF<sub>4</sub>:0.02 Eu, 0.02Tb

Compounds	Content of Sr/mg.g <sup>-1</sup>		Content of Mg/mg.g <sup>-1</sup>	
	Experimental value	Theory value	Experimental value	Theory value
SrMgF <sub>4</sub> :0.02Eu	448.2	453.8	119.8	128.5
SrMgF <sub>4</sub> :0.02Tb	449.6	453.5	116.3	128.4
SrMgF <sub>4</sub> :0.02Eu, 0.02Tb	435.9	441.2	122.6	127.5

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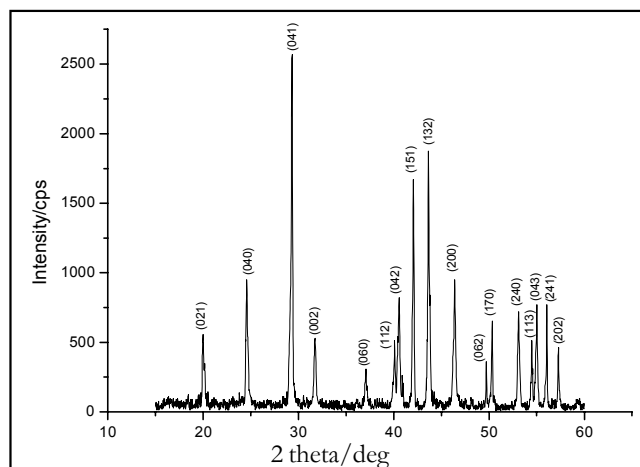


Figure 1: The XRD patterns of  $\text{SrMgF}_4:0.02\text{Eu}, 0.02\text{Tb}$

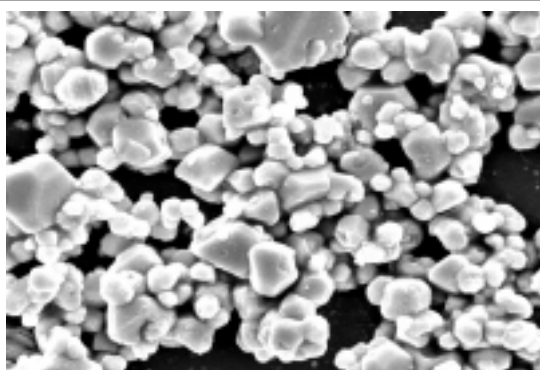


Figure 2: SEM of  $\text{SrMgF}_4:0.02\text{Eu}, 0.02\text{Tb}$

perature. Thus, the borderline conditions for the hydrothermal preparation of the  $\text{SrMgF}_4$  are (1) A temperature higher than  $200^\circ\text{C}$  and (2) A time longer than 72h.

#### 4. Synthesis of $\text{SrMgF}_4:\text{RE}$ (RE=Eu, Tb)

$\text{SrMgF}_4:\text{RE}$  (RE=Eu, Tb) were prepared by hydrothermal synthesis when  $\text{pH}=4$ ,  $T=240^\circ\text{C}$ ,  $t=72\text{h}$ , 0.02mole ratio RE ions doped. The conditions were given as TABLE 2.

#### Characterization of $\text{SrMgF}_4:0.02\text{Eu}, 0.02\text{Tb}$

The contents of Sr and Mg in the  $\text{SrMgF}_4:\text{RE}$  were measured by ICP-AES. TABLE 3 shows that experimental value was lower than theory value and the mole ratio of Sr:Mg is ca. 1:1. This may be for the RE ions doping. In generally, the contents of Sr and Mg of experimental value were agreement with that of theory value.

The XRD patterns of all products were characterized. Figure 1 shows the XRD patterns of

TABLE 4: The XRD data of  $\text{SrMgF}_4:0.02\text{Eu}, 0.02\text{Tb}$

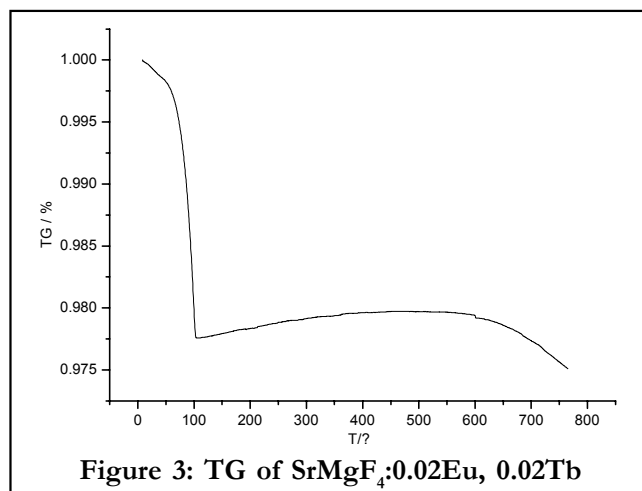
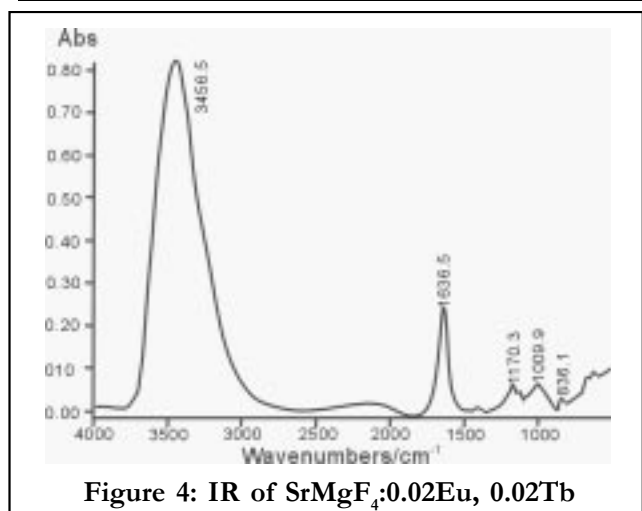
Peak No.	Experimental data		JCPDS Card 32-630 data		
	d value	I/I <sub>1</sub>	d value	I/I <sub>1</sub>	hkl
1	4.4403	22	4.44	20	021
2	3.6132	37	3.61	40	040
3	3.0427	100	3.042	100	041
4	2.8167	21	2.817	20	002
5	2.4210	12	2.410	10	060
6	2.2472	20	2.259	20	112
7	2.2242	32	2.224	30	042
8	2.1474	65	2.150	60	151
9	2.0726	73	2.068	70	132
10	1.9618	37	1.958	40	200
11	1.8319	14	1.831	10	062
12	1.8104	24	1.793	20	152
13	1.7235	28	1.722	30	240
14	1.6830	20	1.683	20	113
15	1.6684	30	1.667	30	043
16	1.6389	30	1.647	30	241
17	1.6077	18	1.607	20	202

$\text{SrMgF}_4:0.02\text{Eu}, 0.02\text{Tb}$ . No other peaks or impurities are detected. Therefore, XRD confirmed the phase purity of the resulting  $\text{SrMgF}_4$  obtained from hydrothermal method. The compound crystallizes in the orthorhombic; the space group is  $\text{Cmcm}$ (no.63); the indexed powder XRD patterns are listed in TABLE 4. The lattice parameters were optimized by least-squares refinements. The unit cell parameters for the product are  $a=3.9236$ ,  $b=14.526$ ,  $c=5.6334$ , which is in good agreement with those given in JCPDS Card 32-630.

The result shows that at the dopant concentration of  $0.02\text{mol}\cdot\text{mol}^{-1}\text{Eu}^{3+}$  and  $0.02\text{mol}\cdot\text{mol}^{-1}\text{Tb}^{3+}$  the obtained product was pure phase of  $\text{SrMgF}_4$ , or the product is free of impurities. It indicated that the product was single phase and the structure could not be changed by a low doping concentration of RE ions.

SEM examined the morphology of the samples at room temperature. Figure 2 shows the scan electron micrograph of  $\text{SrMgF}_4:0.02\text{Eu}, 0.02\text{Tb}$ . As can be seen from this figure, the powder is non-uniform with different grain size, indicating the product is forming. The XRD shows the product is single phase. So, the product crystallinity gradually increases with increasing reaction time.

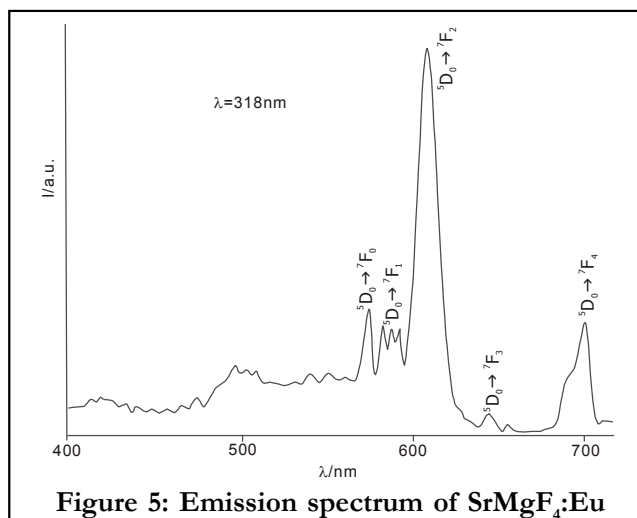
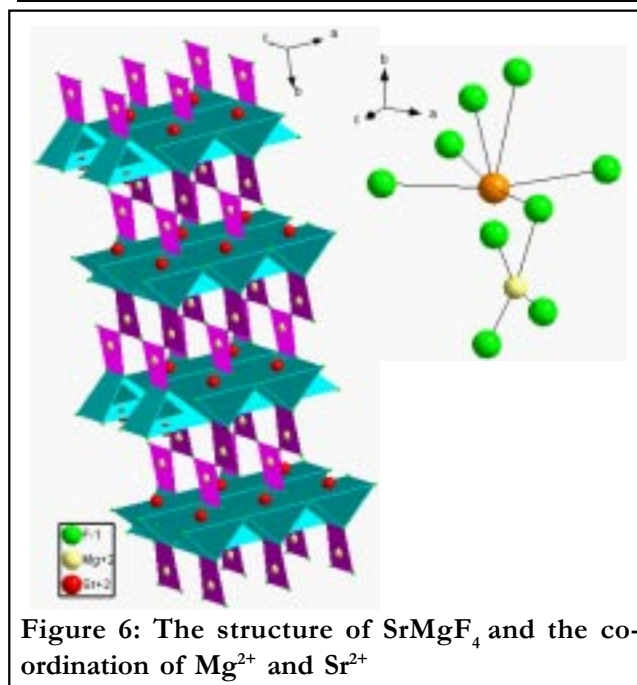
The thermal stability of the  $\text{SrMgF}_4:0.02\text{Eu}, 0.02\text{Tb}$  were studied by TG-DTA analyses in air, as shown in figure 3. There are no phase transforma-

Figure 3: TG of SrMgF<sub>4</sub>:0.02Eu, 0.02TbFigure 4: IR of SrMgF<sub>4</sub>:0.02Eu, 0.02Tb

tions up to 800°C and a small mass of ca. 2.25% surface water was evident at 50–100°C. Then, the weight lost is very slow. 0.25% weight was lost after 600°C, this may be for the decompose of the certain inorganic small molecule of samples or the mixed dust and the grain of filter paper when the sample was filtered. IR of SrMgF<sub>4</sub>:0.02Eu, 0.02Tb (Figure 4) confirms the presence of water. The observation of sharp absorption band around 3456 cm<sup>-1</sup> indicates the presence of terminal hydroxyl groups. The 1637 cm<sup>-1</sup> band is due to the H-O-H bending vibrations of H<sub>2</sub>O molecule, which is diagnostic of the presence of water in the sample. The results show that the sample is stable in air and the surface water is removed upon increasing the temperature.

### Luminescent properties

To study on the luminescent properties of SrMgF<sub>4</sub>:RE (RE=Eu, Tb), we measure their emission spectra after they are dried at 80°C for 2h to removed

Figure 5: Emission spectrum of SrMgF<sub>4</sub>:EuFigure 6: The structure of SrMgF<sub>4</sub> and the coordination of Mg<sup>2+</sup> and Sr<sup>2+</sup>

the surface water.

### 1. Luminescence of SrMgF<sub>4</sub>:Eu

Figure 5 shows the emission spectrum of Eu<sup>3+</sup>-doped SrMgF<sub>4</sub> under 318nm excitation. The main features are the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>J</sub> (J=0, 1, 2, 3, 4) transition of Eu<sup>3+</sup> are observed and are marked in the figure. The intense peak in the spectrum is ~611nm, corresponding to the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> transition as is the case with Eu<sup>3+</sup>-doped samples. It seems that only emission of Eu<sup>3+</sup> ions are observed in SrMgF<sub>4</sub>:Eu. Although Eu<sup>3+</sup> can be reduction to Eu<sup>2+</sup> ions, there is hardly the emission of Eu<sup>2+</sup> in the emission spectrum of SrMgF<sub>4</sub>:Eu which is during 400~500nm. However, the broad-band emission of Eu<sup>2+</sup> which maximum emission

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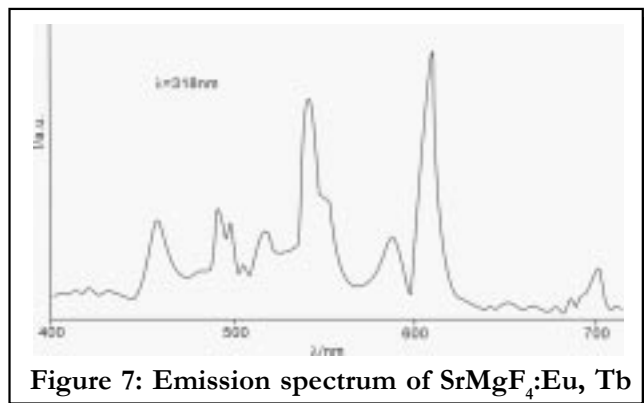


Figure 7: Emission spectrum of SrMgF<sub>4</sub>:Eu, Tb

wavelength is at 420nm can be observed in SrMgF<sub>4</sub>:Eu obtained by solid state reaction at high temperature<sup>9,10</sup>. The phenomenon can be explained as follow: the stable valance of Eu is trivalent charge state(Eu<sup>3+</sup>), the other hand, the reaction temperature of hydrothermal synthesis is lower and the conditions are mild, so the valance change is not easy. Besides these, there are a plenty of F<sup>-</sup> ions in the system, which play role as charge compensation in the SrMgF<sub>4</sub> and make Eu<sup>3+</sup> be stable in the matrix.

It is well know, as is to be expected the spectral energy distribution of the emission from the <sup>5</sup>D<sub>0</sub> level depends strongly on the crystal structure. As far as the Eu<sup>3+</sup> ions occupy one crystallographic site in the host lattice only sharp emission lines are expected; not more than three for the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>1</sub>, not more than five for the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> transition in view of the degeneracy of the level involved. If more than one crystallographic site is occupied, these numbers can be higher due to the presence of different types of Eu<sup>3+</sup> centers. If the Eu<sup>3+</sup> ions would occupy the position with inversion symmetry, the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>1</sub> emission lines

are expected to have the highest intensity in view of their magnetic dipole character<sup>11</sup>. If the Eu<sup>3+</sup> ions would occupy the position which is no inversion symmetry(C<sub>s</sub> symmetry), the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> emission is expected to be dominant<sup>12</sup>. In the case, the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> transitions have the highest intensity and the intensity of the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>4</sub> transition varies strongly as do the number and the width of the lines, demonstrating that the Eu<sup>3+</sup> ions occupy non-centro symmetrical site in SrMgF<sub>4</sub>. The number of the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>1</sub>, <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> transition is not more than 1, 3, 5, respectively. This indicates that the Eu<sup>3+</sup> ions occupy one crystallographic site in the SrMgF<sub>4</sub>. The crystal structure (Figure 6) shows that Sr<sup>2+</sup> ion is surrounded by six fluorine ions and Mg<sup>2+</sup> ions are in octahedral co-ordination. The Sr<sup>2+</sup> ion is in this kind of space group involves only one type of site, which is non-Centro symmetrical. And the ionic radius of Eu<sup>3+</sup>(95pm) is more similar to that of Sr<sup>2+</sup>(112pm) than that of Mg<sup>2+</sup>(66pm). So Eu<sup>3+</sup> ions occupy the Sr<sup>2+</sup> site in SrMgF<sub>4</sub>.

## 2. Luminescence of SrMgF<sub>4</sub>:Eu, Tb

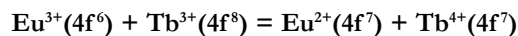
The emission spectrum of SrMgF<sub>4</sub>:Eu, Tb phosphor is given in figure 7. Eu<sup>3+</sup>, Tb<sup>3+</sup> and Eu<sup>2+</sup> can be coexisted in one system. The group of sharp peaks ranging 560~720nm is the emission of Eu<sup>3+</sup>, which due to the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>J</sub>(J=0,1,2,3,4) transition. The emission line at 542nm is a characteristic emission from <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>5</sub> transition of Tb<sup>3+</sup> ion. The Eu<sup>2+</sup> ions exhibit broadband fluorescence, which corresponds to 5d-4f transitions in Eu<sup>2+</sup>. The strongest emission peak is found at 458nm. The Eu<sup>2+</sup> ions occupy the Sr<sup>2+</sup>

TABLE 5: The difference between hydrothermally prepared SrMgF<sub>4</sub>:Eu and that of corresponding SrMgF<sub>4</sub>:Eu synthesized by solid state reaction

SrMgF <sub>4</sub> :Eu synthesized by solid state reaction	SrMgF <sub>4</sub> :Eu synthesized by hydrothermal method
Space group is A2 <sub>1am</sub> (C <sub>2v</sub> <sup>12</sup> ) <sup>14</sup>	Space group is Cmcm
Eu <sup>3+</sup> -O <sup>2-</sup> charge transfer transition with maximum at about 310nm <sup>9</sup>	No remarkable excitation ranging 250~300nm was found
A Eu <sup>2+</sup> broadband emission was found with its maximum at about 420nm <sup>9,10</sup>	There is hardly the emission of Eu <sup>2+</sup> in the emission spectrum of SrMgF <sub>4</sub> :Eu(Figure 5)
The strongest emission is at 573nm when it is excited by 316nm <sup>9,14</sup>	The strongest emission is at 611nm when it is excited by 318nm(Figure 5)
Three crystallographic site are occupied, due to the presence of three different types of Eu <sup>3+</sup> centers <sup>14</sup>	Only one crystallographic site is occupied, because of the presence of different types of Eu <sup>3+</sup> centers

sites of SrMgF<sub>4</sub>. This phenomenon also existed in SrMgF<sub>4</sub>:Eu, Tb synthesized by solid state reaction<sup>[9, 10]</sup>.

Eu<sup>3+</sup> and Tb<sup>3+</sup> is a couple of conjugate rare earth ions, thus, an electron transfer can take place between Eu<sup>3+</sup> and Tb<sup>3+</sup> ions<sup>[13]</sup>:



When Eu<sup>3+</sup> and Tb<sup>3+</sup> are codoped in SrMgF<sub>4</sub> matrix, an electron can be transferred from a Tb<sup>3+</sup>(4f<sup>8</sup>) to an Eu<sup>3+</sup>(4f<sup>6</sup>) to get their half-filled 4f shell configuration(4f<sup>7</sup>). This explanation can be identical with the relative emission intensity. Under the same excitation conditions, the emission intensity of Eu<sup>3+</sup> is decreased whereas that of Eu<sup>2+</sup> is increased.

SrMgF<sub>4</sub>:Eu, Tb(RE=Eu, Tb) phosphors can be prepared by hydrothermal method and solid-state reaction. The difference between them is interested, shown as TABLE 5. The mechanism can't be described though we hope to study them.

## CONCLUSION

SrMgF<sub>4</sub> can be synthesized by mild hydrothermal method. The results show that the molar ratio and pH in the initial reaction mixture associated with the reaction temperature dominate the crystallization of the products. The products are air stable. SrMgF<sub>4</sub>:RE obtained was pure phase of SrMgF<sub>4</sub>. It indicates that doping a low concentration of RE<sup>3+</sup> ions couldn't change the structure. In the co-doped Eu<sup>3+</sup> and Tb<sup>3+</sup> system, Eu<sup>3+</sup>, Tb<sup>3+</sup> and Eu<sup>2+</sup> are observed in one matrix. These phenomena can be explained using an electron transfer theory. These RE ions occupy the sites of Sr<sup>2+</sup> in SrMgF<sub>4</sub>.

## ACKNOWLEDGMENT

This work was supported by National Nature Science Foundation of China (90201032).

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