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Luminescence of Eu^{2+}- and Pb^{2+}-Activated Alkaline-Earth Oxyhalides M_4OX_6 (M = Ca, Sr, Ba; X = Cl, Br)

W. J. Schipper,* Z. A. E. P. Vroon, and G. Blasse

Debye Research Institute, University of Utrecht, P.O. Box 80.000,
3508 TA Utrecht, The Netherlands

Th. Schleid and Gerd Meyer

Institut für Anorganische Chemie, Universität Hannover, Callinstr. 9,
D-3000 Hannover, Germany

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The luminescence properties of $Ba_{3.96}Eu_{0.04}OCl_6$, $Ba_{3.96}Eu_{0.04}OBr_6$, $Sr_{3.96}Eu_{0.04}OCl_6$, $Sr_{3.96}Eu_{0.04}OBr_6$, $Ca_{3.96}Eu_{0.04}OCl_6$, Eu_4OCl_6, and Eu_4OBr_6 are reported and discussed. All compositions show an efficient blue emission under UV and X-ray excitation. From the similarity of the luminescence properties of these materials, it is concluded that the luminescence properties of Eu^{2+} are strongly determined by the oxide ion in the crystal structure. In Eu_4OCl_6 and Eu_4OBr_6 no concentration quenching of the luminescence is observed. The luminescence properties of the alkaline-earth oxyhalides doped with lead are also reported. The Pb^{2+} ion exhibits a blue emission in the strontium oxyhalides. In addition a red emission of unknown nature is observed.

Introduction

In a preliminary paper we reported on the emission and thermoluminescence properties of europium-activated alkaline-earth oxyhalides of the type M_4OX_6.[1] These materials are promising storage phosphors. In this paper the luminescence properties of these compounds are described in more detail and a comparison is made with the pure europium compounds Eu_4OCl_6 and Eu_4OBr_6.[2] All these compounds are isostructural; the structure contains tetrahedral $[M_4O]$ units.[3-5] There are two cation sites with C_{3v} symmetry, which are highly asymmetric: one is coordinated by nine halide ions and one oxide ion, the other by seven halide ions and one oxide ion. Because of this asymmetric coordination, it seemed interesting to study the luminescence of Pb^{2+} in these hosts as well. Ions with s^2 configurations in asymmetrical sites are known to luminesce efficiently with a large Stokes shift.[6]

Experimental Section

The europium-doped alkaline-earth compounds and the pure europium compounds were prepared as powders in tantalum tubes following a procedure described before.[1]

It is also possible to prepare the alkaline-earth oxyhalides by firing stoichiometric amounts of the appropriate halide and nitrate with europium sesquioxide or trihalide at 700 °C under a 5% hydrogen/95% nitrogen flow for 4 h. Powder samples prepared in this way show Eu^{2+} emission with about the same efficiency as the samples prepared in a tantalum tube but contain a small amount of trivalent europium as well.

The lead-doped materials were prepared analogously under nitrogen atmosphere, with Pb^{2+} added as the nitrate. We tried in vain to prepare Pb_4OCl_6 and Ca_4OBr_6 in this way, although the existence of the latter compound has been reported by Frit et al.[7] Samples were checked by X-ray powder diffraction; no other phases were found. Photoluminescence measurements were performed on a SPEX DM3000F spectrofluorometer with two double-grating 0.22-m SPEX 1680 monochromators. This setup is equipped with an Oxford Instruments liquid helium flow cryostat. Decay measurements were performed on a Nd:YAG laser equipped with a frequency-doubled dye laser (setup described in ref 8) and on a Lambda-Physik LPX 105 xenon chloride excimer laser (308 nm). Direct X-ray spectra were recorded using a tungsten Siemens Monodor M. Iontomat X-ray source operating at 85 kV, 26 mA, equipped with a 21-mm aluminum filter.

Table I. Maxima of the $4f^6(^7F_0)5d$ Excitation and Emission Bands (cm^{-1}) of M_4OX_6:Eu^{2+} at 4.2 K

	exc	em	Stokes shift
$Ca_{3.96}Eu_{0.04}OCl_6$	23 950	21 280	2670
$Sr_{3.96}Eu_{0.04}OCl_6$	24 520	22 320	2200
$Sr_{3.96}Eu_{0.04}OBr_6$	24 260	21 830	2430
$Ba_{3.96}Eu_{0.04}OCl_6$	24 800^a	21 930	~2900
$Ba_{3.96}Eu_{0.04}OBr_6$	24 600^a	21 690	~2900
Eu_4OBr_6	23 800^a	21 000	~2800
Eu_4OCl_6	23 900^a	21 140	~2800

^{a} Estimated.

Results

Eu^{2+} Luminescence. All Eu^{2+}-doped compounds show efficient blue emission at room temperature under UV and X-ray excitation. The emission spectra are the same for either way of excitation. The luminescence is ascribed to a $4f^65d$–$4f^7$ transition on the Eu^{2+} ion. This ion is known to luminesce efficiently in this spectral region in a number of hosts.[9-11] The emission spectrum at 4.2 K consists of a single band in all cases in spite of the fact that there are two sites available for the metal ions. The composition of each sample and the position of the maximum of the emission band are given in Table I. The emission spectrum of $Ba_{3.96}Eu_{0.04}OBr_6$ is given in Figure 1 as a representative example.

The excitation spectrum of the emission of $Sr_{3.96}Eu_{0.04}OBr_6$ at 4.2 K is given in Figure 2. For all compositions the excitation spectrum is the same for all wavelengths of the emission band. In the excitation spectra fine structure is observed at liquid helium temperature. This structure is due to the splitting of the lowest excitation band by spin–orbit coupling in the $4f^6$

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* To whom correspondence should be addressed.

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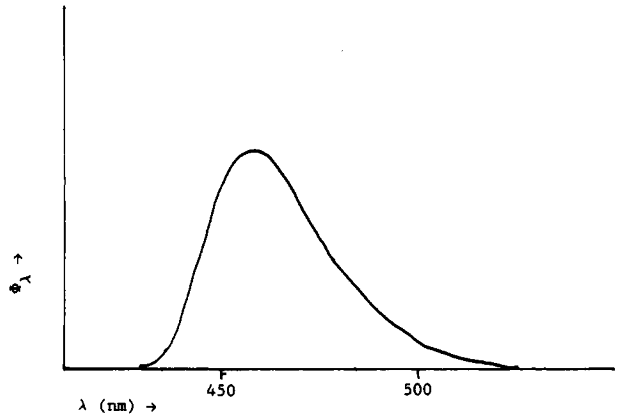

Figure 1. Emission spectrum of $Ba_{3.96}Eu_{0.04}OBr_6$ powder at 4.2 K for λ_{exc} = 300 nm. Φ_λ denotes the radiant power per constant wavelength interval in arbitrary units.

Figure 2. Excitation spectrum of the emission of $Sr_{3.96}Eu_{0.04}OBr_6$ at 4.2 K. The calculated $^7F_{0-6}$ levels of the $4f^65d$ state are indicated. The arrow indicates the Fano antiresonance dip. q_r denotes the relative quantum output. The inset shows the Fano antiresonance profile for $Ba_{3.96}Eu_{0.04}OCl_6$. Here the dip is more clear, since the ^7F_J sublevels are smeared out.

core. The $^7F_{0-6}$ levels of the $4f^6$ core, derived from data for $Eu^{3+}(4f^6)$, are indicated in Figure 2; the agreement is seen to be good.

The knowledge of the position of the $4f^6(^7F_0)5d$ level, the lowest excited level, allows the calculation of the Stokes shift. This is possible only for the strontium and calcium compounds. The Stokes shift for the barium and europium compounds can only be estimated due to the absence of clear fine structure. The position of the $4f^6(^7F_0)5d$ level was estimated by comparison of the shape and the onset of the excitation spectra to those of the strontium compounds. Results are given in Table I.

The luminescence efficiency of the alkaline-earth oxyhalides at 4.2 K and room temperature is the same. The concentrated compounds Eu_4OCl_6 and Eu_4OBr_6 also do not show pronounced temperature quenching; the emission intensity decreases only by a few percent going from 4.2 K to room temperature. The emission intensity of these compounds is high. The decay time of the emission of Eu_4OCl_6 at room temperature is 0.39 μs, whereas the decay time of the diluted systems is about twice as long, viz. 0.79 μs for Ba_4OCl_6:Eu^{2+}. The decay curve for Eu_4OCl_6 shows a slight deviation from single exponentiality. Nevertheless, we can conclude that concentration quenching of the luminescence does not play an important role in these europium compounds.

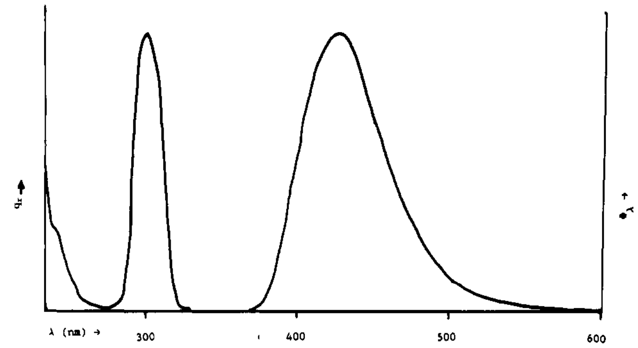

Figure 3. Blue emission band of $Sr_{3.96}Pb_{0.04}OCl_6$ (λ_{exc} = 308 nm) and its excitation spectrum (λ_{em} = 440 nm) at 4.2 K.

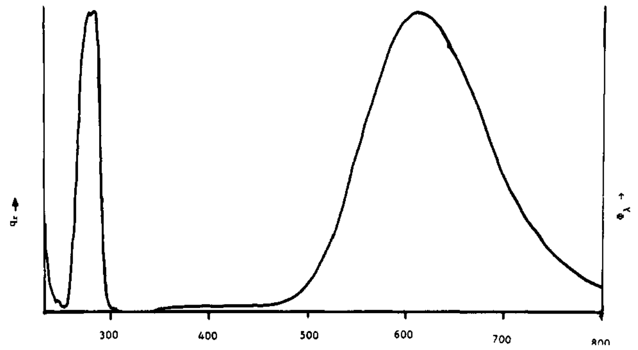

Figure 4. Red emission band of $Sr_{3.96}Pb_{0.04}OCl_6$ (λ_{exc} = 280 nm) and its excitation spectrum (λ_{em} = 600 nm) at 4.2 K.

Table II. Excitation and Emission Band Maxima (cm^{-1}) of Lead-Doped Strontium Oxyhalides at 4.2 K

	blue luminescence			red luminescence		
	exc	em	Stokes shift	exc	em	Stokes shift
$Sr_{3.99}Pb_{0.01}OCl_6$	32 790	23 260	9530	35 710	16 390	19 320
$Sr_{3.99}Pb_{0.01}OBr_6$	30 770	21 740	9030	36 360	16 670	19 690

Pb^{2+} Luminescence. For $Sr_{3.96}Pb_{0.04}OCl_6$ two emission bands are observed at 4.2 K, one peaking at 430 nm and the other at 600 nm (Figures 3 and 4). The intensity of these emission bands is of the same order of magnitude (comparison made at equal excitation photon density). The excitation spectra of these bands are different (Figures 3 and 4). Both emissions occur in the same intensity ratio at all Pb concentrations studied (0.01–1%). This excludes the possibility of Pb pairs causing the red emission. No second phase was found in the X-ray diffraction patterns, and synthesis of the samples with 20% excess of either of the starting materials does not influence the intensity ratio of the bands. The bands are not the product of a photochemical reaction since their intensity does not change in time under irradiation. Also, these emissions are not observed in undoped samples.

For lead-doped strontium oxybromide similar observations are made (Table II). At 4.2 K the barium analogues show only a weak red and blue emission; at room temperature the emission is almost absent, which is in marked contrast to the strontium compounds. The excitation of the red emission now occurs at lower energies than that of the blue one, but due to the low efficiency no reliable results could be obtained; therefore the barium compounds have not been investigated further.

The position of the maximum of the emission bands in $Sr_{3.96}Pb_{0.04}OCl_6$ is temperature dependent. The blue band shifts from 430 to 460 nm between 50 and 80 K. At higher temperatures the maximum shifts back to about 430 nm. There is no decrease of intensity over this temperature range. The maximum of the red band shifts to shorter

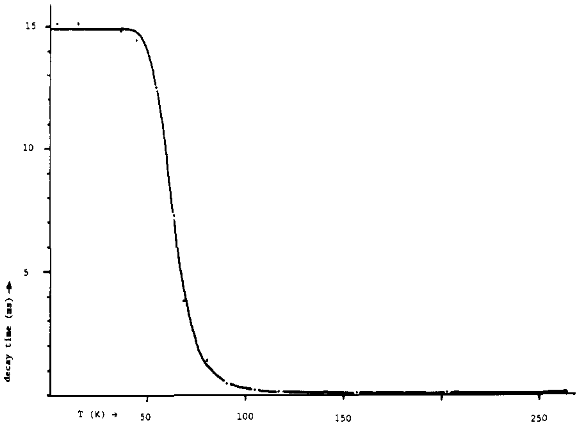

Figure 5. Temperature dependence of the decay time of the blue emission in Sr_4OCl_6:Pb^{2+}. The drawn curve represents a fit discussed in the text.

wavelengths as the temperature increases (from 610 nm at 4.2 K to 550 nm at room temperature). At room temperature the intensity has dropped to about 60% of the original value.

The decay time of the blue emission is plotted as a function of temperature in Figure 5. All decays were single-exponential. The temperature dependence observed is typical for s^2 ions and can be described by a three-level scheme with ground state $^1S_0$ and excited states $^3P_0$ and $^3P_1$, the $^3P_0$ level being metastable.[12] When the temperature increases, the decay time is seen to drop from 15 ms at 4.2 K to 2.4 μs at room temperature. A three-level fit applied to the temperature dependence of the decay time yields an energy difference between the $^3P_0$ and $^3P_1$ levels of 494 ± 9 cm^{-1}. The transition probability from the $^3P_1$ level to the ground state was found to be 5×10^6 s^{-1}, whereas that from the $^3P_0$ level amounts to 67 s^{-1}. Both values are about 1 order of magnitude lower than usually observed for Pb^{2+}.[13] The resulting curve is shown in Figure 5 and gives a good fit to the data.

The decay curve of the red emission is nonexponential at 4.2 K, but above 50 K the decay time is single-exponential. At 50 K its value amounts to 45 μs; this value drops to 15 μs at room temperature.

Discussion

Eu^{2+} Luminescence. Table I shows that the influence of the host lattice on the luminescence properties of Eu^{2+} in the M_4OX_6 series is small.

The position of the $4f^6(^7F_0)5d$ level in the excitation spectra increases in energy in the order Ca < Sr < Ba. Such an effect has been reported before and can be explained by a crystal-field effect: in a smaller cation site the crystal field will be stronger, and hence the lowest $4f^65d$ level will be lower in energy.[10,14] The position of this level is determined not by the crystal-field strength alone but also by the amount of covalency (nephelauxetic effect). Its dependence on M in the [M_3OEu] tetrahedron is not easy to predict. The nephelauxetic effect causes the excitation cutoff of the oxybromides to somewhat lower in energy than the corresponding chlorides.

In the concentrated system the excitation onset is lower in energy than in the strontium compounds (where the cations have about the same size as Eu^{2+}), indicating some interactions between the europium ions. The shape of the excitation spectra of the concentrated compounds is different from that of the diluted systems. The difference is ascribed to a considerably higher absorption strength.

The excitation spectra of the diluted systems show dips around 320 nm (see arrow in Figure 2). These are ascribed to Fano antiresonance between the $4f^65d$ level and the ^6D_J levels of the $4f^7$ configuration.[15] Because the background cannot be estimated reliably, a detailed analysis is not possible.

The values of the Stokes shift are larger than the Stokes shifts derived in the same way for divalent europium in alkaline-earth haloborates (520–1560 cm^{-1} (ref 16)) and barium bromosilicate (750 cm^{-1} (ref 17)). Due to the absence of groups like borate and silicate, the surroundings of the europium ion in the M_4OX_6 lattice are less rigid. This will allow a larger relaxation after excitation, resulting in a larger Stokes shift.[18]

In the oxyhalide series, the Stokes shift is smallest in the strontium compounds. The values for $Ca_{3.96}Eu_{0.04}OCl_6$ and the barium compounds are larger and comparable to each other within the experimental error. The fact that the Stokes shift is not solely governed by the size of the cation in the host lattice indicates that there are two counteracting effects. In fact, the Stokes shift is governed by two factors: the space available for the luminescent ion at the cation site and the stiffness of the lattice (related to the polarizability of the neighboring cations).[18] The equilibrium distance between the europium ion and its ligands decreases after excitation. In the series Ca^{2+}–Sr^{2+}–Ba^{2+}, where the cation size increases and the lattice stiffness decreases in this order, there are therefore two effects that counteract each other: in a barium compound the lower stiffness causes a larger Stokes shift, but the larger cation site causes a smaller Stokes shift. The former effect will have a marked influence only in the absence of structure elements which give stiffness to the lattice as in the present case.[18] This explains why the Stokes shift is larger for the barium oxyhalides: a higher lattice relaxation is possible due to the relative softness of the barium ions. Here the structural unit [Ba_3OEu] should be kept in mind: the barium ions are close to the luminescent center. In calcium oxychloride[5] the small cation site causes the Stokes shift to be larger than in the strontium compounds, as is usually observed.

Since the luminescence properties of the europium ion are only slightly influenced by the choice of M^{2+} in the M_4OX_6 host lattice and since there is no detectable difference in luminescence between europium ions on the two different cation sites, the luminescence properties seem to be mainly determined by the oxide ion in the center of the [M_3OEu] tetrahedron. With Pauling's rule[19] it can be found that the oxide ion is undersaturated. This implies a strong chemical bonding between Eu^{2+} and O^{2-}. If a strong chemical bonding in the Eu–O complex is assumed, the lowest lying 5d orbital will be either nonbonding or weakly δ-antibonding; its energy will be influenced less by the oxide ion than the energy of the other d-orbitals. Since the position of the $4f^7$ ground state is certainly not influenced, the luminescence transitions are indeed expected to be independent of the composition of the host lattice. We note in passing that a similar asymmetric coordination as in M_4OX_6 has recently been found in $Ba_5SiO_4Br_6$.[20]

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The luminescence properties of Eu^{2+} in this lattice show a striking similarity to those of M_4OX_6:Eu^{2+}. Both materials are efficient photostimulable storage phosphors.

Let us now consider the compounds Eu_4OX_6 in more detail. These compounds luminesce efficiently at room temperature with decay times only slightly shorter than those of the diluted systems. Therefore, energy migration is not efficient enough to reach quenching sites in the lattice.

Energy migration is expected to be of a complicated nature: energy transfer within the $[Eu_4O]$ tetrahedron is expected to be much faster than transfer to a neighboring tetrahedron (at a larger distance). For the calculation the spectral overlap was estimated from the room-temperature excitation and emission spectra of Eu_4OCl_6; its value was found to be 0.12 eV^{-1}. The total Eu^{2+} f-d oscillator strength was assumed to be 0.01. The lowest $4f^65d$ level with which the spectral overlap occurs contributes less than 10% to the total first 4f-5d band, so that the oscillator strength involved is less than 10^{-3}. With this value a critical distance for energy transfer of 13 Å was calculated.[21]

From the formula[21]

$$P_{\text{transfer Eu-Eu}} = (R_c/R_{\text{Eu-Eu}})^6 \times P_{\text{rad,Eu}}$$

with $P_{\text{rad,Eu}} = 1.2 \times 10^6$ s^{-1}, an Eu-Eu transfer rate of about 10^9 s^{-1} is found for transfer between europium ions in the $[M_4O]$ tetrahedron ($R_{\text{Eu-Eu}} = 3.8$ Å[22]). As this calculation does not take energy transfer by exchange into account, which is expected to be efficient at 3.8 Å, the transfer rate is probably even higher. As a result, the excitation energy can be thought of as smeared out over the tetrahedron on the time scale of transfer to another tetrahedron. The distance between the centers of the tetrahedra is 6.5 Å. In this way the transfer rate between two tetrahedra is estimated to be 10^8 s^{-1} or less. The calculated value is 2 orders of magnitude faster than the radiative decay time of the europium ion. The mean migration length is then about 60 Å; within this distance there are obviously only a few effective quenchers, i.e. defects or impurities that accept the excitation energy with a rate faster than the transfer rate. Therefore it is concluded that migration can take place, but its range is restricted.

Pb^{2+} Luminescence. In Pb^{2+}-doped Sr_4OCl_6 samples a blue and a red emission band are observed. A blue lead emission is quite common but a lead emission in the red spectral region and with such a large stokes shift (17 000 cm^{-1}) is unusual, although it has been observed in $PbGa_2O_4$[6] and recently in $RbPb_2Cl_5$.[23] A blue emission similar to the one observed here has been found in $PbCl_2$. This emission was ascribed to 6s-6p transition on an extrinsic lead site in which one of the coordinating chloride ions has been replaced by an oxide ion.[24] In ref 7 it is shown that the metal sites in the M_4OX_6 structure can be derived from the metal site in $BaCl_2$, which is isostructural with $PbCl_2$, by replacing one of the chloride ions by an oxide ion. Since the extrinsic site in $PbCl_2$ and the intrinsic sites in the M_4OX_6 structure are similar, we ascribe the emission band at 430 nm to emission from the 6s6p ($^3P_{1,0}$) levels of the lead ion. This is confirmed by the temperature behavior of the decay time of this emission which is typical for s^2 ions; this is not the case for the red emission.

The excitation spectrum of the blue emission consists of two bands. The band at 310 nm is ascribed to the transition to the $^3P_1$ level; the onset of the transition to the $^1P_1$ level can be seen at wavelengths shorter than 270 nm. The energy difference between the $^1P_1$ and $^3P_1$ levels is estimated to be 10 000 cm^{-1}, a common value.[13] In the oxybromide the $^3P_1$ excitation is at lower energy which is ascribed to the stronger nephelauxetic effect of the bromide ion.

From the temperature dependence of the decay time it is found that the energy difference between the lowest and one-but-lowest excited state is about 500 cm^{-1}. About the same value was found in $PbAl_2O_4$ and $PbGa_2O_4$.[6] The transition probabilities for the $^1S_0$-$^3P_{0,1}$ transitions are both lower than usual. Since the $^1S_0$-$^3P_0$ transition borrows its intensity from the $^1S_0$-$^3P_1$ transition, the fact that both values are low is not surprising. If we assume that the luminescence transitions are localized in a Pb-O complex due to strong Pb-O bonding, we can distinguish two sets of molecular orbitals: those with A_1 symmetry (composed of 6s and $6p_z$ on Pb^{2+} and $2p_z$ on O^{2-}) and those with E_1 symmetry (composed of $6p_x$,$6p_y$ on Pb^{2+} and $2P_x$,$2p_y$ on O^{2-}) taking the point group $C_{\infty v}$ for the Pb-O complex. The former are σ-bonding, the latter π-bonding. The 6s-6p transition will be a transition from a σ^* orbital to a π^* orbital. This transition may well be spatially restricted, so that the transition probability is relatively low.

Since the blue emission can be successfully ascribed to intrinsic lead ions, the red emission must be of a different nature. The behavior of the decay time excludes that this emission is due to isolated lead ions. Although our experiments seem to exclude that the red emission should be ascribed to lead ions in a second phase or to Pb^{2+} ion pairs, it cannot be excluded that it is caused by a lead oxychloride phase, possibly on the surface. Since the red emission is excited efficiently in a region where the main phase shows strong absorption according to the reflection spectra, a surface impurity is an obvious possibility.

Another possible explanation for the red luminescence is a charge-transfer (CT) transition. Since the oxide ion is undersaturated, a low-lying oxide-lead charge-transfer state does not seem unrealistic. With such an assignment it can be understood why the position of the excitation band of the red emission is more strongly influenced by the choice of the cation than by the choice of the halide ion. The three M^{2+} cations in the $[M_3OPb]$ tetrahedron will certainly influence the position of an oxide-lead charge-transfer transition if a strong Pb-O bonding is assumed. When the potential energy curve of the CT excited state in the configurational coordinate model is lowered, the luminescence is more easily quenched. Indeed the excitation and emission energy of the red luminescence are lower in the barium compounds than in the strontium compounds, and strong quenching occurs.

A charge-transfer transition from Br^- to the $6s^2$ ion Bi^{3+} has been observed before with decay times similar to those of the present red emission.[25] A halide-lead CT seems unlikely in the present case, since the CT excitation is at almost the same spectral position in strontium oxybromide and strontium oxychloride. In this assignment it remains to be explained why the red and blue emissions can be excited separately, since some population from the blue to the red emitting state is to be expected, especially at higher temperatures.[25] Therefore we feel that the nature

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of the red emission remains a problem.

Conclusions

Europium-doped alkaline-earth oxyhalides and the pure compounds Eu_4OCl_6 and Eu_4OBr_6 show efficient blue emission under excitation with UV and X-rays. Because the excitation and emission spectra of all these compounds are similar, it is concluded that the luminescence properties of Eu^{2+} in this structure are mainly governed by the oxide anion in the [M_4O] tetrahedron, although some influence of the halide is observed. Due to a relatively small spectral overlap there is no concentration quenching in Eu_4OCl_6 and Eu_4OBr_6. In the alkaline-earth oxyhalides the Pb^{2+} ion shows emission in the blue. In addition to this emission there is a broad, strongly Stokes-shifted red emission, the nature of which remains obscure.

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Registry No. $Ca_{3.96}Eu_{0.04}OCl_6$, 140225-34-9; $Sr_{3.96}Eu_{0.04}OCl_6$, 140225-35-0; $Sr_{3.96}Eu_{0.04}OBr_6$, 140225-36-1; $Ba_{3.96}Eu_{0.04}OCl_6$, 140225-37-2; $Ba_{3.96}Eu_{0.04}OBr_6$, 140225-38-3; Eu_4OBr_6, 12506-22-8; Eu_4OCl_6, 12506-73-9; $Sr_{3.99}Pb_{0.01}OCl_6$, 140225-39-4; $Sr_{3.99}Pb_{0.01}OBr_6$, 140225-40-7; Eu^{2+}, 16910-54-6; Pb^{2+}, 14280-50-3.

Epoxidized Triglycerides as Renewable Monomers in Photoinitiated Cationic Polymerization

J. V. Crivello* and R. Narayan

Department of Chemistry, Polymer Science and Engineering Program, Rensselaer Polytechnic Institute, Troy, New York 12180

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A wide variety of epoxidized triglyceride oils was examined as renewable monomers in photoinitiated cationic polymerization. Unsaturated triglyceride oils were obtained from commercial sources and exhaustively epoxidized and characterized by chemical and spectroscopic methods. The oils were photopolymerized as thin films using diaryliodonium and triarylsulfonium salt photoinitiators bearing long-chain alkoxy substituents. The course of the photopolymerizations was monitored using differential scanning photocalorimetry. The effects of the structures of both the cation and the anion of the photoinitiator on the polymerization rates were investigated. The photopolymerization rates were also found to be dependent on the structure and epoxy content of the monomers. The photopolymerized polymer networks were characterized by thermal analysis as well as by mechanical techniques.

Introduction

One of the current challenges in polymer chemistry today is to develop polymeric materials which are environmentally compatible. Ideally, such materials should have their origins in renewable sources.[1] Monomers derived from botanical sources are particularly attractive. It would also be advantageous if the monomers could be converted to polymers with worthwhile properties by environmentally acceptable methods. Thus, processes are sought which employ rapid, energy efficient, nonpolluting polymerization techniques. Finally, the resulting polymers should be biodegradable such that these materials constitute minimal potential accumulation problems in the environment. Biodegradation by adventitious organisms present in the environment is desirable; however, it would be much more attractive if such materials could be largely recovered and reused, for example, by fermentation techniques. Clearly, the discovery of polymers and polymerization processes possessing all of the above attributes simultaneously is improbable, but efforts toward achieving a substantial portion of the goals outlined above are already in progress in a number of academic and industrial laboratories.

The recent focus of research activity in this laboratory has been directed toward the investigation of various aspects of the photoinitiated cationic polymerization of epoxides using various photosensitive onium salts.[2] Photoinitiated polymerizations in general and photoinitiated cationic polymerizations in particular are highly attractive techniques for many thin-film applications such as inks, coatings, and adhesives. Using photoinitiated cationic polymerizations, it is possible to prepare cross-linked polymer films from multifunctional epoxy and vinyl ether monomers at a high speeds, with approximately one-tenth the expenditure of energy necessary to polymerize these monomers using thermal techniques. Furthermore, such polymerizations can be carried out on the liquid monomers without the need for volatile organic solvents. These photopolymerizations are, therefore, essentially nonpolluting processes.[3] Further, cationic photopolymerizations are not subject to oxygen inhibition and can be carried out in the presence of ambient air without the requirement for an inert blanketing atmosphere.

The development of photosensitive onium salt photoinitiators has made it possible to polymerize virtually all types of cationically polymerizable monomers. More specifically, the development of this chemistry has led us to consider what potential monomers might be available from renewable sources which could be polymerized using these photoinitiators. Glycerol triesters of fatty acids are produced by most members of the plant and animal kingdoms as means of energy storage. Those oils which

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* To whom correspondance should be addressed.

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