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Ultraviolet Luminescence from Hafnium Pyrophosphate (HfP_2O_7)

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Under X-ray excitation hafnium pyrophosphate (HfP_2O_7) shows an intense ultraviolet emission with a band maximum at 305.5 nm. © 1991 Academic Press, Inc.

Introduction

Closed-shell oxocomplexes of the transition metal ions are among the most efficient luminescent centers in solids. They have been reviewed by one of us (*1*). The most well-known case is undoubtedly $CaWO_4$, a luminescent material in use for some 75 years (*2*). In this compound the tungstate group is the luminescent center. Research has been performed for decades in order to find out which members of this group of complexes show luminescence and which do not.

Next to the tungstate group, the molybdate and titanate groups were found to emit (*3*). That of the vanadate group became of interest after the invention of the red phosphor YVO_4 : Eu (*4*). Then followed the niobate group [$YNbO_4$, Ref. (*5*)]. For the zirconate and tantalate groups it was necessary to excite with high energy, since their absorption edge is at too high an energy to excite with conventional ultraviolet (*1*). As far as we are aware no emission has been reported for the permanganate group. The chromate group is a borderline case with a weak emission (*6, 7*). This leaves the hafnate group as the one for which luminescence is expected but has not been reported until now.

Ackerman (*8*) has reported a luminescence for Cs_2HfCl_6 which is very similar to that of Cs_2ZrCl_6. The emission band maximum is at 400 nm, and the transition was ascribed to a charge-transfer transition in the $HfCl_6^{2-}$ complex, similar to the emission of all complexes mentioned above. In the present communication we report also luminescence for the oxidic compound of hafnium(IV) HfP_2O_7. In this way the total picture of the luminescence of these

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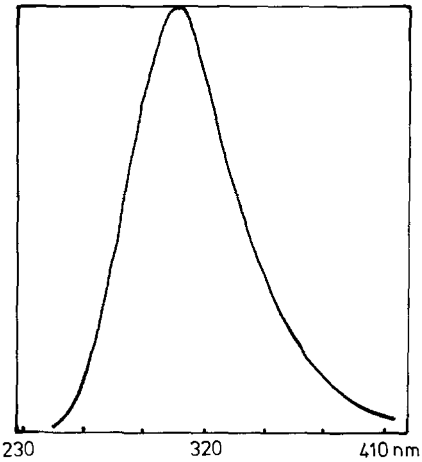

FIG. 1. Emission spectrum of HfP_2O_7 at 300 K under X-ray excitation.

closed-shell oxocomplexes is further completed.

Experimental and Results

Samples of HfP_2O_7 were prepared by interacting HfO_2 (Johnson Matthey AESAR spectroscopic grade, containing 105 ppm Zr) and $NH_4H_2PO_4$ (Johnson Matthey AESAR grade) at 300°C for 10 hr. After ball-milling this precursor it was pressed into a 1-in. diameter pellet and fired at 600, 800, 1000, and 1400°C for 4 hr each. The resulting material was single phase and yielded a refined cell constant in Pa3 symmetry of 8.187 Å. The X-ray-excited luminescence measurements were carried out as described before (*8*).

Under X-ray excitation the samples of HfP_2O_7 show a strong ultraviolet luminescence. The emission spectrum is given in Fig. 1. It consists of a broad band with a maximum at 305.5 nm. In addition there is a weaker visible emission.

Discussion

In a very old, and often overlooked, paper Bril and Klasens (*10*) reported ultraviolet emission for ZrP_2O_7 under cathode-ray excitation. Later, by comparison with BaZr Si_3O_9 with similar luminescence properties, it was shown that this emission presents the charge-transfer transition in the zirconate group (*11*). The emission maximum is at about 285 nm. Excitation with ultraviolet radiation is only possible for $\lambda < 220$ nm.

In view of the strong similarity between the emission spectra of ZrP_2O_7 (cathode-ray excitation) and HfP_2O_7 (X-ray excitation), we ascribe the emission of HfP_2O_7 to a charge-transfer transition in the hafnate (HfO_6^{8-}) group. This extends the group of luminescent closed-shell oxocomplexes. The reason that this luminescence has not been observed before is probably due to the fact that hafnium compounds are not frequently studied and also to the fact that conventional ultraviolet excitation does not excite this emission, as is the case for ZrP_2O_7.

The fact that the HfP_2O_7 emission is at slightly longer wavelength than that of ZrP_2O_7 should not be taken too serious. Not only are we comparing data under different excitation sources and measured at different times, but also the crystal structure involved is complicated by a superstructure with slightly different metal ion sites. This was used by Donker *et al.* (*12*) to explain the appearance of two luminescent Te^{4+} centers in their samples of ZrP_2O_7 : Te. Since the ionization potentials of zirconium and hafnium are very similar (*13*), the charge-transfer spectra are expected to be in the same spectral range.

Shidlovsky *et al.* (*14*) have reported the cathodo- and photoluminescence of HfP_2O_7; they consider this luminescence to be "self-activated." Their emission maxima vary slightly and are at somewhat shorter wavelengths than ours (~285 nm). This variation was interpreted in the same way as we did by "internal defects."

There is, however, one problem with our interpretation. The starting material HfO_2

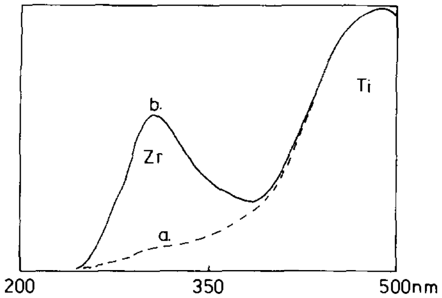

FIG. 2. Emission spectra of HfO_2 (100 ppm Zr) (a) and HfO_2(1.5% Zr) (b) at 300 K under X-ray excitation.

contains about 100 ppm zirconium. Although in this way it is the purest HfO_2 available commercially, it cannot be excluded that Zr^{4+} ions in HfP_2O_7 act as traps for the charge carriers and are responsible for the emission, instead of the hafnate group. Actually there is also present another impurity, titanium. This ion is responsible for the visible emission of HfP_2O_7 which was also reported in Ref. (*14*). This effect was studied at length by Sarver for ZrO_2-Ti (*15*).

However, the HfP_2O_7 and ZrP_2O_7 structure with its defects is not the most suitable one to investigate this possibility any further. Therefore the X-ray-excited luminescence of HfO_2(100 ppm Zr) and HfO_2(1.5% Zr; Reactor grade) was measured. The resulting emission spectra are given in Fig. 2.

Dominating is a broad emission band with a maximum at about 490 nm. This emission is ascribed to titanate impurities. It coincides with the titanate emission of $ZrO_2:Ti$ (*15*) and has also been observed for the compound $La_2Hf_2O_7$ (*16*). Pure ZrO_2 does not emit at room temperature (*15*); neither do all other metal oxides with d^0 ions (TiO_2, V_2O_5, Nb_2O_5, MoO_3, Ta_2O_5, WO_3) (*17, 18*). Therefore, it seems reasonable to assume that pure HfO_2 also does not emit. However, in addition to the visible emission our samples also show an ultraviolet emission (see Fig. 2), the intensity of which increases as a function of the zirconium concentration. It seems obvious to ascribe this emission to impurity zirconate.

It is important to realize that titanate is obviously a better trap for the excitation energy than zirconate. This is clear from our experiment, but follows also from the energy levels which are much lower in energy for titanate. In HfO_2(100 ppm Zr) the UV emission is indeed very weak. In HfP_2O_7, prepared from this HfO_2 the UV emission is more intense than the visible emission. This shows that energy transfer to the trapping centers is of less importance in HfP_2O_7, which can be related to the longer Hf–Hf distance in HfP_2O_7 compared to HfO_2. The possibility that the UV emission of HfP_2O_7 contains a certain amount of zirconate emission cannot be excluded. However, the fact that at least a substantial part of this emission is due to hafnate emission is of importance here.

In conclusion, the oxohafnate luminescence is expected to be similar to that of the analogous zirconate group. Its emission maximum is at about 300 nm. The compound HfP_2O_7 appears to present the first example of this emission.

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