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THE I.R. PHOTOLUMINESCENCE EMISSION BAND IN ZnO

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Abstract – Measurements of emission spectra, excitation spectra, intensity dependence of the luminescence, decay of the luminescence, and temperature dependence of the luminescence in ZnO are reported. The results for the emission at 1·70 eV, with the exception of the decay of the luminescence, were found to be similar to those of the yellow (2·02 eV) emission band in ZnO. Both bands could be excited at the band edge and directly, the intensity of both bands was found to be linear with excitation strength and the asymptotic regions of the temperature dependence of both bands could be approximated by exponential functions. It is proposed that the luminescent transition is an electron transition from the edge of the conduction band to a hole trapped in the bulk at 1·60 eV above the edge of the valence band, and that the luminescence center is an unassociated acceptor-like center.

1. INTRODUCTION

BECAUSE of their extremely rapid decay times and their relatively high efficiencies, the near u.v. 'edge emission' and the broad band green (2·44 eV) emission of ZnO have been the subject of a large number of investigations during the past decade. The near u.v. 'edge emission' has been identified with and consistently interpreted in terms of the exciton structure of ZnO[1]. The center responsible for the green emission, although extensively studied[2] is still the subject of much controversy. A recent study based on a comparison of Zeeman data and electron spin resonance (ESR) data has suggested that one possibility for the center involved is a substitutional Cu impurity at a regular Zn lattice site[3]. In addition to these two efficient photoluminescence processes, a third emission process which has also received a good deal of attention in the literature[4] is a broad band emission peaking in the yellow–orange at 2·02 eV. This center has also not been unambiguously identified, although recent work[5] involving the comparison of polarized photoluminescence measurements and ESR data has suggested that one possibility for the center giving rise to this emission is a Li acceptor substituting at a regular Zn lattice site. In addition to these three extensively studied emissions, a fourth emission band at 1·70 eV has been observed[6, 7]. In this study, the 1·70 eV emission appeared as a lower intensity side band on the 2·02 eV emission. The 1·70 eV emission band, which is narrower than either the green or yellow bands, has received far less attention in the literature, and the atomic origin of the luminescence is an open question. Based on the results of this study, it is necessary to consider, in addition to the previously proposed models[6, 7] for the 1·70 eV luminescence center, a bulk charge transfer center as being responsible for the emission. This center is necessarily similar in nature to the proposed Li acceptor center which gives rise to the 2·02 eV emission.

2. EXPERIMENTAL

The samples used in this study included both powder phosphors and single crystals of ZnO. The samples were prepared by subjecting high purity ZnO powder and Airtron ZnO single crystals to various oxidizing conditions. In general, it was found that the 1·70 eV emission band was generated by heating at temperatures between 900–1000°C in an O_2 ambient. No coactivation such as the use of a halide flux was necessary to obtain the 1·70 eV emission.

The emission spectra were measured using

1/4-m scanning Jarrell–Ash monochromator (Model No. 82-410), and either an EMI-9558Q photomultiplier or a cooled RCA 7102 photomultiplier. The emission spectra have been corrected for the optical response of the system. The excitation spectra were measured by setting the Jarrell–Ash at the peak of the emission spectrum, and then scanning the incident 450 W xenon radiation using a 500mm Bausch and Lomb monochromator and suitable filters. The excitation spectra have been corrected for variations in the incident photon flux.

The temperature dependence of the emission bands were measured by setting the Jarrell–Ash at the peak of the emission spectrum (first at 2·02 eV and then at 1·70 eV) and the Bausch and Lomb at the peak of the intrinsic excitation (3·30 eV). The incident xenon radiation was chopped (12 Hz) and a PAR HR8 lock in amplifier was used to detect the output of the photomultiplier. The resolution of the Bausch and Lomb monochromator was approximately 130 Å; hence, any shift of the excitation peak with temperature would have little affect on the measured temperature dependences. Also, the emission peak position was found to shift 0·14 eV toward lower energy when the temperature was raised from 80 to 270°K; this effect, however, was not large enough to significantly affect the data. In addition, the temperature dependences were measured by exciting the sample at 3·30 eV and rapidly scanning (1 scan/5°K) the emission spectrum during the warming cycle. The results obtained in this manner were identical to those obtained by the first method. Finally, to assure that the temperature dependence of the individual bands were being measured, the Jarrell–Ash was set at the peak of the emission spectrum (first the 2·02 eV emission and then 1·70 eV emission) and the Bausch and Lomb at the peak of the direct excitation of each emission band. The incident xenon radiation was chopped and the resultant photoluminescence was detected by using a PAR lock-in amplifier to measure the output of the photomultiplier. These results were qualitatively the same as those obtained by the two previous methods.

3. RESULTS AND DISCUSSIONS

Figure 1 shows a typical photoluminescence emission spectrum. In all cases studied, it was found that the 2·02 eV emission band was present when the 1·70 eV band was observed. By taking the difference between the 2·02 eV band as reported in the literature[4], and the measured emission spectrum, the 1·70 eV band can be isolated. This is shown by the dashed curve in Fig. 1. Figure 2 shows the excitation spectra for both the 2·02 eV emission band and the 1·70 eV emission. From this figure, it is clear that both emissions are excited at the band edge (3·30 eV) as well as at lower energies unlike the green (2·44 eV) emission which was found to be excited only at the band edge. If the low energy tail of the peak at 3·30 eV in the excitation spectrum of the 2·02 eV band is extended in the same manner as the low

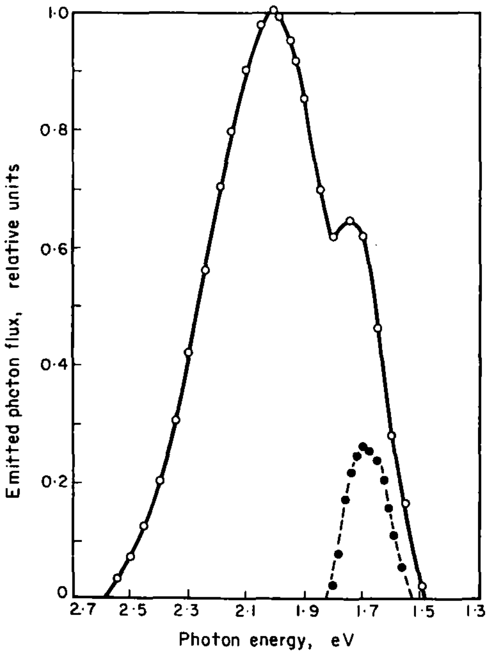

Fig. 1. Typical photoluminescence emission spectrum for ZnO. Measured spectrum- ○. Resolved 1·70 eV emission band- ●.

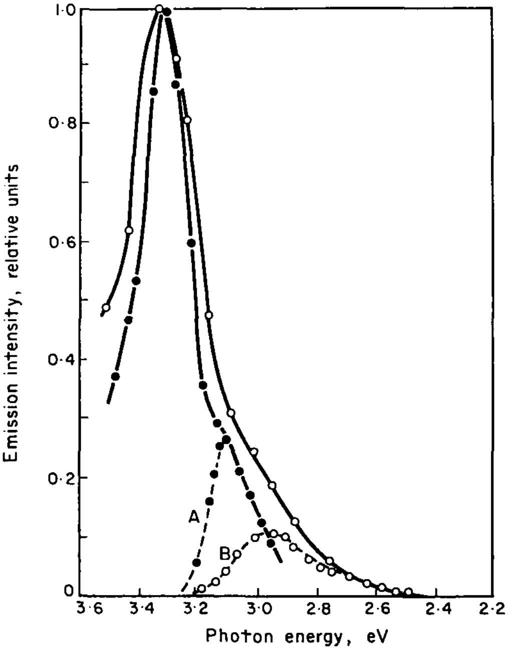

Fig. 2. Excitation spectra for the 2·02 and 1·70 eV emission bands in ZnO. The direct excitation of the 2·02 eV band is shown by curve A, and that of the 1·70 eV band by curve B.

energy tail of the excitation spectrum of the 2·44 eV band, and the result is subtracted from the measured data, then a nearly symmetric band peaking at 3·10 eV remains as shown by curve A in Fig. 2. If the same procedure is followed for the excitation spectrum of the 1·70 eV emission band a single symmetric band is not found. However, if the two bands which were resolved in the excitation spectrum of the 2·02 eV emission are subtracted, then a single symmetric band peaking at 2·94 eV remains as shown by curve B in Fig. 2. Therefore, it is concluded that the excitation of the 1·70 eV emission band consists of three bands. The same two bands which are found in the 2·02 eV excitation spectrum are present plus an additional band that excites only the 1·70 eV emission. Based on this analysis, the lowest energy band in each case is attributed to the direct excitation of the luminescence centers. If these are the direct excitation bands then it is possible to excite the 1·70 eV emission in the direct excitation band of the 2·02 eV emission. This effect is observed experimentally, but is not unambiguous because of the overlap of the two bands.

The temperature dependences of both the 2·02 and 1·70 eV emissions are given in Fig. 3. The temperature dependences of the two emissions are qualitatively similar; in both cases the asymptotic regions of the temperature dependence of the luminescence intensity (I) can be approximated by an exponential function of the form $I = I_0/(1+ce^{-E/kT})$. In this expression, c is a constant and E the activation energy of the thermal quenching process. The intermediate temperature region in both cases is more complex and not readily describable by a simple function. The activation energies for the 1·70 eV band are larger than the corresponding energies for the 2·02 eV band. These temperature dependences are markedly different from that of the green band which was found to go through a maximum at approximately 165°K. Based on these

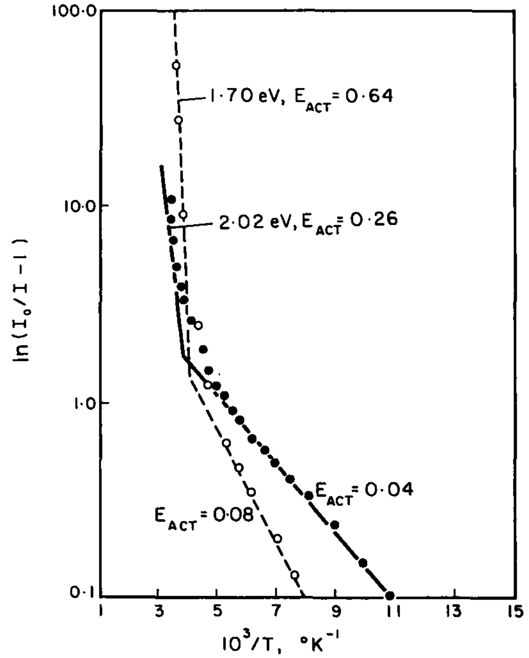

Fig. 3. Temperature dependence of the 2·02 eV (●) and the 1·70 eV (○) emission bands.

thermal quenching data, an energy level scheme could be deduced. The most likely assignments would be to identify the larger activation energies in each case with the direct thermal excitation of trapped holes into the valence band, and to identify the smaller activation energies in each case with metastable excited states of the trapped holes. However, because of the complexities of the thermal quenching process, expecially in the transition region between the two exponentials, these identifications are at best tentative and should not be considered too seriously. Additional measurements revealed that both the 1·70 eV band and the 2·02 eV band are present in all the thermoluminescence peaks, and that both emission bands could be stimulated by i.r. radiation (broad band tungsten light through a Si filter).

The only appreciable qualitative difference observed in the two emission processes was in the decay times. It was found that the decay of the 2·02 eV band could be described by the sum of the two exponentials, one with a time constant of approximately 13·7 sec and the other with a time constant of approximately 1·4 sec. The decay of the 1·70 eV emission was sufficiently fast that it could not be detected by using d.c.-techniques. Attempts to measure the decay using a flash lamp were unsuccessful. From these experiments it is possible only to place an upper limit of approximately 5 msec on the decay time of the 1·70 eV emission. Hence, the 2·02 eV band decays with appreciable phosphorescence while the decay of the 1·70 eV band is much faster.

The difference in the decay of the luminescence could be a result of the nature of the excited state of the 2·02 eV emission. Since the long decay is observed only in the 2·02 eV band and not the 1·70 or 2·44 eV bands, and since all three emission bands are present in thermoluminescence, it is not likely that this extended decay is a result of deep electron trapping. It is more likely that the phosphorescence is a result of the lifetime of the excited state of the luminescence center. If the excited state of the luminescence center, regardless of its atomic origin, is independent of both the conduction and/or the valence bands, then the requisite lifetime for the state can be readily postulated. For example, if it is assumed that the 2·02 eV luminescence center is a substitutional Li at a Zn lattice site then the following argument regarding the nature of its excited state can be made. Since the final state of the Li center can be regarded as a linear combination of Γ_1 states of the wurtzite space group C^4_{6v} the 2·02 eV emission should be polarized parallel to the *c*-axis if the transition originates from the edge of the Γ_1 conduction band. Schirmer and Zwingel[5] were unable to observe the complete polarization of the 2·02 eV emission, and therefore concluded that the transition originated from localized states slightly below the edge of the Γ_1 conduction band. If this is the case, the long decay time of the 2·02 eV emission can be ascribed to the lifetime of this excited state.

Based on these results, it is believed that the center responsible for the 1·70 eV emission is a charge transfer center with many properties in common with the 2·02 eV luminescence center. Indeed, if the lower energy subbands in the excitation spectra are the direct excitation of the luminescence centers, then from the peak maxima a Stokes shift of 1·08 eV is calculated for the 2·02 eV band and a Stokes shift of 1·24 eV is calculated for the 1·70 eV emission band. This leads to a ratio of 1·54 and 1·73 between excitation and emission of the 2·02 and 1·70 eV emission bands respectively. The approximate agreement between these two ratios indicate that both luminescence centers interact with the host ZnO lattice in approximately the same manner. Because of the similarities in the two luminescence processes, it is postulated that the 1·70 eV emission process, like the proposed Li center model[5] for the 2·02 eV emission process, involves an electronic transition into a trapped hole. In the case of the 1·70 eV emission, the transition is assumed to originate from the edge of the conduction band because of its different decay properties from the 2·02 eV emission. The 2·02 eV emission is assumed to originate in donor centers slightly below the edge of the conduction band. Both emission processes have similar final states, i.e., trapped holes, but different initial states. The 2·02 eV center can be consistently interpreted as an associated donor-acceptor center, while the 1·70 eV center is an unassociated acceptor-like charge transfer center. For the 1·70 eV emission, the trapped hole is approximately 1·60 eV above the edge of the valence band. This model is supported by the presence of both the 2·02 and 1·70 eV emission bands in thermoluminescence and also the i.r. stimulation of the two emission bands.

The atomic nature of the 1·70 eV luminescence center remains unresolved. It has been previously suggested[6] that the center responsible for this emission was a N–H pair that substituted at O sites in the ZnO lattice. Gerbshtein and Zelikin[7] disagree with this identification. They propose that the 1·70 eV emission arises from the oxidation of excess surface Zn. The results of this study suggests that neither of these models are consistent with the experimental data. Clearly, the 1·70 eV emission band is present in our samples in the absence of doping with N and H. The peak in the excitation spectrum of the 1·70 eV band at 3·30 eV indicates that surface effects are not involved in the luminescence process. Because of the increase in optical absorption in the region of the band edge, fewer and fewer bulk luminescence centers are excited in this energetic region. This effect causes the excitation spectrum to peak in the vicinity of the band edge and then fall off on the high energy side. If the 1·70 eV emission band is a result of radiative recombination at localized surface states, then the excitation spectrum for this band should not decrease at energies greater than 3·30 eV, but remain high since the same number of surface states would be excited independent of increases in excitation energy. In addition, the intensity of the luminescence is approximately independent of the type of sample. That is the magnitude of the 1·70 eV emission band is nearly the same in powder phosphors as it is in single crystals when both have been oxidized sufficiently. These results strongly suggest that surface effects are not dominant.

There seems to be several other logical defect centers that might qualify as the luminescence center. Since it is virtually impossible to eliminate Na (or other alkali metal impurities), it is necessary to consider defects such as Na at a Zn lattice site as likely candidates, since they would behave in a manner analogous to Li at a Zn lattice site. Also, Zn vacancies which have been observed in ZnO crystals[8] cannot be disregarded. These centers certainly could give rise to the observed luminescence in a manner similar to the 'self-activated' center of ZnS.

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