Inorganica Chimica Acta, 95 (1984) 65–68

A Study of the Absorption and Emission Behaviour of U(VI) in some Glassy Matrices

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Received November 15, 1983

The absorption and emission spectra of xSiO_2/yNa_2O/zPbO glasses doped with U(VI) show the influence of the lead oxide on the formation of the UO_2^{2+} ion, that can exist only when PbO is absent or present at most in a mole percentage about 29%. This is due to a destruction of the random three-dimensional network by PbO and to the consequent steric impossibility for the hexavalent uranium to form the UO_2^{2+} linear ion.

Introduction

We are interested in materials that can have applications as lasers and for this reason we began to study the radiation absorption and emission of some glasses whose composition is xSiO_2/yNa_2O/zPbO doped with U(VI). The choice of characterizing the optical properties of such systems is due to the uncertainty of the presence of U(VI) as UO_2^{2+} in lead silicate glasses. Bearing in mind that the UO_2^{2+} system has a peculiar absorption and emission spectrum, this allows us to confirm or not the presence of this ion.

Experimental

The composition of the glasses under investigation and the nature of the doping salts are reported in Table I.

TABLE I. Compositions of the Glasses under Investigation.

Sample	mol %				Doping salt
	SiO_2	PbO	Na_2O	U	
1)	49.50	49.50	–	1.00	$UO_2(OCOCH_3)_2$
2)	61.50	37.50	–	1.00	$UO_2(OCOCH_3)_2$
3)	61.50	37.50	–	1.00	UO_3
4)	61.50	37.50	–	1.00	Na_2UO_4
5)	61.66	28.67	8.67	1.00	$UO_2(NO_3)_2$
6)	61.66	24.67	12.67	1.00	$UO_2(NO_3)_2$
7)	61.66	21.67	15.67	1.00	$UO_2(NO_3)_2$
8)	61.66	19.67	17.67	1.00	$UO_2(OCOCH_3)_2$
9)	59.50	–	39.50	1.00	$UO_2(OCOCH_3)_2$

The batches were prepared by mixing reagent grade (RP Carlo Erba) SiO_2, PbO and Na_2CO_3 with the appropriate uranium compounds of the same purity. The mixtures were melted in air in a 50 cm^3 platinum crucible at 1250 °C for four hours in an electrically heated muffle furnace. The melts were then quenched on a stainless steel plate. Clear and homogeneous glasses were obtained, whose colours depended on the composition. They were green-yellow when PbO was absent or its concentration was low, and orange-yellow when the PbO percentage was higher. The samples were cut and polished to 0.2 mm thickness for optical measurements. Absorption spectra in the visible and near UV regions were measured by a Cary 14 spectrophotometer at room temperature, liquid nitrogen and liquid helium temperatures in a continuous flow Oxford CF 100 cryostat. Luminescence spectra were obtained by means of the following experimental set-up. The exciting light was sent to the sample using a high

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TABLE II. Maxima Positions (cm^{-1}) of the Absorption and Emission Spectra.

Sample	Absorption	Emission
1)	19850	–
2)	19850	–
3)	19850	–
4)	19850	–
5)	20195; 24100	18685(low intensity)
6)	20012; 24190	17927(sh); 18585; 19230
7)	20200; 24230	18033; 18698; 19330
8)	20350(sh); 24200	17240(sh); 17655(sh); 18077; 18741; 19395
9)	20548; 21092(sh); 23873	17203(sh); 17600(sh); 18024; 18684; 19330

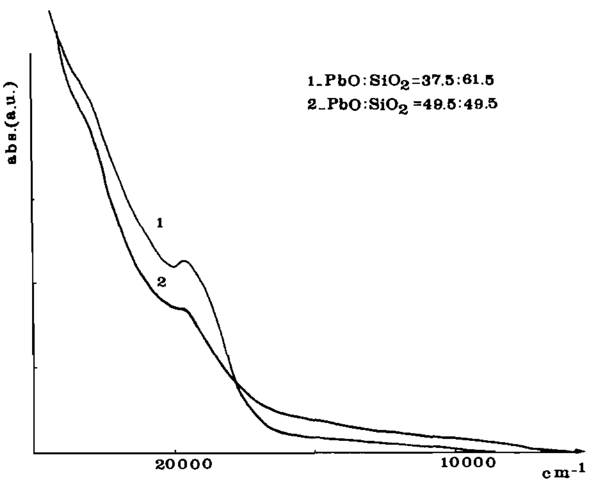

Fig. 1. Absorption spectra of some lead silicate glasses doped with U(VI) compounds.

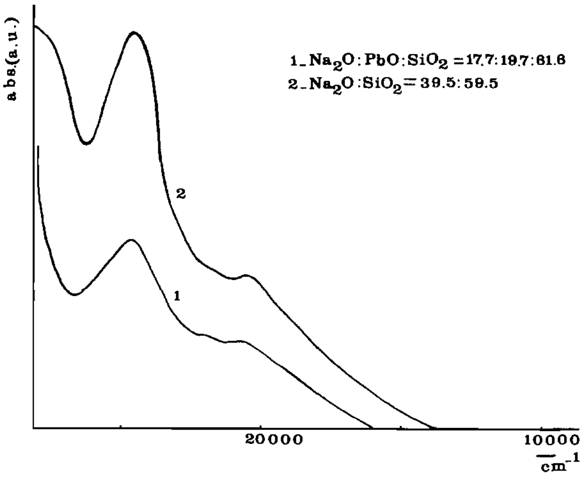

Fig. 2. Absorption spectra of some sodium silicate and sodium lead silicate glasses doped with U(VI) compounds.

pressure Xe lamp (Osram X BO 150 W/1) and a 0.5 meter Jarrel-Ash monochromator; the emission light, taken at a right angle, was analyzed by a MRS_2 Jobin-Yvon monochromator, detected by an EMI 9558 QAM photomultiplier cooled to –25 °C, and processed by a Keithley 417 picoammeter.

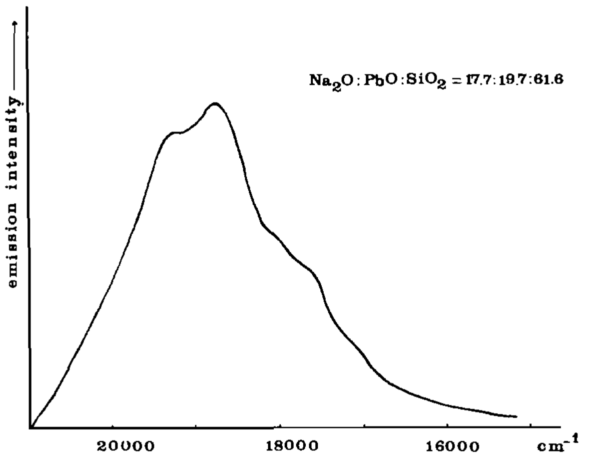

Fig. 3. Fluorescence spectrum of a sodium lead silicate glass doped with U(VI).

The temperature variation leaves the absorption and emission electronic spectra unaffected.

Results and Discussion

Some of the absorption and emission spectra of the glasses are reported in Figs. 1, 2 and 3 and the maxima of the bands are summarized in Table II.

The samples containing Na_2O show an absorption spectrum in which two well-resolved bands appear, but those without Na_2O show only a shoulder at about 19850 cm^{-1}. It is clear that the nature of the spectra does not depend on the doping uranium salts. As for the emission spectra, the band between 16000 and 21000 cm^{-1} is relatively well-resolved and from the analysis of the shape we suggest that it is due to a superposition of emissions from slightly different sites. It is important to point out that the intensity of the bands of samples of the same thickness always depends on the PbO percentage. When the PbO/Na_2O ratio increases, the intensity of the highest wave-

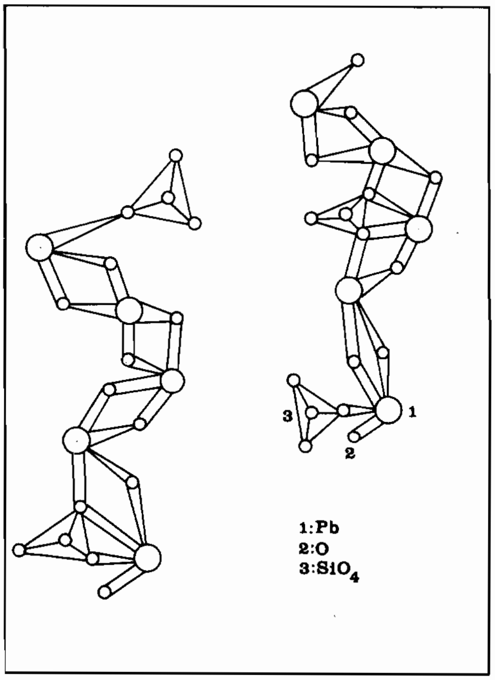

Fig. 4. Structure of lead silicate glass (taken from ref. [4]).

number absorption band decreases, and for the luminescence, it almost disappears when the mole percentage of PbO and Na_2O is 29% and 9% respectively.

Regarding the absorption spectra of the systems $SiO_2/Na_2O/U(VI)$ and $xSiO_2/yNa_2O/zPbO/U(VI)$, it is quite sure that the band in the region of the highest wavenumbers is due to the absorption of the UO_2^{2+} ion [1], that in our case is stabilized in a strongly basic medium for the presence of the Na_2O in the glassy matrix. This behaviour is very strange, for Weyl [2] discovered that U(VI) is stabilized as UO_2^{2+} especially in acid glasses, but in the basic ones U(VI) is present as UO_4^{2-} and/or $U_2O_7^{2-}$.

The absorption spectra of all the $SiO_2/PbO/U(VI)$ systems do not show the peculiar absorption bands of the UO_2^{2+} ion: this could mean that the presence of high lead oxide percentages does not allow the formation of the linear ion UO_2^{2+} because, according to Weyl [2], the lead oxide destroys the glass structure and so the U(VI) can enter into the network to form more complex U(VI) oxides. These experimental results can be confirmed from the analysis of the emission spectra. The luminescence of the $SiO_2/Na_2O/U(VI)$ and the various $SiO_2/Na_2O/PbO/U(VI)$ systems is certainly due to the UO_2^{2+} ion [3]. As we pointed out, the emission intensity decreases with increasing PbO percentage, and this means a decreasing of the UO_2^{2+} concentration. Moreover, the absence of any kind of luminescence in the case of the $SiO_2/PbO/U(VI)$ system suggests that the UO_2^{2+} ions and other possible emitting centres (*e.g.* UO_4^{2-} groups) are not present in this matrix. It is reasonable therefore to suggest that the lead oxide from qualitative and quantitative points of view is fundamental in the formation of the UO_2^{2+} ion.

An explanation of this behaviour could be found from structural considerations about U(VI) complexes with oxygen atoms as surroundings, silicate and lead silicate glasses [4–7]. In the case of silicate glasses, the structure (that has not been yet completely defined) is made by SiO_4 tetrahedra linked in a three-dimensional network. In such a steric situation, it seems possible for the U(VI) ion to enter an interstitial site and form a UO_2^{2+} molecular ion. On the other hand, when we add PbO, which enters as a network former and a network modifier, the system then becomes much more distorted owing to the strong covalency of the Pb–O bond (obviously respect to the Na–O bond): a consequence is the formation of bidimensional chains or $(Si_2O_5)_n$ layers linked by Pb bridges [4] (Fig. 4). This steric situation probably is highly unfavourable to the formation of the UO_2^{2+} linear ion or to its presence in the interstices. In this case, the uranium ions can also replace silicon (even if their ionic radii are strongly different) in a network former site, probably with a strongly distorted tetrahedral symmetry because of the different size of uranium and silicon. Another possibility is an octahedral coordination, which because of the remarkable randomness of the system, cannot be regular.

From considerations about the symmetry of the U(VI) surroundings, it seems highly probable that it is lower than cubic, and for this reason the highly symmetric UO_4^{2-} or UO_6^{6-} ions are absent or their concentration is very low. Obviously this can have important consequences for optical properties.

It is well known that the symmetry around the U(VI) ions is fundamental as being directly responsible for the emission properties, that are enhanced by high symmetries [8]. All this is supported by the experimental results on the absence of any kind of luminescence (due to UO_2^{2+}, UO_4^{2-} or UO_6^{6-} ions) in systems containing only PbO as network modifier, and the decreasing of the peculiar UO_2^{2+} emission in the $SiO_2/Na_2O/PbO$ systems when the PbO percentage increases.

The absorption band present in the lead and lead-sodium silicate glasses at about 19850 cm^{-1} could be due to the presence of very low symmetry uranium–oxygen complexes.

Conclusions

As a continuation of this work we propose the preparation of appropriate glasses doped with rare earth ions. In fact the excited UO_2^{2+} ion may perform energy transfer to lanthanides, and this property could be used in order to develop solid state laser technology.

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