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No. 2349 - 9443 Synthesis and Luminescence Characterstics of Inorganic Borate (Na₃Y(BO₃)₂))



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Abstract

The photoluminescence properties of inorganic borate host material $Na_3Y(BO_3)_2$ doped with Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} as reported. The material $Na_3Y(BO_3)_2$ was prepared by novel technique which is a slight variation of solution combustion synthesis. The synthesis is based on the exothermic reaction between the fuel (urea) and oxidizer(ammonium nitrate). The structure of the prepared sample was confirmed by powdered investigated.Under the uv excitation (254nm), $Na_3Y(BO_3)_2$ shows interbroademission band peaking at 409 nm. The effect of concentration Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} ions on the PL intensity has also been investigated. It has been observed that the powdered sample exhibits highest PL emission intensity for Eu $^{3+}$ concentration of about 0.05 molest has been observed.

Keywords:Photouminescence, Synthesis, Exothermic Reaction, Interbroademission

Introduction

Luminescence is "cold light" that can be emitted at normal and lower temperatures. In luminescence, some energy source kicks an electron of an atom out of its lowest energy "ground" state into a higher energy "excited" state; then the electron returns the energy in the form of light so it can fall back to its "ground" state. With few exceptions, the excitation energy is always greater than the energy (wavelength, color) of the emitted light. There are several varieties of luminescence, each named according to the source of energy, or the trigger for the luminescence: Fluorescence and Photoluminescence are luminescence where the energy is supplied by electromagnetic radiation. Photoluminescence is generally taken to mean "luminance from any electromagnetic radiation", while Fluorescence is often used only for luminescence caused by ultraviolet, although it may also be used for other photoluminescence. Fluorescence is seen in fluorescent lights, amusement park and movie special effects, the redness of rubies in sunlight, "day-glow" or "neon" colors, and in emission nebulae seen with telescopes in the night sky. Bleaches enhance their whitening power with a white fluorescent material.

Photoluminescence should not be confused with reflection, refraction, or scattering of light, which cause most of the colors you see in daylight or bright artificial lighting. Photoluminescence is Luminescence is traditionally classified, as Fluorescence and Phosphorescence depending upon time lag.

Types of Luminescence

- 1. Chemiluminescence
- 2. Bioluminescence
- 3. Electroluminescence
- 4. Cathodoluminescence
- 5. Radio luminescence
- 6. Triboluminescence
- 7. Thermo luminescence
- 8. Optically stimulated

Characteristics of Luminescence

For understanding the mechanism and uses of any phenomenon, its characteristics play an important role.Some of the important characteristics of luminescence are as follows:

1) Luminescence power

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- 2) Energy and quantum yield
- 3) Luminescence spectrum
- 4) Excitation spectrum
- 5) Rise and decay of luminescence

Application of Luminescence

- Luminescence finds a lot of application. Some important applications are given below:
- 1. Luminescent materials are also used in scintillation counters wherebynucleons can be detected.
- Luminescent materials are used in fabricating x-ray imaging plates, which haspresently replaced x-ray photographic films.
- Asian Resonance 3. X-ray fluorescence is used in non-destructive
 - testing of rocket and shipMaterials.Phosphors are used in fluorescent tubes, energy saving lamps, etc.
 - 5. Cathodoluminescence phosphors are used in the screens of television, cathoderay oscilloscope, radar, electron microscope, night vision devices, etc.
 - 6. Luminescent materials are also used in fabricating the detectors for ultravioletFluorescence and phosphorescence are two special aspects of luminescence.

Different forms of L	Luminescence
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Excitation source	Luminescence type	Applications	
Photons	Photoluminescence Radiophoto-luminescence (RPL) Optically stimulated luminescence	Fluorescent lamps, Phototherapy Lamps, Light Source, Highlighting Paints and inks, Image intensifier, PLLCD, PDP and other Display devices, Optically pumped solid state lasers, Up conversion lasers, Luminescent solar concentrators, Diagnosis Dosimetery of ionizing radiations OSL dating	
Ionizing radiations like X ray, ray or rays.	Radio luminescence Long lasting (Delayed) Radio phosphorescence	Watch dial, standard light source	
	Photo-stimulated luminescence (PSL)	X ray imaging, dosimetry	
	Thermo luminescence (TL)	Dosimetry of ionizing radiation, Environmental monitoring, Personnel monitoring, Geological dating, Archaeological dating	
	Lyoluminescence (LL)	Dosimetry of ionizing radiation, Detectors, Analytical devices, Personnel monitoring	
	Radio luminescence (Prompt)	X ray screen, X ray scintillators, Scintillation detectors	
Electric field	Electroluminescence	LEDs, EL displays, Diode lasers, TFEL display, TV screens	
Electrons	Cathodoluminescence	CRO, TV screens, Monitors, FED	
Biochemical reaction energy	Bioluminescence	Analytical chemistry	
Chemical reaction energy	Chemiluminescence	Analytical chemistry	
Mechanical energy	MechanoluminescenceTribomechano- luminescence	Used in radiology, toxicology, pediatric cardiology,For writing messages for reading in dark, Calculation of surface charge density	
Ultrasound	Sonoluminescence	Acts as a catalyst in many situations	

Fundamental aspects of Photoluminescence Principle

The luminescent system generally consists of a host lattice and a luminescent centre, often called as 'activator'. In general, the host needs to be transparent to the radiation source used for excitation process. The activator absorbs the exciting radiation and is raised to an excited state. The excited state returns to the ground state by emission of radiation or by nonradiativedecay. It is necessary to suppress this nonradiative process. In some materials the activator does not absorb the exciting radiation but the other ion may absorb the exciting radiation and subsequently transfer it to the activator. In this case, the absorbing ion is called as a 'sensitizer'. In many cases the host lattice transfers its excitation energy to the activator, so that, the host lattice acts as the sensitizer. High–energy excitation always excites the host lattice. Direct excitation of activator is only possible with ultraviolet and visible radiation.

Excitation

In general luminescence may be excited by a number of agents such as light, cathode rays or positive ion bombardment or X-rays, by contact with flame, or by friction. The region of wavelengths for which a given material can be excited by optical means with high efficiency, usually consists of one or more broad bands, which are characteristic of both the host material and the

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activator. The position of the bands evidently is of much importance for practical purposes. For example it is important that the given material possess a prominent excitation band at 253.7 nm, if it is to be excited by radiation from a low-pressure mercury discharge. It should be emphasized that not all crystals possessing a high efficiency for optical excitation, also posses a high efficiency for excitation by cathode rays. It has generally been observed that the efficiency of excitation of luminescence decreases, reversibly, as the temperature is raised sufficiently. Luminescence may be regarded as a way of converting various kinds of energy, such as optical, nuclear, electric, mechanical and chemical in to light emission (detection of invisible radiation). This forms a background for a great variety of the ways for the application of luminescence. It is possible to set apart the type of luminescence depending upon the type of energy employed for their excitation.

Emission

The emission spectra of luminescent material usually consist of one or more bands whose position is related to the activator. In general, peaks become narrower and narrower in the crystalline materials as the temperature of the specimen is lowered and they approximate sharp lines near the absolute zero of the temperature. It is clear that if the electrons, which absorb energy and radiate light, are in the well shielded inner shells of the atom (for example rare earth ions), excitation may have relatively little effect upon the chemical binding, in which case, the degradation of energy will be smaller than it would be if the electrons that are to be excited are in the outermost shell.

Decay Characteristics

An examination of the decay properties of the luminescent materials indicates that they fall in to two broad classifications.

Decay Equation of first Type

In first type, the decay equation is given by:

 $I(t) = I_o \cdot exp(-\alpha t)$

Where,

- I_o is the initial intensity,
- I (t) is the intensity at time t

α is a constant.

This resembles closely the process governing the progress of monomolecular reaction. This behavior suggests that in these cases the luminescence takes place by simple excitation with subsequent optical emission in the active centre, the excitation energy remaining closely localized in the centre between excitation and emission. The decay constant is independent of temperature and is small.

Decay Equation of Second Type

Most of the luminescent materials, which are valued for their long decay characteristics, obey a decay equation of second type:

$$I(t) = I_0 / (\beta t + 1)n$$

Where,

- I_o is the initial intensity,
- I(t) is the intensity at time t,
- β and n are constants.

This equation is similar to the rate equation for the bimolecular reaction. The constant β is dependent on temperature. The atoms or clusters of atoms become

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ionized during the excitation and the luminescent radiation is emitted during recombination of the free electrons and the ionized centres. Johnson has suggested that essentially all centres become ionized during excitation and that a majority of free electrons are recaptured into a state, which has a very long lifetime (of the order of milliseconds). This is because the optical transition to the ground state is forbidden. These electrons contribute an exponential component to the decay curve. The remaining electrons are captured at the trapping centres and are released over a period of time that is long compared to the life times of the excited state of the fluorescing centre. The second class of electrons is responsible for the bimolecular component of the decay curve.

Configurationallycoordinate Model

The configurationally coordinate model describes the electronic transitions of absorption and emission. It shows the potential energy curves of the absorbing centre as a function of configurationally coordinates. In optical absorption the centre is promoted from its ground state to the high vibrational level of the excited state. The centre returns first to the lowest vibrational level of the excited state giving up excess energy to the surroundings. From the lower vibrational level of the excited state the system can return to the ground state spontaneously under emission of radiation.





By emission the centre reaches a high vibrational level of the ground state. Again the relaxation occurs to the lowest vibrational ground state. This is schematically shown in Figure 1.1

The activator ions possess energy levels that can be populated by direct activation or indirectly by energy transfer and are responsible for the luminescence. Generally, two types of activator ions can be distinguished. In the first type the energy levels of the activator ions involved in the emission process show only weak interactions with the host lattice (e.g. Many of the lanthanide ions Ln^{3+}). The characteristic line emission spectra can be observed in this case. The second types of activator ions strongly interact with the host lattice (e.g. Mn^{2+} , Eu^{2+} , Ce^{3+} , Pb^{2+} , etc.).

The strong coupling of the electronic states with vibrational modes of the lattice mainly lead to more or less broad bands in the spectrum. Full width at half maximum (FWHM) is related to the Stokes shift S, that

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is the energy difference between absorption and emission maximum.

$FWHM = \sqrt{8\ln 2} \sqrt{2kT} \sqrt{S} [eV]$

 $S = S_e h_{\omega e} + S_g h_{\omega g}$

 S_e and S_g are Huang-Rhys parameters for the excited and ground state respectively. Phosphors that show an emission with a large Stokes shift usually exhibit a low quenching temperature, which is disadvantageous for many applications.

In general the luminescent process can be divided into the steps of energy absorption, energy transfer and emission. Energy absorption need not take place at the activator ion itself but can occur at random place in the lattice. This implies that energy transfer of the absorbed energy to the luminescent centre takes place before emission can occur. The migration of energy absorbed by the lattice can take place through one of the following processes:

- 1. Migration of electric charge (electrons, holes),
- 2. Migration of excitons,
- 3. Resonance between atoms with sufficient overlap integrals,
- 4. Reabsorption of photons emitted by another activator ion or sensitizer.

The occurrence of energy transfer within a luminescent material has far-reaching consequences for its properties as a phosphor. On the one hand the absorbed energy can migrate to the crystal surface or to the lattice defects, where it is lost by radiation less deactivation. As a consequence the quantum efficiency of the phosphor declines.

Instrumentations

The instrumentation used for synthesis of material and study of different aspects, with complete specifications is discussed in the following section.

- 1. Mettler Balance
- 2. Combustion Chamber
- 3. X-Ray Diffractometer
- 4. Fluorescence Spectrophotometer
- 5. Sources of Excitation
- 6. A thermoluminescence glow curve reader
- 7. Thermoluminescence emission spectra

Synthesis of Borate

Borate

Borates are naturally occurring minerals containing boron, the fifth element on the periodic table. The element boron does not exist by itself in nature. Rather, boron combines with oxygen and other elements to form inorganic salts called borates. Boron has an ionic radius 0.11 A and hence can occur in both triangular (BO3) and tetrahedral (BO4) coordination where bonded to oxygen .BO3 groups have an average B-O bond-valance approximately equal to 1 v.u. and BO4 groups have an average B-O bond-valance approximately equal to 3/4 v.u. Hence both (BO3) and (BO4) groups can polymerize by sharing corners with out violating the valance sum rule. Such polymerization is very common in both minerals and synthetic inorganic compounds. In general, a borate structure contains clusters of corner sharing (BO3) and (BO4) polyhedra, which occur as discrete polyanions to form larger clusters, chains, sheets or frameworks. Since, the boron

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atom is capable of coordination in either trigonal or tetragonal mode borate anions exist in numerous structural types. There are hundreds of different structures with various borate anionic groups as basic structural units in the known borate crystals. However, there are only a few types of basic structural units of borates of practical interest-

(i) (BO3) ³⁻	(ii) (BO4)	⁵⁻ (iii) (B2O	5) ⁴⁻ (iv)
(B2O7) ⁸⁻	(v) (B3O6) ³⁻	(vi) (B3O7) ⁵⁻	(vii)
(B3O8) ⁷ -	(viii) (B3O3 ^{) 9-}	(ix) (B5O10) ⁵⁻	(x) (B4O9)

Applications of Borate Host Materials

Solid state inorganic borates have become a focus of technological interest due to a variety of physical and chemical features exhibited by these compounds . Owing to possible three-, or four-fold coordination of borate atoms, borates form a great number of compounds having diverse structures. Borates intrinsically possess characteristics that are advantageous for optical materials, which include wide transparency range, large electronic band gap, good thermal and chemical stability, low preparative temperature, optical stability with good nonlinear characteristics and exceptionally high optical damage threshold. The unique crystal structure of borates determines their enhanced UV transparency, good nonlinearity and relatively high resistance against laser induced damage. Recent research on inorganic borates has been focused on the synthesis and characterization of compounds with potential application as optical material. Borate compounds currently have been of considerable interest to the scientific community owing to their wide range of applications: Laser, NLO material, Phosphor material and Scintillator material etc. Most of the borates are polyfunctional materials with nonlinear optical, piezo- electrical and acoustic- electrical properties. Some borates are also suitable as a laser material for miniature laser . Borate crystals with the structure of the naturally occurring mineral huntite CaMg3(CO3)4 are widely known as polyfunctional materials having device potential due to their good thermal and chemical stabilities. The general formula of huntite borate is LnM3(BO3)4, Ln=rare earth element and M=Al, Ga, Cr, Fe, Sc. Among them, rare earth aluminium borates LnAl3(BO3)4 have attracted considerable attention for their luminescence properties and possible application as single crystal minilaser. In the following sections the applications of inorganic borate compounds as LASER& NLO material and Phosphor material are discussed.

Inorganic Borate As Phosphor Material

During the past few years, a number of borate materials have been studied extensively due to their unique combinations of large electronic band gaps, strong nonlinear optical properties, chemical and environmental stabilities, and mechanical robustness. Due to their large electronic band gaps, borate materials are excellent host lattices for luminescent ions. Rare earth borate compounds normally have high UV transparency and exceptional optical damage threshold, which makes them attractive for numerous practical such as, in lamps and display applications. There are many excellent phosphors in the borate family, for

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example, YBO3: Eu3+, m GdBO3: Eu3+ and LnMgB5O10, etc. which has been applied in the region of UV- excited phosphors and integrated optics. Rare earth borate compounds are an interesting class of luminescent materials. The rare earth borate phosphors were first introduced by R.I.Smirnova et al. and have been of little or no interest for two decades. More recently due to rising demand for new efficient phosphors for various applications such as Lamp Phosphor, FPD, PDP etc. rare earth borates have attracted attention. Rare earth orthoborates, RBO3 (R=Y, La, Gd), doped with rare earth ions (Eu3+ and Tb3+) are interesting luminescent materials. Rare earth borates doped with Eu3+ are potential red emitting phosphors. Gadolinium borate phosphors ranging from orthoborates to pentaborates have proved to be potential candidates for practical applications in fluorescent lamps due to their high efficiency.

Haloborates activated by Ce3+ ions have been recently shown to be a promising material for detecting thermal neutrons. Strontium haloborates doped with Eu2+ are well known X- ray storage phosphors.

Plasma display panels (PDP) are regarded as the most promising candidate for large sized flat panel displays (FPD). Phosphors for the application in PDP are required to have high conversion efficiency by VUV radiation of 147 and / or 172 nm from the Xe gas plasma. The inorganic borate compounds have strong absorption in the VUV region and therefore widely used as host lattices of phosphors for PDP applications. LnBO3 doped with Eu3+ has been widely used as a luminescent material in plasma display panels (PDP) due to the high quantum efficiency and good color coordinates under 147 nm VUV excitation . At present, the most widely used red emitting phosphor for PDP is (Y Gd)BO3: Eu3+. The doped YAI3(BO3)4 can be utilized as red PDP phosphor Borate host Inorganic Luminescent materials

S.No.	Inorganic Borate	Applications		
1	(CeGd)MgB5O10	Red Emitting Phosphor in		
		Special deluxe lamps		
2	(CeGd)MgB5O10	Green Emitting Phosphor in		
	: Tb3+	Tricolor lamps		
3	Ca4GdO(BO3)3:E	Potential Red Lamp		
	u3+	phosphor		
4	GdB3O6:	Potential Green Lamp		
	Ce3+,Tb3+	phosphor		
5	SrBPO5: Eu3+	Storage phosphor		
6	CaLaB7O13:	Green emitting phosphor in		
	Ce3+,Tb3+	low pressure Hg vapor lamps		
7	CaLaB7O13:	Red emitting phosphor in low		
	Eu3+	pressure Hg vapor lamps		
8	SrB4O7: Sm2+	Optical pressure Gauge		
9	(Sr0.89Na0.05)BPO5	Green Emitting Phosphor in		
	Ce0.05,Tb0.01	Tricolor lamps		
10	Sr2B5O9Br: Ce3+	Potential storage phosphor		
		for thermal neutron		
11	SrB4O7: Eu2+	Commercial UV emitting		
		phosphor in medical lamps		
12	Sr2B5O9CI: Eu2+	Blue component of day		
		light phosphor		

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13	Sr2B5O9CI:	Blue component in FED	
	Eu2+(Thin Film)		
14	Ba2B5O9Br:Eu2+	X-ray storage phosphor	
15	SrB2Si2O8:Eu2+	Blue emitting phosphor	
16	InBO3: Tb3+	Green emitting phosphor in	
		CTV screens.	
17	La(BO3,PO4):Ce3	Green Emitting Phosphor in	
	+ Gd3+ Tb3+	high quality Tricolor lamps	
18	Ba2B5O9CI:Tb3+	Green emitting phosphor in	
	(Thin Film)	FED	
19	Ba2B5O9CI:Eu2+	Blue emitting phosphor in	
	(Thin Film)	flat panel display (FPD)	
20	YBO3: Eu3+	Red emitting VUV phosphor	
21	YAI3(BO3)4:Ho,Yb	Up conversion phosphor	
22	CaBPO5: Tb3+	Green emitting VUV phosphor	
23	Y3BO6: Eu3+	Red phosphor in vacuum	
		discharge lamps or screens	
24	(YGd)BO3:Tb3+	Green component in PDP	
25	(YGd)BO3:Eu3+	Red component in PDP	
26	GdAl3(BO3)4:Eu3+	Red component in PDP	
27	(YGd)Al3(BO3)4:Eu3	Pod component in PDP	
	+	Red component in PDP	
28	GdAl3(BO3)4:Tb3+	Green emitting VUV phosphor	
29	BaZr(BO3)2:	Red component in PDP	
	Eu3+	Red component in PDP	
Con	abuation Synthesia		

Combustion Synthes

The solid state synthesis using boric acid as the boron source allows the preparation without melting the constituents which is essential for avoiding glass formation. This requires longer reaction times. Evapopration of boric acid may cause nonstoichiometry. Recently, oxide materials have been prepared using the self heat generating methods, popularly termed as combustion sysnthesis. The heat generated in the exothermic chemical reactions is used for the sysnthesis.

The combustion systhesis is a convenient method for rapid systhesis of phosphors. The method makes the use of the heat produced in exothermic reaction between metal nitrates & urea. In particular, the urea act as fuel & metal nitrates help it to be so.

- 1) Use of relatively simple equipment
- 2) Formation of high-purity products
- 3) Stabilization of metastable phases and
- 4) Formation of virtually any size and shape products

This technique involves a highly exothermic reaction in aqueous solution between an organic fuel and metal nitrates (oxidizers). The reaction is initiated at low temperatures (~500 °C) and goes to completion in less than ten minutes. The peak temperature of the reaction is dependent upon the molar fuel to oxidizer ratio, f/o. The optimal f/o ratio depends on the desired final composition, and has been found to occur when the reactants are present in stoichiometric proportions. The relation of a given F/O ratio to the optimal f/o ratio is known as the elemental stoichiometric coefficient, ϕ e. This coefficient is determined by:

- $\phi_e = \frac{\sum total \ valencies \ of \ oxidizing \ elements \ in \ the \ nitrates \ and \ fuel}{\frac{1}{2}}$
 - $(-1)\sum$ total valencies of reducing elements in the nitrates and fuel Stoichiometric proportions of the reactants yield

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 $\varphi e = 1$, fuel-lean proportions yield $\varphi e > 1$, and fuel-rich proportions yield $\varphi e < 1.9$.

The reaction is self-propagating and can produce temperatures in excess of 1500 oC long enough (~45 s for the reaction to come to completion) to synthesize the desired product. As the flame propagates in the reaction vessel, a solid powder grows, while inert gases, such as H2O, CO2 and N2, are also released, which create porosity in the growing powder. In the end, the reaction yields a porous mass of powder with a large surface area, which fills the volume of the reaction vessel.

Following equation can be used to approximate the adiabatic flame temperature for a combustion reaction [McKittricket al., 1999]:

$$T_f = T_o + \frac{\Delta H_r - \Delta H_p}{c_p}$$

where Δ Hr and Δ Hp are the enthalpies of formation of the reactants and products, respectively, cp is the heat capacity of products at constant pressure, and To is 298 K. Measured flame temperatures are typically lower than calculated values of flame temperature as a result of heat loss.

Synthesis of Nabab9o15

The inorganic borates NaBaB9O15 were synthesized by solution combustion synthesis method. The stoicheometric amounts of the ingredients were thoroughly mixed in an Agate Mortar, adding little amount of double distilled water and obtained an aqueous homogeneous solution. The aqueous solution was then transferred in to a china basin and introduced in to a preheated muffle furnace maintained at 550°C. The solution boils; foams and ignites to burn with flame and obtained a voluminous, foamy powder. The entire combustion process was over in about 5 minutes.Following the combustion, the resulting fine powders were annealed in an open air at temperature 800°C for 90 min. and then suddenly quenched to room temperature.

NaBaB9O15-	Merck	Merck	IRE Ltd	Merck	Merck	Merck
Eu ²⁺	EP	EP	99.9	GR	GR	GR
Ingredients	NaNO3	Ba(NO3)2	Eu(NO3)3	H ₃ BO ₃	NH2CONH2	NH4NO3
Molar ratio	1	0.99	0.01	9	7	14
Weights (gms)	0.8499	2.5874	0.0446	5.8439	4.2042	11.2056

Precautions

- One has to do the stoichiometric calculations very precisely in order to get the desire equimolar ratios & the weight has to be taken accordingly.
- 2.) The ratio of fuel (urea) to oxidizer (ammonium nitrate) should be taken such that it will generate heat required for the combustion synthesis.

Asian Resonance Result and Discussion



Fig. A shows the excitaion and emission spectra of Na₃Y(BO₃)₂ :Eu³⁺ .The excitation spectra of abroad band peaking at 250.7 nm followed by a series of lines between 289-403 nm. The emission spectrum under UV (254 nm) excitation consists of an intense red emission line at 611 nm corresponding to (${}^{5}D_{0}{-}{}^{7}F_{2}$) transition of **Eu**³⁺. The other emission lines 580,587,592 nm (${}^{5}D_{0}{-}{}^{7}F_{1}$) and 630,652 (${}^{5}D_{0}{-}{}^{7}F_{3}$) are very weak , indicating that a **Eu**³⁺ ion coordination environment without symmetry is the most probable.

Reference

- A.V.Sidorenko, A.J.J.Bos, P.Dorenbos, P.A.Rodnyi, C.W.Evan Eijk , I.V. Berezovskaya, V.P.Dotsenko, J Phys: Condens Matter 15(2003) 3471.
- A.V.Sidorenko, A.J.J.Bos, P.Dorenbos, P.A.Rodnyi, C.W.Evan Eijk , I.V. Berezovskaya, V.P.Dotsenko,O.Guillot –Noel,D.Gourier,J Phys: Condens Matter 16 (2004) 4131.
- A.V.Sidorenko,P.A.Rodnyi, C.W.Evan Eijk , O.Guillot –Noel,D.Gourier, J Phys: Solid State 45 (2003) 1597.
- I.V.Berezovskaya, V.P.Dotsenko, N.P.Efryushina, A.S.Voloshinovskii : Matter Chem Phys 77 (2002) 141.
- 5.) I.V.Berezovskaya, V.P.Dotsenko, N.P.Efryushina, M.V.Ryzhkov : Red Measurements 33 (2001) 755.
- 6.) T.R.N. Kutty: Mater Res Bull 25(1990) 343.
- 7.) T.R.N. Kutty: Mater Res Bull 25(1990) 485.