Chem. Mater. **1995,** *7,* 738−743

Structure and Luminescence of Barium Uranium Disilicate ($BaUO_2Si_2O_6$)

J. R. Plaisier,[†] D. J. W. IJdo,[†] C. de Mello Donegá,[‡] and G. Blasse[*,‡]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, Postbox 9502, 2300 RA Leiden, The Netherlands, and Debye Institute, University of Utrecht, Postbox 80.000, 3508 TA Utrecht, The Netherlands

Received November 8, 1994. Revised Manuscript Received February 6, 1995[⊗]

The structure and luminescence of $BaUSi_2O_8$ are reported and discussed. $BaUSi_2O_8$, orthorhombic, *Cmcm*, $a = 5.7027(4)$ Å, $b = 16.4636(10)$ Å, $c = 7.4956(5)$ Å, $V = 703.74(8)$ Å^3, $Z = 4$, $D_x = 5.281$ Mg m^{-3}. The structure has been refined by Rietveld analysis of neutron diffraction data recorded at room temperature. $R_p = 4.43\%$, $R_{wp} = 6.24\%$. The structure is related to $SrVSi_2O_7$, haradaite. The luminescence spectra are characteristic of the uranyl group. At low temperatures the energy migration is hampered by the presence of two sets of uranyl groups and inhomogeneous broadening. At somewhat higher temperature the uranyl traps can be reached by migration, and trap emission occurs until the temperature is high enough for detrapping. The spectra show a progression in the symmetrical stretching frequency of the uranyl group. The radiative decay time is 1.1 ms. The spectroscopic results suggests that the proposed structure cannot be correct in all details.

Introduction

Silicates of uranium, not containing water, such as coffinite ($USiO_4$)[1] and uranosilite (USi_7O_{17}),[2] are known, but they have not been studied in detail. Recently, however, knowledge of compounds resulting from reactions between uranium and fission products has become increasingly important in nuclear safety studies. When in a severe nuclear accident the reactor core has melted through the reactor vessel, the formation of quartenary uranium silicates may occur. The abundant uranium and fission products combined with silica in the concrete may lead to the formation of such compounds. Research in the system $BaO-UO_3-SiO_2$ led to $BaUSi_2O_8$. In the first section of this paper the crystal structure will be discussed. On the other hand, the luminescence properties of uranate groups are well-known. They have been discussed extensively.[3−5] The luminescence of the UO_2^{2+} (uranyl) group has been discovered by Stokes long ago (1852), whereas that of groups such as octahedral UO_6^{6-} and tetrahedral UO_4^{2-} was reported more than a century later. In U(VI) compounds, energy migration is a common phenomenon, and at low temperatures the emission consists of uranate traps.[4,6]

The uranate emission is a parity-forbidden transition.[5] Decay times may be as long as milliseconds. If, however, the inversion symmetry is lifted, the decay times become shorter. For example, UO_2MoO_4 with an uranyl group with unequal U−O distances (1.81 and 1.76 Å) and a 5-fold equatorial oxygen coordination, has a radiative decay time of about 100 μs.[6]

In $BaUSi_2O_8$ UO_6 groups occur. These can be described as distorted octahedra with U−O distances of 1.83 and 1.86 Å, and four equatorial U−O distances of 2.230 Å. The oxygens involved in the latter are also bound to silicon, those in the former are not. Therefore the formula may be written as $Ba(UO_2)Si_2O_6$, i.e., a uranyl silicate. The site symmetry of uranium is C_{2v}; inversion symmetry is lacking. The luminescence properties of this compound are discussed in the second part of this paper. This study reveals further details on the crystal structure, whereas the luminescence properties can be explained in terms of models which have been proposed before.[4,6]

Experimental Section

$BaUSi_2O_8$ was prepared by heating a stoichiometric mixture of $BaCO_3$, U_3O_8 and SiO_2 in a platinum crucible at 1200 °C for 1 week interrupted by repeated grinding. A pure product was obtained in this way.

This product was examined with a Philips PW 1050 X-ray diffractometer using monochromated Cu Kα radiation. The data were collected digitally in steps of 0.05° 2θ and 3 s counting time in the range $10° \le 2\theta \le 70°$. The product was also examined with a Siemens Elmiscope 102, fitted with a 40° double tilt and lift cartridge operating at 100 kV. All data were collected at room temperature.

The X-ray diffraction pattern could be indexed with the ITO computer program[7] with an orthorhombic unit cell with $a = 5.6996(5)$, $b = 16.455(1)$, and $c = 7.4922(8)$ Å.

The reflections absent in the electron diffraction patterns, as well as in the X-ray diffraction pattern indicated the space group *Cmcm* or a lower one.

Because no single crystals were avaialable, Rietveld's method[8] was used for refinement of neutron diffraction data. The neutron diffraction pattern was obtained on the powder diffractometer at the Petten high-flux reactor in the range $5° \le 2\theta \le 155°$, with $\Delta 2\theta = 0.1°$, $\lambda = 2.57168(3)$ Å. In this range there are 108 contributing reflections. For the calculation the

---

[†] Leiden University.

[‡] University of Utrecht.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

(1) Fuchs, L. H.; Gerbert, E. *Am. Mineral.* **1958**, *43*, 143.

(2) Walenta, K. *Neues Jahrb. Mineral. Monatsch.* **1983**, *259*.

(3) Bleijenberg, K. C. *Struct. Bonding* **1980**, *42*, 97.

(4) Powell, R. C.; Blasse, G. *Struct. Bonding* **1980**, *42*, 43.

(5) Denning, R. G. *Struct. Bonding* **1992**, *79*, 215.

(6) Smit, W. M. A.; Blasse, G. *J. Lumin.* **1984**, *29*, 367; **1985**, *34*, 117.

(7) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.

(8) Rietveld, H. M. *J. Appl. Cryst.* **1969**, *2*, 65.

0897-4756/95/2807-0738$09.00/0

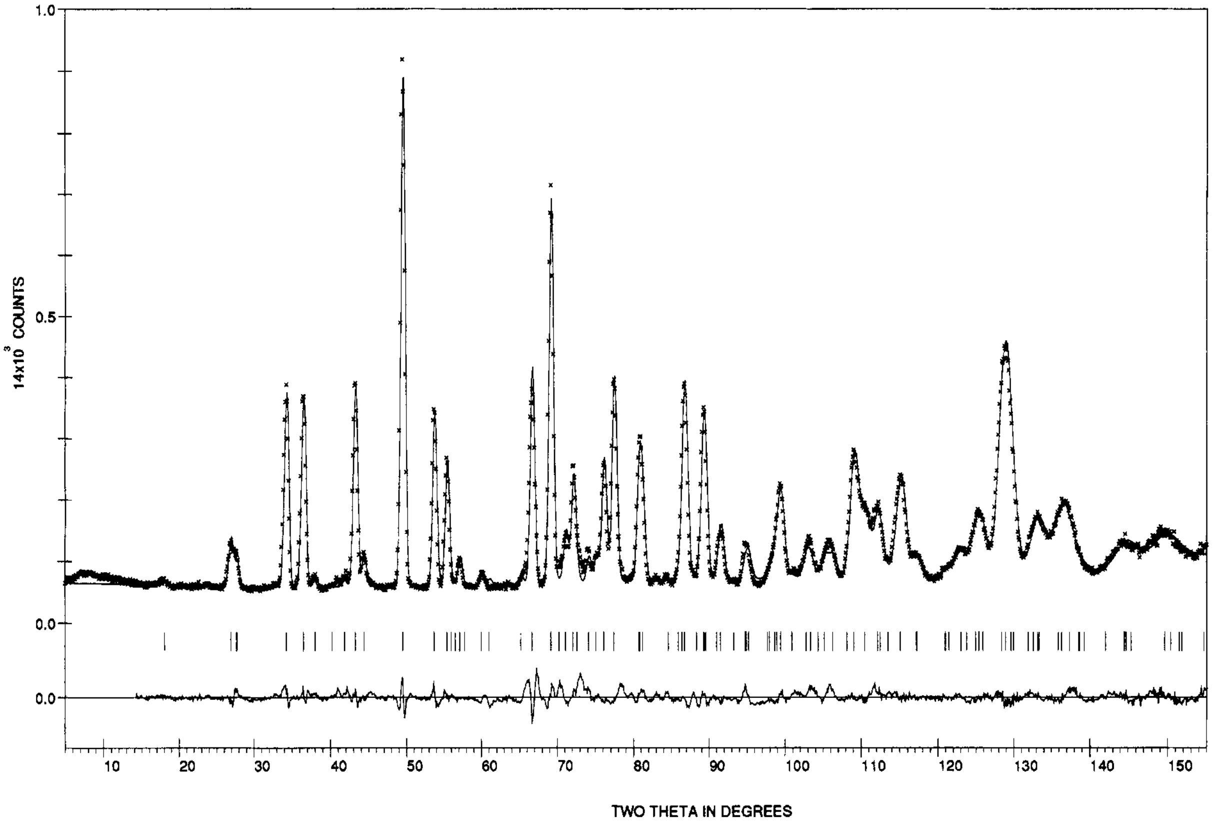

Figure 1. Observed (crosses) and calculated (continuous) profile of $BaUSi_2O_8$. Tick marks below the profile mark the position of allowed reflections. A difference curve ($I_{obs} - I_{calc}$) is plotted at the bottom.

DBW program version 8804[9] was used. The trial model for the refinement was derived from the structure of haradaite, $SrVSi_2O_7$[10] with lattice parameters similar to those of $BaUSi_2O_8$. The position of the uranium atom could be derived from a direct methods program for powder structure determination POWSIM.[11] This position was similar to the vanadium position in haradaite.

Fifty-four parameters were used in the refinement: a scale factor, three half-width parameters, defining the Gaussian-like shape of the reflections, six background parameters, the zero count error, the unit-cell parameters, the atomic positional parameters, and anisotropic thermal parameters.

Refinement of this model in the space group *Cmcm* converged to $R_{wp} = 6.24\%$.

Refinements in lower space groups did not improve the results.

The greater part of the optical measurements were performed on a Spex Fluorolog spectrofluorometer equipped with a liquid helium cryostat as described before.[12]

The used laser setup is given in this reference as well.

The Crystal Structure: Results and Discussion

The atomic parameters are given in Table 1 , and some selected distances in Table 2. The agreement between the observed and the calculated profiles of the data is shown in Figure 1. A projection of the structure of $BaUSi_2O_8$ is given in Figure 2. The structure consists of chains of corner-shared SiO_4 tetrahedra parallel to the *c* axis. The unbranched chains have a periodicity of four tetrahedra. In the strongly folded unbranched chains the loops between the chain tetrahedra are closed by rigid UO_6 groups. The same configuration is found in haradaite, in which the loops are closed by VO_5 groups.

Table 1. Fractional Atomic Coordinates of $BaUSi_2O_8$ at Room Temperature

atom	*x*	*y*	*z*
Ba	0.0	0.2158(5)	0.25
U	0.5	0.3795(5)	0.25
Si	0.5	0.0974(6)	0.0418(15)
O(1)	0.2709(7)	0.1384(4)	−0.0390(5)
O(2)	0.5	0.0	0.0
O(3)	0.0	−0.0073(7)	0.25
O(4)	0.5	0.1065(9)	0.25
O(5)	0.0	0.2319(5)	0.75

Table 2. Selected Bond Lengths in $BaUSi_2O_8$

Ba−O(1) (4×) 2.950(5)	U−O(1) (4×) 2.230(4)	Si−O(1) 1.590(8)
Ba−O(1) (4×) 3.158(8)	U−O(3) 1.863(14)	Si−O(2) 1.634(10)
Ba−O(4) (2×) 3.372(9)	U−O(5) 1.834(12)	Si−O(4) (2×) 1.568(11)
Ba−O(5) (2×) 2.979(3)		

Barium can be considered as 12 coordinated with Ba−O bond lengths ranging between 2.950 and 3.372 Å. The UO_6 octahedra are distorted; there are two short U−O distances and four longer ones (1.83, 1.86 and 2.230 Å). O(3) forms only a bond with U and O(5) has only three nearest neighbors (U and 2Ba). The U−O(3) and U−O(5) distances are very short in order to compensate for the deficiency of charge on these oxygen atoms. The linear group O−U−O with two short U−O bonds (about 1.8 Å) and an equatorial group of four or more O atoms is very common in so-called uranyl compounds. It is also found in $BaUO_4$ (U−2O 1.807, U−2O 2.208, U−2O 2.186 Å).[13]

---

[9] Wiles, D. B.; Young, R. A. *J. Appl. Cryst.* **1982**, *15*, 149.

[10] Takeuchi, Y.; Joswig, W. *Mineral. J.* **1967**, *5*, 98.

[11] Jansen, J. Thesis, University of Amsterdam, 1991.

[12] de Mello Donegá, C.; Meijerink, A.; Blasse, G. *J. Phys.: Condens. Matter* **1992**, *4*, 8889.

[13] Loopstra, B. O.; Rietveld, H. M. *Acta Crystallogr.* **1969**, *B25*, 787.

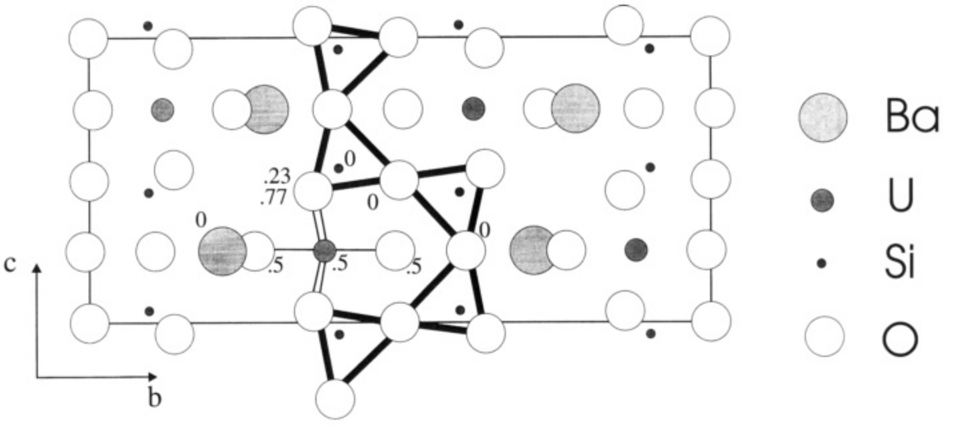

Figure 2. Projection of the structure of $BaUSi_2O_8$ along [100].

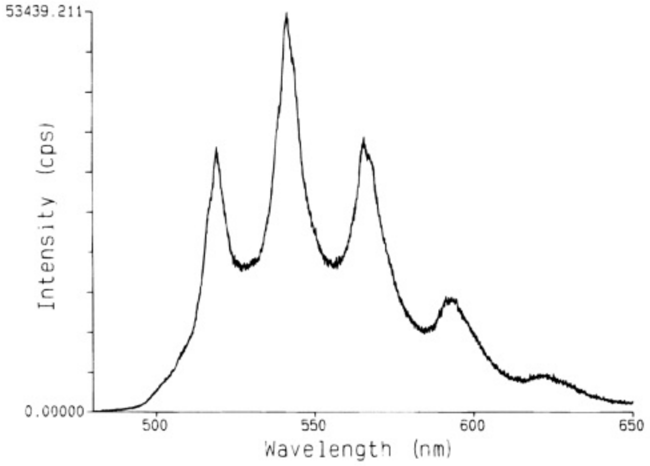

Figure 3. Emission spectrum of $BaUSi_2O_8$ at 300 K. Excitation wavelength 335 nm.

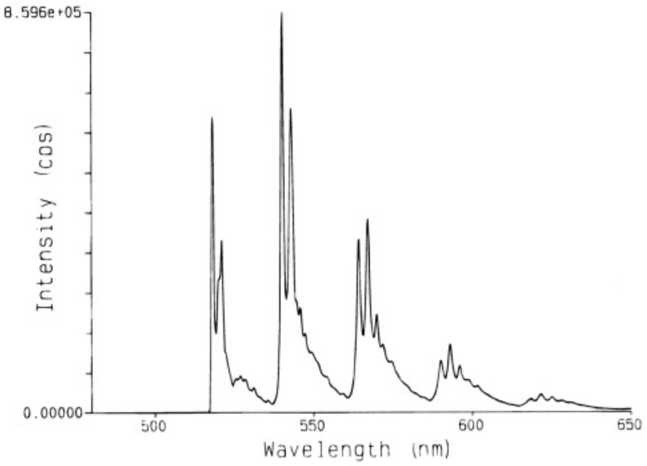

Figure 4. Emission spectrum of $BaUSi_2O_8$ at 4.2 K. Excitation wavelength 320 nm.

The thermal parameters of most atoms are highly anisotropic.

Because the results of the refinement were not optimal, high-resolution electron microscopy was performed with a Philips CM30ST electron microscope operating at 300 kV and equipped with a side entry 25°/25° tilt specimen holder at the Technical University Delft. The diffraction patterns showed the actual structure to be much more complicated. The electron diffraction patterns suggest that the a and b axes are doubled. However, this could not be confirmed by X-ray and neutron diffraction.

In the unbranched chain the O(2) atom lies in an inversion center, and thus the Si−O−Si angle is 180°. This angle is not often found in silicates but does also occur in $Sc_2Si_2O_7$, thortveitite.[14] Changing the angle away from 180° may lead to a deformation of the chains as well as a doubling of the axis.

The Luminescence: Results and Discussion

Results. The compound $BaUSi_2O_8$ shows an intense yellow-green photoluminescence at room temperature. At liquid helium temperature (LHeT) the emission intensity has increased about 1-order of magnitude.

Figure 3 shows the emission spectrum at room temperature. It consists of one broad structured band which is typical of uranyl. The progression frequency amounts to approximate 770 cm^{-1}. The excitation spectrum of this emission consists of a very broad band in the region $250 < \lambda < 370$ nm, whereas the region $\lambda > 370$ nm is structured. Progressions with repetition frequencies of about 670 cm^{-1} can be distinguished.

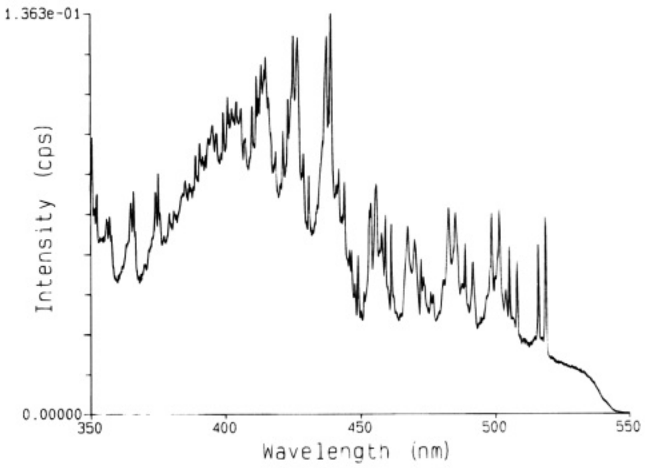

Figure 5. Excitation spectrum of the emission $BaUSi_2O_8$ at 4.2 K. Emission wavelength 593 nm. Many lines occur in pairs.

The decay curve at room temperature is nonexponential. There is an exponential tail with $\tau = 56$ μs.

At LHeT the spectra show considerably more detail. Figure 4 gives the emission spectrum. The progression frequency is 785 cm^{-1}. This spectrum starts with a sharp zero-phonon line at 518.3 nm. Figure 5 presents the corresponding excitation spectrum. In the longer

---

[14] Smolin, Y. I.; Shepelev, Y. F.; Titov, A. P. *Sov. Phys. Crystallogr.* **1973**, *17*, 749.

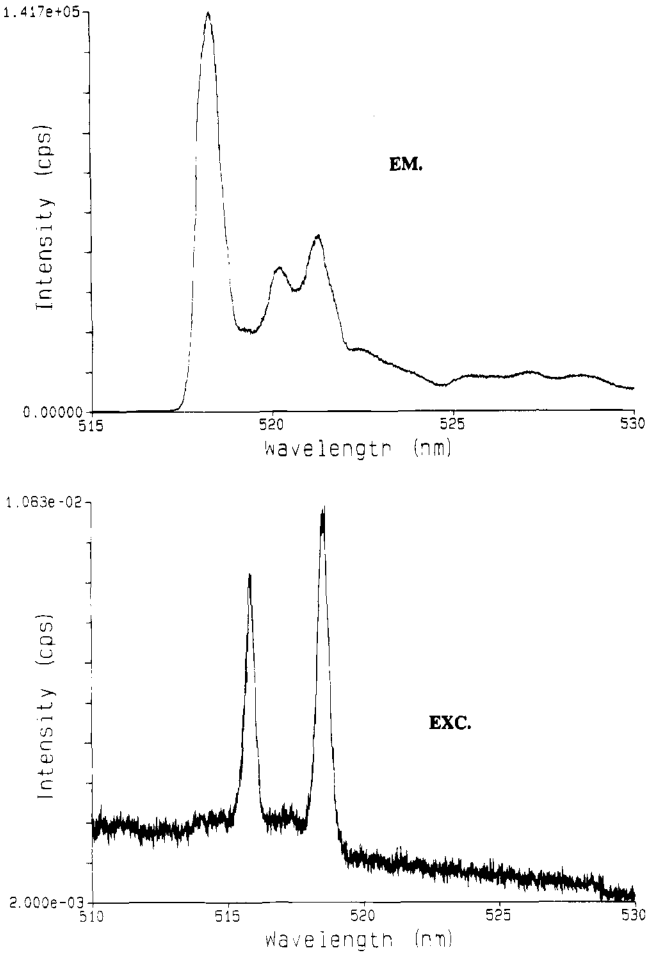

Figure 6. Emission and excitation spectra of the luminescence of $BaUSi_2O_8$ at 4.2 K in the zero-phonon region.

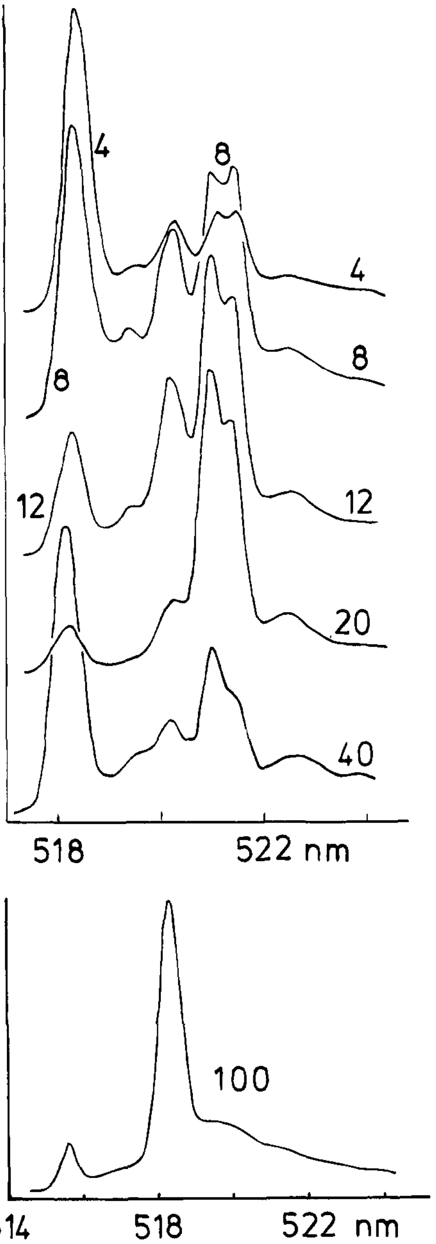

Figure 7. Temperature dependence of the emission spectrum of $BaUSi_2O_8$ in the region close to the zero-phonon line. Temperatures are 4, 8, 12, 20, 40, and 100 K.

wavelength region it can be clearly seen that many lines are doubled. The energy distance involved is 100 cm^{-1}. It is also possible to find progressions in this spectrum with a repetition frequency of 660 cm^{-1}.

Figure 6 shows the emission and excitation spectra in the zero-phonon region. Within the accuracy of the instrument, the zero-phonon emission line coincides with the lowest zero-phonon excitation line. The latter is followed by another line at 101 cm^{-1} higher energy. Actually, these two lines are the lowest pair of the pairs of excitation lines mentioned above. The emission and excitation spectra are not mirror symmetric.

The emission spectrum of $BaUSi_2O_8$ is strongly temperature dependent. This is shown in Figure 7, where the region close to the zero-phonon line is depicted for a few temperatures. Note first that the zero-phonon line itself is rather broad ($\Delta_{1/2} \sim 20$ cm^{-1}). Above LHeT the peaks at longer wavelengths become more intense, but above 25 K their intensity starts to decrease again. These lines are assigned to trap emission.[4,6] We observe at least five of these lines with trap depths of 40, 70, 102, 115, and 155 cm^{-1}. At even higher temperatures, there appears an anti-Stokes line at 100 cm^{-1} higher energy than the zero-phonon line. This line coincides with the higher energy pair line in the excitation spectrum (Figure 6).

The decay curve at LHeT is practically exponential (Figure 8). The corresponding decay time is 1.1 ms. High-resolution emission spectra using the 1 m Spex monochromator confirm the observations reported above and show the complex structure of the zero-phonon line as well (Figure 9).

Discussion. The luminescence of $BaUSi_2O_8$ shows similarities with that of UO_2MoO_4[6] and the classic case of $Cs_2UO_2Cl_4$.[15,16] The main features of the emission spectrum at 4.2 K can be described by the expression

$$\nu = \nu(0-0) - n\nu_s - m\nu_{as}$$

where $\nu(0-0)$ is the wavenumber of the zero-phonon emission line, ν_s that of symmetrical UO_2^{2+} stretching mode, ν_{as} that of asymmetrical stretching mode, $n = 0$, 1, ..., 4, and $m = 0$ or 1. The values of ν_s and ν_{as} are 785 and 880 cm^{-1}, respectively. For UO_2MoO_4 these values are 745 and 885 cm^{-1},[6] for $Cs_2UO_2Cl_4$ 835 and 910 cm^{-1}. The other lines in the emission spectrum are

---

(15) Krol, D. M. *Chem. Phys. Lett.* **1980**, *74*, 515.

(16) Denning, R. G.; Ironside, C. N.; Thorne, J. R. G.; Woodwark, D. R. *Mol. Phys.* **1981**, *44*, 209.

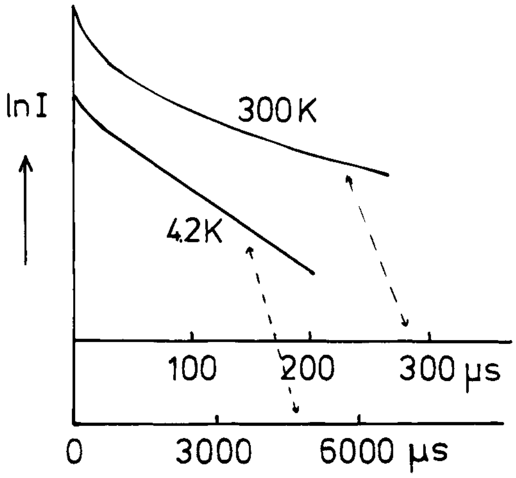

Figure 8. Decay curves of the emission of $BaUSi_2O_8$ at 4.2 and 300 K. Excitation wavelength 308 nm. For clarity the curves have been shifted relative to each other.

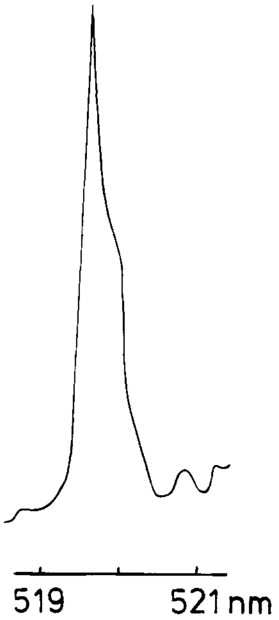

Figure 9. High-resolution emission spectrum of $BaUSi_2O_8$ at 4.2 K in the zero-phonon line region.

hard to assign, since at lower temperatures they are overlapped by trap emission lines and at higher temperature they are strongly broadened.

The excitation spectrum of this emission starts with a zero-phonon transition which coincides with the zero-phonon emission line. This show that the LHeT emission originates mainly from intrinsic UO_2^{2+} groups. Conspicuous and remarkable are the occurrence of line pairs in the excitation spectrum. The pair lines are of comparable intensity and strongly suggest the presence of two different UO_2^{2+} groups whose energy levels are 100 cm^{-1} different from each other. Emission at low temperatures originates only from the one with the lower energy levels with a high efficiency. However, since the shortest U−U distances are about 6 Å, such a transfer is feasible. The transfer rate is expected to be $10^{10\pm1}$ s^{-1},[6] which is much higher than the radiative decay time ($\sim10^3$ s^{-1}).

The progression frequency in the excitation spectrum is considerably lower than in the emission spectrum, indicating a weaker uranyl bond in the excited state.

The temperature dependence of the emission spectrum is remarkable (see Figure 7). At LHeT the emission is mainly from the intrinsic UO_2^{2+} groups with the lower energy levels. This changes dramatically upon increasing the temperature. In the region up to 25 K several uranyl trap lines increase strongly in intensity. This shows that the excitation energy of uranyl centers emitting at 4.2 K becomes mobile and migrates to the trap centers from where emission occurs. Above 25 K detrapping becomes possible again and at even higher temperatures the traps are too shallow to play any role. Simultaneously the total emission intensity decreases considerably, which indicates that the migrating excitation energy reaches also quenching sites where the excitation energy is lost nonradiatively. These phenomena are well-known for uranium compounds, although usually the trap emission dominates already at LHeT.[4,6] The following comments on the case of $BaUSi_2O_8$ are noteworthy.

(a) The absence of long-range migration at LHeT may have two reasons. First we know already that the uranyl groups occur in two sets of comparable concentration. The higher energy set transfers its energy to the lower energy set. Back-transfer at LHeT is impossible in view of the 100 cm^{-1} energy difference. Therefore energy migration is possible only in the sublattice of the lower energy set. However, the number of nearest neighbors will decrease, and the distance concerned will increase as a consequence of the fact that the uranyl centers occur in two sets with different energy levels. In the second place the inhomogeneous broadening of the emission lines in $BaUSi_2O_8$ is about 1 order of magnitude larger than in single-crystalline $Cs_2UO_2Cl_4$[15] and twice that of UO_2MoO_4 powder.[6] This indicates that the degree of imperfection in the $BaUSi_2O_8$ lattice is rather high. As a consequence there will be small energy mismatches in the set of lower energy uranyl groups which hamper energy migration at LHeT.

(b) This high degree of imperfection is also clear from the large number of different traps. The values of the trap depths are comparable to those in other uranium compounds.[4,6,15]

(c) At 100 K the emission spectrum shows emission from the set of uranyl centers with the higher-energy levels as well (see Figure 7). The intensity ratio $I_{0-0}(\mathrm{high})/I_{0-0}(\mathrm{low})$ is about 0.19. Assuming that the ratio of the transfer rates between uranyl groups of the sets is given by $\exp(-\Delta E/kT)$ where ΔE is their energy difference, viz., 100 cm^{-1}, and that the radiative rate of both groups is equal, the expected ratio is 0.22. This can be considered as a satisfactory agreement with experiment.

At this point the question rises whether the presence of two sets of uranyl groups is due to the presence of two crystallographically different groups or to crystal-field and/or Davydov splitting. In our opinion the latter possibility can be excluded in view of the large energy difference (100 cm^{-1}). For UO_2MoO_4 the crystal field and Davydov splitting is about 10 cm^{-1},[6] for $Cs_2UO_2Cl_4$ only 2 cm^{-1}.[15] Actually in $BaUSi_2O_8$ the Davydov splitting is probably also some 10 cm^{-1} in view of the vague splitting of the zero-phonon emission line under high-resolving power (see Figure 9). At room temperature the emission spectrum is considerably broadened, so that only the progression in the symmetrical stretching vibration can be observed. Also the excitation spectrum cannot offer much information anymore.

The decay curves confirm the physical behavior deduced from the spectroscopic data. At LHeT the decay curve is nearly exponential. Since energy migration is very much restricted, this has to be expected. The decay time derived from this curve is 1.1 ms; it has to be considered as a radiative decay time. Its value is not unusual for uranyl and suggests that the deviation from inversion symmetry at the uranium site cannot be large.

The nonexponential decay curve at room temperature with an exponential tail with $\tau = 56$ μs points to diffusion-limited energy migration to quenching sites.[17] This is well in line with the model used above to explain the spectroscopic data.

Comparison between the Crystallographic and Spectroscopical Results

Denning[5] has presented a relation between the energy of the first excited state of the uranyl group and the U−O bond length. Using the position of the lowest zero-phonon line, this relation yields for $BaUSi_2O_8$ a U−O distance of 1.85 Å, equal to the average of the values found from the diffraction data.

The radiative decay time of the emission (1.1 ms) corresponds to a uranyl group with two nearly equal distances. The overall picture of the emission spectrum is characteristic of the uranyl group.[5,6,15] In passing we note that recently the luminescence of $(PPh_4)UOCl_5$ has been described.[18] The $UOCl_5$ anion has C_4 symmetry with distances U−O 1.76, U−Cl (trans) 2.43, and U-Cl (equatorial) 4 × 2.54 Å. The lifetime is 2 μs. This low value was ascribed to the absence of inversion symmetry.

A striking contradiction between the crystallographic and spectroscopical results is the presence of two sets of uranyl groups with an energy difference of 100 cm^{-1} which cannot be due to Davydov and/or crystal-field splitting. The diffraction data indicate only one crystallographic site for uranium. It should be realized that diffraction results relate to long-range order, whereas the spectroscopical results relate to the local situation. Another aspect of the U(VI) polyhedron, which is not understood, is the following. The U−O(3) distance is longer than the U−O(5) distance (see Table 2), whereas the O(3) ion has no further direct neighbors, but the O(5) has in addition two Ba^{2+} ions. It can, therefore, not be excluded that the proposed crystal structure is more complicated than originally thought. This is also indicated by the high-resolution electron microscopy results.

Finally it should be realized that the presence of two sets of uranyl groups is based on spectroscopical data obtained at 4.2 K, whereas the crystallographic data were obtained at room temperature. A possible phase transition between these two temperatures could also be responsible for the contradiction observed.

Conclusions

The system $BaO-UO_3-SiO_2$ is of interest for nuclear safety studies. When in a severe nuclear accident the reaction core has melted through the reactor vessel, formation of quartenary compounds in this system may occur. As a first result the new compound $BaUSi_2O_8$ has been described. Its crystal structure contains corner-shared SiO_4 chains parallel to the *c* axis. The crystal structure is related to $SrVSi_2O_7$, haradaite.

The compound $BaUSi_2O_8$ shows an efficient uranyl photoluminescence. At 4.2 K energy migration seems to be strongly hampered. At higher temperatures trap emissions appear, indicating energy migration. The trap emissions disappear at even higher temperatures. The presence of two sets of uranyl groups in the spectra are at variance with the proposed crystal structure which seems to deserve further study.

Acknowledgment. The authors are indebted to Mr. A. Bontenbal of the Netherlands Energy Research Centre (ECN), Petten, for the collection of neutron powder diffraction data, to Mr. G. H. Renes for the collection of the electron diffraction patterns, and to Dr. H. W. Zandbergen of the Technical University Delft for the collection of high-resolution electron micrographs.

CM9405077

---

[17] See, e.g.: Blasse, G. *Prog. Solid Chem.* **1988**, *18*, 79.

[18] Bartleet, J. M.; Denning, R. G.; Morrison, I. D. *Mol. Phys.* **1992**, *75*, 601.