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Abstract. The optical absorption and luminescence spectra of the uranyl-doped fluorophosphate glasses $75NaPO_3$–$24.5SrF_2$–$0.5UO_2F_2$ and $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$ are discussed. The absorption spectrum of the uranyl ion in glasses shows less fine structure than the spectra of uranyl complexes in solution. The glass samples exhibit a strong luminescence typical for the uranyl ion, and the luminescence spectrum is well resolved. It was found that the force constant of the vibrations in the ground state is intermediate between that in fluoride and phosphate glasses. During the glass preparation, reduction of uranyl to tetravalent uranium is often observed.

1. Introduction

From the beginning of the 19th century until the Second World War, uranyl ions were used to give an attractive yellowish green colour to glasses. These glasses were known under the name *Vaseline glass*, and were used for vases, drinking vessels, candlesticks and even jewellery [1]. Afterwards uranium glasses gained interest, because of the possibility of enclosing nuclear waste into glasses. In comparison to studies of the uranyl ion in solutions and in single crystals, only relatively few spectroscopic studies have been devoted to the uranyl ion in glasses. Most of the work in this field has been done by Jørgensen and Reisfeld [2–7]. Bettinelli *et al* [8] studied the optical absorption spectrum and emission spectrum of uranyl in SiO_2–PbO–Na_2O oxide glasses. Pandey studied nonradiative energy transfer from uranyl to Sm^{3+} and Pr^{3+} in a sodium borate glass [9]. The state of the art of the knowledge about the electronic structure of uranyl ions has been reviewed by Denning [10].

In this paper, we discuss the spectroscopic properties of the uranyl ion in the fluorophosphate glasses $75NaPO_3$–$24.5SrF_2$–$0.5UO_2F_2$ and $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$. Our results obtained for uranyl ion fluorophosphate glasses will be compared with the behaviour of uranyl in other glasses.

2. Experimental details

The glass samples were prepared by melting the required amounts of sodium metaphosphate and the fluoride compounds in a platinum tube. After melting, heating was continued for

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15 minutes to homogenize the melt. Then, the melt was cast in a brass mould (preheated to 250–300 °C). In order to remove strain, the glass samples were annealed for four hours in an oven at 270 °C. Finally, the glass samples were cut and polished. Absorption spectra were recorded with an AVIV 17DS spectrophotometer, equipped with a continuous-flow cryostat (Oxford Instruments). Luminescence spectra were recorded with a home-built apparatus. A water-cooled 450 W xenon lamp was used as the excitation source. Wavelength selection was achieved by a Sciencetech Model 9050 monochromator. Luminescence was measured at an angle of 90° with respect to the excitation beam. The emission light was analysed by a McPherson monochromator (1200 lines mm^{-1}) and detected by a single-photon counting detector (photomultiplier and Stanford Research Systems SR400 two-channel gated photon counter).

3. Results and discussion

Several glasses were prepared with the general compositions $75NaPO_3$–$24.5MF_2$–$0.5UO_2F_2$ and $60NaPO_3$–$24.5MF_2$–$15LiF$–$0.5UO_2F_2$, where M = Mg, Ca, Sr, Ba, Zn. A major problem we were faced with during the synthesis of the uranyl-doped glasses was reduction of the uranyl group to the tetravalent uranium ion (U^{4+}). Whereas a glass containing only UO_2^{2+} and no U^{4+} shows a yellow–green colour, several of our glasses had a dark green colour. The absorption spectrum showed that these glasses contained a mixture of UO_2^{2+} and U^{4+}, or even only U^{4+} [11]. Because the equilibrium $UO_2^{2+} \leftrightarrow U^{4+} + O_2 + 2e^-$ depends on the partial oxygen pressure above the melt, we prepared the glasses in an air atmosphere and not in an inert atmosphere. We found that a glass which was poured into the brass mould when the melt was dull red produced a glass with a lower U^{4+} content than when a glass with the same composition was poured into the mould at orange–red glowing heat (at higher temperature). Only for the glass compositions $75NaPO_3$–$24.5SrF_2$–$0.5UO_2F_2$ and $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$, we were able to obtain glasses with a very low U^{4+} content. Because the spectroscopic properties of these two glass compositions are very much alike, we will mainly focus on the $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$ glass. Also Jørgensen and Reisfeld had problems with the reduction of uranyl to tetravalent uranium in fluoride and in phosphate glasses [3, 7]. Culea *et al* found that an increase in melting time of borate glasses enhances the reduction of U^{6+} to U^{4+} [12].

The absorption spectrum of the glass $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$ at liquid helium temperature is shown in figure 1. The main feature is an absorption band between 19 500 and 27 000 cm^{-1}. Even at cryogenic conditions the fine structure of this band is not as well resolved as in (room temperature) solution spectra. This is due to inhomogeneous line broadening. It is worth mentioning that only a minor improvement of the resolution of the glass spectrum is observed when going from room temperature to liquid helium temperature. The absorption spectrum shows several shoulders which could be resolved into ten Gauss curves. The uranyl ion has a $5f^0$ electronic configuration. The absorption band is caused by an oxygen to uranium charge transfer excitation [13] in which an electron is moved from a molecular orbital of odd parity (mainly from oxygen 2p orbitals) to the empty 5f shell. The fine structure is due to vibronic transitions, i.e. transitions on which vibrational transitions are superimposed. Because of its linearity, the uranyl ion possesses three fundamental vibration modes: symmetric stretching, asymmetric stretching and bending vibrations. The bending vibration is twofold degenerate, because bending can occur in two mutually perpendicular planes. In the uranyl ion, the symmetric vibration at ~750 cm^{-1} is preferentially excited. So one can conclude that the uranyl ion retains its linearity during excitation. Therefore, the
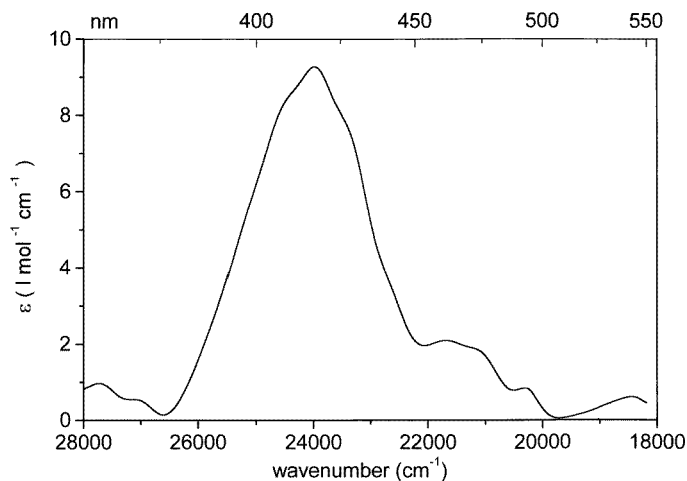
Figure 1. Absorption spectrum of the uranyl-doped glass $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$ at liquid helium temperature (4.2 K).

transitions observed in the absorption spectrum are characterized by the wavenumber

$$\bar{v} = \bar{v}_E + n_S \bar{v}_S \tag{1}$$

where $\bar{v}_E$ is the wavenumber of the electronic transition, $\bar{v}_S$ is the wavenumber of the symmetric vibration and n_S is the number of quanta associated with the symmetric vibration. The low intensity of the transition in the absorption spectrum ($\varepsilon < 10$ mol l^{-1} cm^{-1}) can be explained by the Laporte forbidden character of the transition. If the uranyl ion in the glass is considered as a free uranyl ion, the local symmetry is $D_{\infty h}$. In $D_{\infty h}$ symmetry, an inversion centre is present. It was found by Görller-Walrand and De Jaegere that transitions in uranyl complexes with an inversion centre have a much lower intensity than without an inversion centre [14, 15].

The uranyl glass samples exhibit a very intense yellowish luminescence. The strongest intensity was observed when the samples were irradiated at 415 nm (24 100 cm^{-1}). The emission is due to transitions from the lowest excited electronic state to the different vibrational levels of the ground state. In contradistinction to the absorption spectrum, the luminescence spectrum shows fine structure (even at room temperature). In figure 2, the luminescence spectrum of the glass $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$ at 77 K is shown. Five peaks are detected: at 20 124, 19 314, 18 496, 17 682 and 16 868 cm^{-1}. The transition at 16 868 cm^{-1} is observed only as a shoulder. The peak at 20 124 cm^{-1} coincides with the Stokes threshold and the others are due to the vibrational progression. These peaks are equidistant with separations of $\sim$814 cm^{-1}. This value is intermediate between the 770 cm^{-1} found for uranyl in a fluoride glass [7] and the 880 cm^{-1} in a phosphate glass [3]. The vibrational progression is more widely spaced in the luminescence than in the absorption spectrum, because the excited state has a lower force constant than the ground state [6]. The intensity distribution is influenced by the Franck–Condon principle. The equilibrium distance U–O in the uranyl ion is longer in the excited state than in the ground state, so that the configurational coordinate diagram of the excited state has been shifted to longer equilibrium distances with respect to the diagram of the ground state. Because during the transition the U–O equilibrium distance is not changed (Franck–Condon principle), it is not the $0' \rightarrow 0$ transition (peak at 20 124 cm^{-1}) that is the most intense transition, but the $0' \rightarrow 1$ transition (peak 19 314 cm^{-1}). The presence of fine structure in the luminescence spectrum of uranyl in glasses is not evident [2, 3]. Fine structure
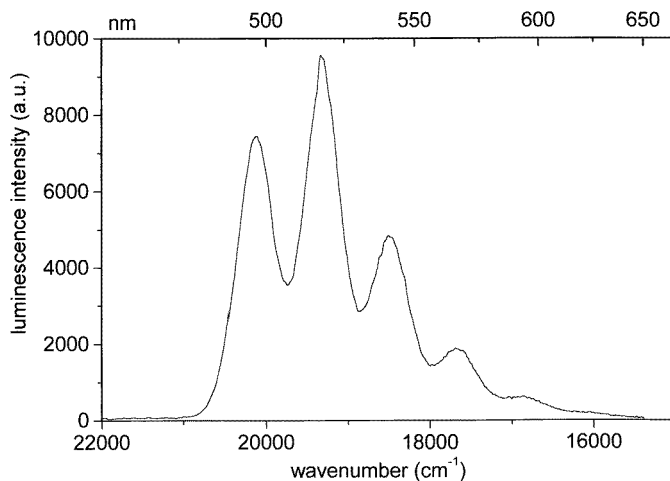
Figure 2. Luminescence spectrum of the uranyl-doped glass $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$ at liquid nitrogen temperature (77 K). The excitation wavelength is 415 nm.

is observed for the uranyl ion in silicate, in fluoride and in phosphate glasses. On the other hand, uranyl in borate and germanate glasses only gives a broad irregular spectrum. The presence of fine structure in the luminescence spectrum of uranyl ions in fluorophosphate glasses, proves that U^{6+} is present in the form of linear triatomic uranyl groups (UO_2^{2+}) and not as octahedral UO_6^{6-} clusters.

The glass samples $75NaPO_3$–$24.5SrF_2$–$0.5UO_2F_2$ and $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$ give virtually the same spectra, so that the glass composition does not seem to be a critical factor for the spectroscopic properties, as long as the same anionic groups are present in the glasses. It can be assumed that in the fluorophosphate glasses, the uranyl groups are surrounded by both fluoride ions and phosphate groups. Thus small composition changes in the glass cannot be used to improve the luminescence in the glasses. The mechanical properties and the resistance against corrosion are more important parameters in the choice of the glass composition of uranyl-doped glasses. This is very much the same as what we found for trivalent lanthanide ions in glasses [16].

4. Conclusions

The spectroscopic behaviour of uranyl ions in fluorophosphate glasses is intermediate between the behaviour in fluoride and phosphate glasses. The fine structure of the luminescence spectrum gives evidence for the presence of discrete triatomic uranyl groups (UO_2^{2+}), and not the octahedral UO_6^{6-} groups as found in borate and germanate glasses. On the other hand, no detailed fine structure could be observed in the absorption spectrum. This is due to inhomogeneous line broadening. The glass samples used in this study, $75NaPO_3$–$24.5SrF_2$–$0.5UO_2F_2$ and $60NaPO_3$–$24.5SrF_2$–$15LiF$–$0.5UO_2F_2$, give very similar spectra, so that the glass composition does not seem to be a critical factor for the spectroscopic properties, as long as the same anionic groups are present in the glasses. However, the chemical composition of the fluorophosphate glasses has a significant influence on the reduction of UO_2^{2+} to U^{4+}.

Acknowledgments

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