

Luminescent Properties of Eu^{3+} -Activated Rare-Earth Phosphates

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Eu^{3+} 로 활성화된 희토류 인산염의 발광 특성

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ABSTRACT

Spectral properties of europium activated intermediate compounds in the system $\text{R}_2\text{O}_3\text{-P}_2\text{O}_5$ ($\text{R}=\text{La}$, Y , and Gd) are presented, including also phosphors with bismuth and vanadate sensitization. The sensitized phosphors are less efficient than unsensitized phosphors. (The ratio of oxygen to phosphorus effects the charge transfer band.) Most phosphors have low efficiencies, but La_3PO_7 and Gd_3PO_7 hosts are possible for commercial luminescent materials.

요 약

$\text{R}_2\text{O}_3\text{-P}_2\text{O}_5$ ($\text{R}=\text{La}$, Y , and Gd)계의 희토류 인산염들을 Eu 로 활성화 시켰을 때와 Bi 와 V 를 증감제로 사용하였을 때의 발광특성을 고찰하였다. Bi 와 V 으로 증감유발한 발광체가 Eu 으로만 활성화된 발광체보다 낮은 photon flux 값을 나타낸다. 본 연구에서 고찰한 대부분의 희토류 인산염이 낮은 발광특성을 보이고 있으나, La_3PO_7 과 Gd_3PO_7 은 우수한 발광물질로 사용될 가능성이 높다.

1. INTRODUCTION

Several rare-earth phosphates have interesting luminescence when excited by ultraviolet radiation. The europium-activated yttria has been used as the red phosphor in color television tubes. The rare-earth orthophosphates have been widely used as host materials for the preparation of luminescent compou-

nds. A large number of europium activated rare-earth phosphate phosphors have been studied¹⁻⁹, but except for the work of Agrawal and Hummel¹¹, no systematic study of the luminescence of the intermediate compounds occurring in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$, $\text{Y}_2\text{O}_3\text{-P}_2\text{O}_5$, and in the $\text{Gd}_2\text{O}_3\text{-P}_2\text{O}_5$ systems has been investigated.

Bril and Wanmaker²¹ studied the properties of

europium-activated gadolinium phosphors and deduced from the excitation spectra that energy absorbed by gadolinium ions can be transferred to the europium ions. Wanmaker et al.³⁾ studied the properties of some europium-activated some rare-earth orthophosphates and found that the emission wavelengths and intensities depended strongly on small variations in the surroundings of the europium ion. Blasse⁴⁾ discussed the position of the ultraviolet absorption bands of Eu^{3+} and Bi^{3+} in LaPO_4 and YPO_4 . Ropp⁵⁾ studied the spectral properties of rare-earth oxide phosphors. He showed that the wavelength of emission lines was similar, but that the total energy efficiency and the intensity of the emission lines were influenced by changing the host material. He also studied the reflectance spectra of unactivated rare-earth orthophosphates and found that TbPO_4 and EuPO_4 produce luminescence when excited by radiation of the proper wavelength⁶⁾. Blasse and Brill⁷⁾ investigated the mechanism of energy transfer from Bi^{3+} and Ce^{3+} to Eu^{3+} in YPO_4 . Their results showed that energy transfer was observed in Bi^{3+} to Eu^{3+} , but no energy transfer in Ce^{3+} to Eu^{3+} . Nakazawa and Shiga⁸⁾ studied the luminescence-excitation spectra and diffuse reflection spectra of rare-earth orthophosphate phosphors with europium activator in the vacuum ultraviolet region. They concluded that the narrow excitation band at the absorption edge (145–160nm) of the hosts was assigned to an intramolecular transition of PO_4^{3-} ions.

Blanzat et al.⁹⁾ investigated the luminescence and spectral properties of some rare-earth pentaphosphates. They argued that Eu^{3+} occupied a site symmetry of c_2 that was determined from the position and intensity of emission lines. Agrawal and Hummel¹⁰⁾ studied the luminescent behavior of Eu^{3+} in the intermediate compounds of the Y_2O_3 - P_2O_5 and Gd_2O_3 - P_2O_5 systems. They showed that Eu^{3+} activated ortho- and penta-phosphates had moderate luminescent intensity, but other phosphate phosphors had no measurable luminescent intensity relative to the

standard phosphor $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$.

The purpose of this work is to investigate the luminescence of europium-activated lanthanum, yttrium and gadolinium phosphates.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Phosphors.

All the phosphors, except pentaphosphates were, prepared by solid state reactions using europium ion as activator. Intimate mixtures of high purity (99.9%) oxides and diammonium hydrogen phosphate were obtained by grinding in a porcelain mortar under acetone. After drying, the mixtures were pre-fired to drive out the volatiles (NH_3 and H_2O) and after another grinding procedure they were fired at an appropriate temperature. The rare-earth pentaphosphate phosphors were prepared by precipitation from phosphoric acid solutions at temperature ranging from 450°C to 750°C. The phase identification of the phosphors was checked by X-ray analysis using a Philips diffractometer equipped with an AMR focusing monochromator.

2.2. Luminescence Measurements.

All the samples used to make luminescence measurements were in powder form. The samples used for emission measurements were simply packed into circular brass holders and excited with 253.7 nm radiation from a filtered low-pressure mercury lamp. The emission spectra obtained using a Spex Mono 1402 double monochromator were recorded on magnetic tape using an Interdata 7/16 minicomputer-controlled emission spectroradiometer. The intensity of each sample was measured relative to that of a sodium salicylate standard. The emission spectra were read from the magnetic tapes, corrected for instrument response, and plotted on an x-y recorder, which was driven by the Interdata computer. The excitation spectra were obtained on powdered samples packed into sample holders having a silica glass window. Corrections for transmission of ultraviolet

radiation through the window were made by recording the excitation spectrum of a Rhodamine B dye solution. The excitation spectra were recorded with a Perkin-Elmer MPF-44A fluorescence spectrophotometer. To record the excitation spectra, the analyzer monochromator was set to the wavelength at which the maximum intensity of the emission occurred. If there were more than one strong peak in the emission spectrum, the excitation spectra were recorded at these different wavelengths to determine if more than one luminescence center were present.

3. RESULTS and DISCUSSION

3.1. Emission Spectra

All the 5 mole% europium-activated intermediate compounds in the three systems give a red or orange emission when excited under 253.7 nm radiation. The emission spectra were scanned from 560 nm to 720 nm. Table 1 gives the relative photon fluxes and the relative percentage intensities of three main groups of europium emission lines considering the intensity of the standard to be one hundred percentage. The emission spectra of europium-activated rare-earth

phosphates are shown in Fig.1. Three main groups of europium emission lines have been observed: one is 585 to 600nm(${}^6D_0-{}^7F_1$ transition), the second 610 to 625nm(${}^5D_0-{}^7F_2$ transition), and the third 680 to 705 nm(${}^5D_0-{}^7F_4$ transition). In general, all the yttrium phosphates have very low emission intensity. In oxyphosphate phosphors, $La_3PO_7 : Eu$, $La_2P_3O_{13} : Eu$ and $Gd_3PO_7 : Eu$, the red emission lines near 610–625

Table 1. The Relative Photon Fluxes and Relative Intensities of Different Transitions for the Europium Activated Phosphors. (Sodium Salicylate Standard Photon Flux and Peak Intensity is 100.)

Phosphors	Relative Intensities Photon Flux	${}^5D_0-{}^7F_1$	${}^5D_0-{}^7F_2$	${}^5D_0-{}^7F_4$
La_3PO_7	14.4	7.1	56.0	15.4
$La_2P_3O_{13}$	10.4	5.2	33.9	9.2
$LaPO_4$	45.9	73.1	44.4	103.0
$La(PO_3)_3$	23.2	32.7	56.9	86.0
LaP_5O_{14}	4.3	8.5	12.4	23.4
$Y_3P_2O_{17}$	13.3	4.1	17.9	8.9
Y_3PO_7	8.6	2.7	9.5	5.2
Gd_3PO_7	32.6	12.4	85.4	35.2
$GdPO_4$	38.9	93.1	41.8	90.7
$Gd_2P_4O_{13}$	31.4	73.1	37.1	69.5

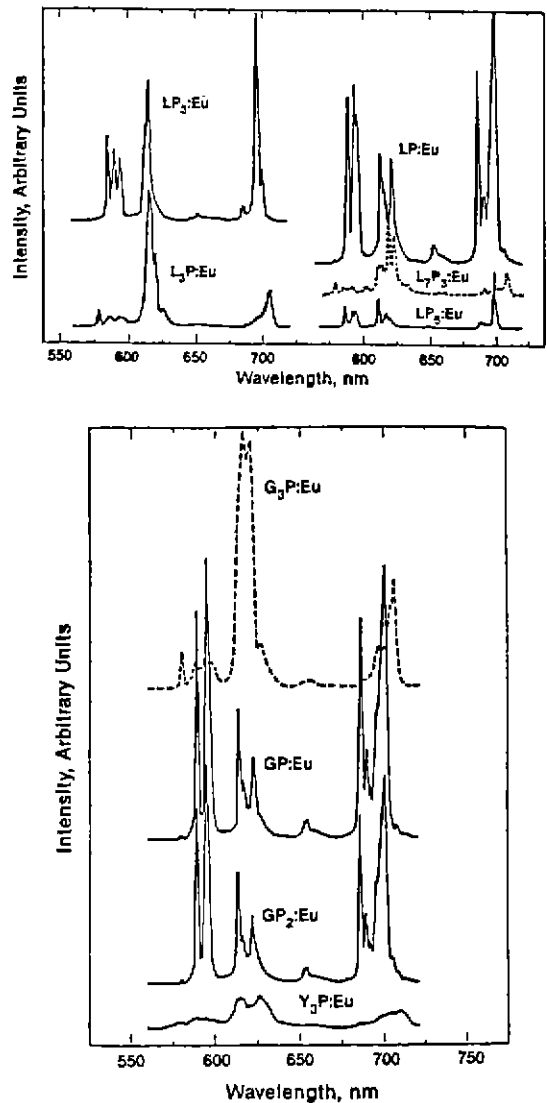


Fig.1. Europium emission spectra in rare-earth phosphates.

nm are predominant. However, in the others, $\text{LaPO}_4 : \text{Eu}$, $\text{GdPO}_4 : \text{Eu}$, $\text{Gd}_2\text{P}_4\text{O}_{13} : \text{Eu}$, $\text{La}(\text{PO}_3)_3 : \text{Eu}$ and $\text{LaP}_5\text{O}_{14} : \text{Eu}$, the deep red emission lines at 680–705nm and the orange lines at 580–600nm predominate. For commercial application, the emission should consist principally of the lines at 610–625nm. The phosphors prepared, which satisfy this requirement, are $\text{La}_3\text{PO}_7 : \text{Eu}$ and $\text{Gd}_3\text{PO}_7 : \text{Eu}$. In an

attempt to produce stronger europium emission, the Bi^{3+} or V^{5+} sensitizers were used in the LaPO_4 , La_3PO_7 , and Gd_3PO_7 compounds. The results are shown in Table 2 and Fig.2.

As may be seen from Table 2 and Fig.2, the emission spectra of bismuth or vanadate-sensitized phosphors do not change, but the sensitized phosphors are less efficient than unsensitized phosphors.

Table 2. Sensitization with Bi^{3+} or V^{5+} on Eu^{3+} Activated Phosphors.

Bi Addition	LaPO_4	La_3PO_7	Gd_3PO_7
0	198	57	129
5	94	26	115
10	75	26	102
V Addition (%)			
0	198	57	129
5	—	10	26
10	—	14	17

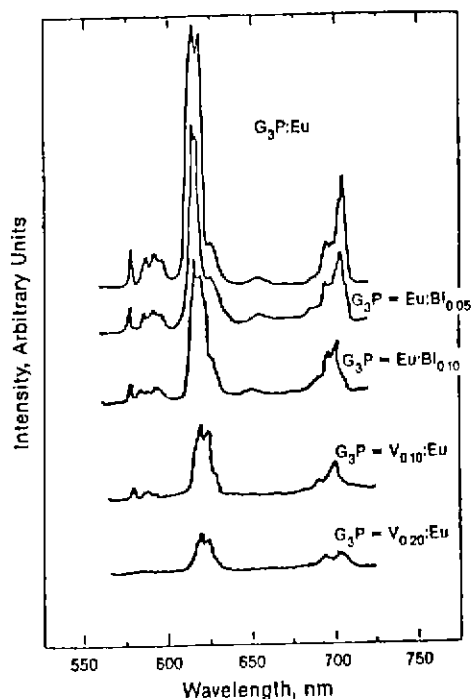
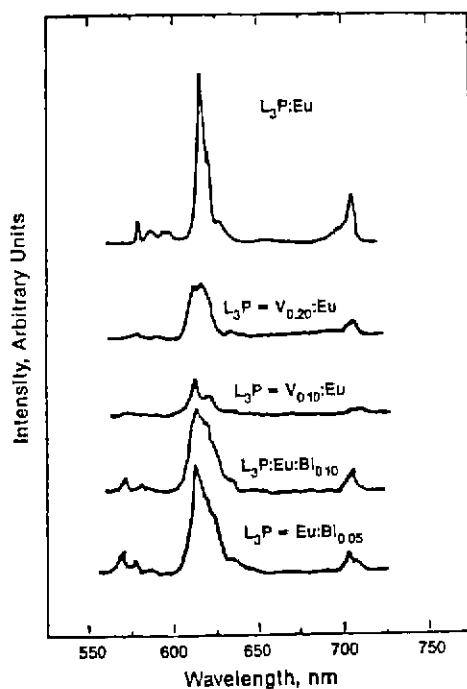
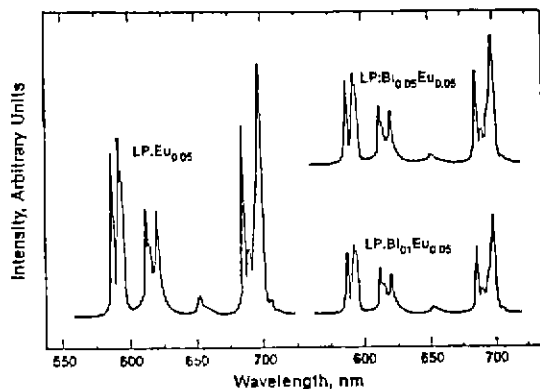


Fig.2. Europium emission spectra in LaPO_4 , Gd_3PO_7 , and La_3PO_7 with Bi^{3+} or V^{5+} sensitization.

Therefore Bi^{3+} absorbs the energy in a broad band centered at 250nm(Fig.3). The energy absorbed by bismuth is dissipated nonradiatively resulting in decreased efficiency of the europium emission. Partial substitutions of vanadate for phosphate decrease the emission of these phosphors. According to the Agrawal and Hummel¹¹, only ortho- and penta-phosphates have moderate luminescent intensity; the other phosphates have no measurable luminescent intensity relative to the ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ transition(613.5nm peak) of the standard phosphor $\text{Y}_2\text{O}_3\text{:Eu}$. However, our results concluded that the integrated intensities of $\text{LaPO}_4\text{:Eu}$, $\text{Gd}_3\text{PO}_7\text{:Eu}$, and $\text{GdPO}_4\text{:Eu}$ have moderate values, but $\text{La}_3\text{PO}_7\text{:Eu}$ and $\text{Gd}_3\text{PO}_7\text{:Eu}$ have moderate intensity at 615nm(${}^5\text{D}_0\text{-}{}^7\text{F}_2$ transition) relative to a sodium salicylate standard. These differences might be caused by the different wavelengths of excitation.

The emission peaks of the oxyphosphate phosphors are broader than those of the others. This broadening possibly arises since these compounds are structurally

disordered. The well-known europium emission is due to radiative transitions from the ${}^5\text{D}_0$ level to the ${}^7\text{F}_j$ manifold($j=0$ to 6). Symmetry center on the site of the europium ion is of importance. If such a center is present, the magnetic-dipole transition(${}^5\text{D}_0\text{-}{}^7\text{F}_1$) dominates. If inversion symmetry is absent, the forced electric dipole transitions(${}^5\text{D}_0\text{-}{}^7\text{F}_j$; $j=2, 4, 6$) are allowed. In $\text{GdPO}_4\text{:Eu}$, $\text{Gd}_2\text{P}_2\text{O}_7\text{:Eu}$, and $\text{LaPO}_4\text{:Eu}$, the magnetic-dipole transition dominates with the forced electric-dipole transition still having moderate intensity; this implies that the europium ion occupies a site symmetry that does not have pure inversion symmetry. The oxyphosphate($\text{La}_7\text{P}_3\text{O}_{18}$, La_3PO_7 , Gd_3PO_7 , Y_3PO_7 and $\text{Y}_4\text{P}_2\text{O}_{17}$) phosphors have no inversion symmetry since the magnetic-dipole transition peak is very weak. The ${}^5\text{D}_0\text{-}{}^7\text{F}_0$ transition is strongly forbidden, being a $j=0$ to $j=0$ transition, but $\text{La}_3\text{PO}_7\text{:Eu}$, $\text{Gd}_3\text{PO}_7\text{:Eu}$, and $\text{La}_7\text{P}_3\text{O}_{18}\text{:Eu}$ phosphors have weak band at 580nm due to highly forbidden ${}^5\text{D}_0\text{-}{}^7\text{F}_0$ transition. In order to explain the appearance of

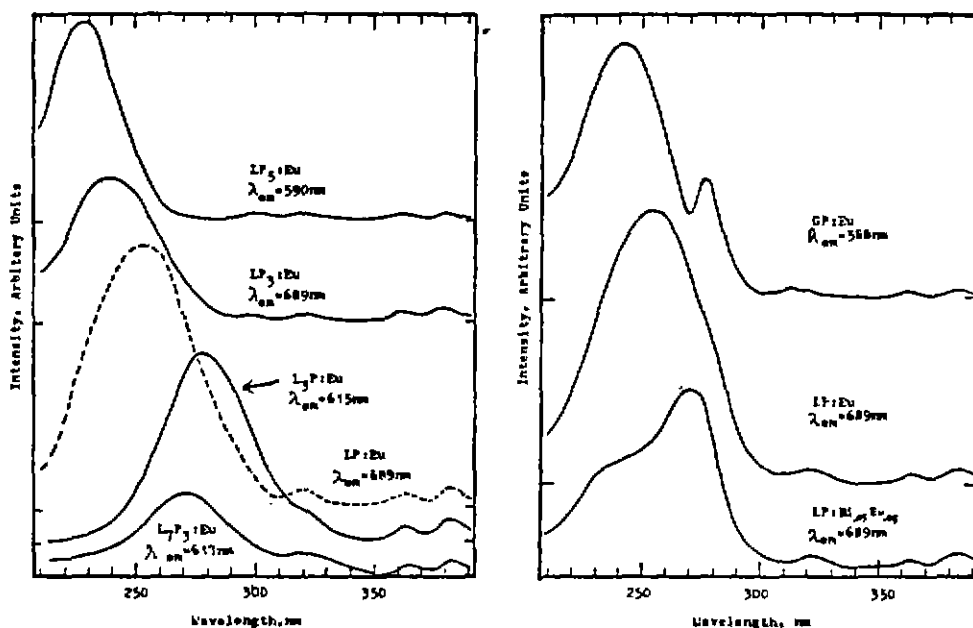


Fig. 3. Excitation spectra of europium-activated lanthanum phosphates and gadolinium orthophosphate.

this band in the emission spectra of europium ion, Nieuwpoort and Blasse¹¹⁾ concluded that the transition could occur if the europium ion occupied a site symmetry, which allows a linear crystal field term (i. e., symmetries of C_s , and $C_{n\nu}$). The site symmetry of europium ion in these compounds is not yet known, but it might belong to one of the C_s or $C_{n\nu}$ symmetries.

Excitation Spectra

The excitation spectra of europium-activated lanthanum phosphates and gadolinium orthophosphate are shown in Fig.3. The spectra consist of several broad bands. The broad band located between 220nm and 290nm corresponds to a charge transfer transition in which an electron is promoted from the highest filled oxygen orbital to the 4f shell of the europium ion. These charge transfer bands shift to shorter wavelengths as the amount of phosphate is increased, indicating that the binding energy of electrons to the phosphate anions increases as the molecular weight of the anions increases, which is shown in Fig.4. The

oxyphosphates and orthophosphates contain isolated $(\text{PO}_4)^{-3}$ ions, the metaphosphates, $\text{Ln}(\text{PO}_3)_3$, contain ring anions of $(\text{P}_3\text{O}_9)^{-3}$, and the pentaphosphates contain infinite double chain anions. In addition to the charge transfer band, some weak excitation peaks are also found at wavelengths of 320nm, 365nm, and 385 nm. These peaks correspond to direct excitation of the europium ions. In gadolinium orthophosphate phosphor, the excitation spectrum of the europium emission shows a sharp peak at 275nm corresponding to the $^8\text{S}-^6\text{I}$ transition in the gadolinium ions. This is an example of energy transfer from gadolinium ion to europium ion, which has been reported for other phosphors²¹⁾. As can be seen from Fig.3, bismuth-sensitized lanthanum orthophosphate phosphor has maximum peak at 270nm, corresponding to bismuth absorption band. This is an example of the energy transfer from bismuth ion to europium ion, but its efficiency is very low since the intensity of europium emission is decreased, which is shown in Fig.2.

4. SUMMARY

Luminescent properties of 5 mole% europium-activated intermediate compounds in the three systems, $\text{Y}_2\text{O}_3\text{-P}_2\text{O}_5$, $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$, and $\text{Gd}_2\text{O}_3\text{-P}_2\text{O}_5$, are studied. Most of the europium-activated rare-earth phosphates have low efficiencies, but La_3PO_7 and Gd_3PO_7 hosts are possible for commercial luminescent materials. In bismuth or vanadate-sensitized La_3PO_7 and Gd_3PO_7 phosphors, in order to improve efficiencies, the emission spectra of them are not changed, but the sensitized phosphors are less efficient than unsensitized phosphors. The excitation spectra consist of a big broad band located between 220nm and 290nm, corresponding to a charge transfer of the europium ion. These charge transfer bands shift to shorter wavelengths as the amount of phosphate is increased.

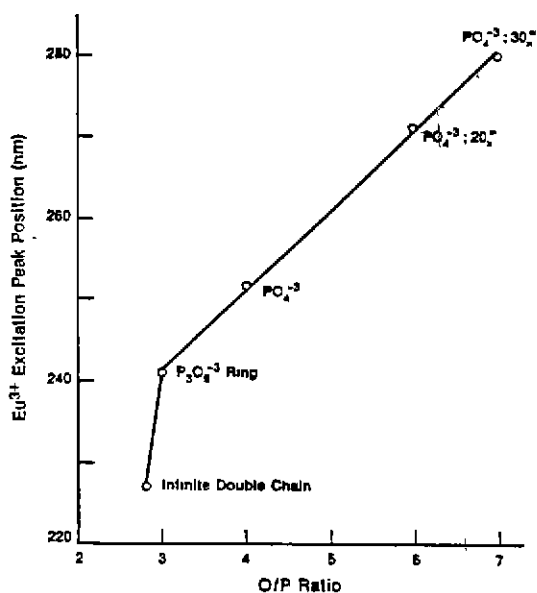


Fig.4. Effect of O/P ratio on O^{2-} to Eu^{3+} charge transfer band.

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REFERENCES

1. D.K. Agrawal and F.A. Hummel, "Phase-Relationships, Vibrational Spectra and Luminescence Studies in Rare-Earth(Yttrium, Gadolinium) Phosphate," PhD. Thesis, Pennsylvania State University(1979), University Microfilms International #8010013.
2. A. Bril and W.L. Wanmaker, "Fluorescent Properties of some Europium-Activated Phosphors," *J. Electrochem. Soc.*, **111** (12) 1363-1368 (1964).
3. W.L. Wanmaker, A. Bril, J.W. ter Vrugt, and J. Broos, "Luminescent Properties of Euctivated Phosphors of the type $A^{III}B^VO^V$," *Philips Res. Repts.*, **21**, 270-282 (1966).
4. G. Blasse, "The Ultraviolet Absorption Bands of Bi^{3+} and Eu^{3+} in Oxides," *J. Solid State Chem.*, **4**, 52-54 (1972).
5. R.C. Ropp, "Phosphors Based on Rare-Earth Phosphates I," *J. Electrochem. Soc.*, **115** (8) 841-845 (1968).
6. R.C. Ropp, "Phosphors Based on Rare-Earth Phosphates II," *J. Electrochem. Soc.*, **116** (5) 623-629 (1969).
7. G. Blasse and A. Bril, "Study of Energy Transfer from Sb^{3+} , Bi^{3+} , Ce^{3+} to Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} ," *J. Chem. Phys.*, **47** (6) 1920-1926 (1967).
8. E. Nakazawa and F. Shiga, "Vacuum Ultraviolet Luminescence-Excitation Spectra of $RPO_4 \cdot Eu^{3+}$ ($R=Y, La, Gd$ and Lu)," *J. Luminescence*, **15**, 255-259 (1977).
9. B. Blanzat, J.P. Dennis and J. Lories, "Luminescence, Structural Properties and Energy Transfer Mechanisms in some Rare-Earth Ultraphosphates," Proc. Rare Earth Res. Conf., 10th 1973, 2(CONF-730402-P2), 1170-1177.
10. G. Blasse, A. Bril and W.C. Nieuwpoort, "On the Eu^{3+} Fluorescence in Mixed Metal Oxides. I. the Crystal Structure Sensitivity of the Intensity Ratio of Electric and Magnetic Dipole Emission," *J. Phys. Chem. Solids*, **27** (10) 1587-1592 (1966).
11. W.C. Nieuwpoort and G. Blasse, "Linear Crystal-Field Terms and the 5D_0 - 7F_0 Transition of the Eu^{3+} Ion," *Solid State Commun.*, **4** (5) 227 (1966).