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Photoluminescence and optical properties of $Mg_xZn_{1-x}Te$ alloys

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The photoluminescence and optical properties of $Mg_xZn_{1-x}Te$ alloys have been studied in the composition range $0 < x < 0.48$. The results are discussed taking into account the formation of band tails due to the alloying effect or random distribution of impurities. The role of residual defects in magnesium-rich alloys is emphasized. On the other hand, a preliminary investigation showed that it is possible to incorporate lithium by high-temperature diffusion in $Mg_xZn_{1-x}Te$ alloys without altering the magnitude or the homogeneity of the magnesium concentration. Evidence is obtained for an increased quantum efficiency after lithium doping.

1. Introduction
In recent years, the successful preparation of high quality $Mg_xZn_{1-x}Te$ crystals has stimulated an interest in this material for the purpose of application in the field of light-emitting diodes (LEDs). The fundamental energy gap of the alloy varies with x within the range 2.27 eV (ZnTe) to 4 eV (MgTe), i.e. suitable for application in the green and the blue ranges of the visible spectrum [2–7].

Some of the fundamental properties of unintentionally doped crystals have already been investigated using luminescence, electrical and wavelength-modulated reflectivity measurements [3–9]. In this paper, we present a further study of the luminescence properties and a preliminary investigation of the effect of lithium doping on those properties. We also report on the optical properties (transmission and reflectivity) of undoped alloys which has so far been given relatively little attention in previous investigations [2, 3].

2. Experimental techniques
The $Mg_xZn_{1-x}Te$ crystals used in the present study were grown from tellurium-rich solutions using the Bridgman technique [1]. The growth temperature varied within 1050 to 1150° C, depending on the composition [1].

The photoluminescence was excited using the 454.5 nm or 478.5 nm line of an argon laser source type Spectra Physics 265 delivering 20 mW on the sample surface. Transmission and reflectivity measurements were carried out using a double beam spectrophotometer type Beckman UV 5240.

For measurements as a function of temperature, the sample was mounted in a liquid helium cryostat which allows a temperature control between 1.6 and 300 K.

3. Results
3.1. Photoluminescence
The photoluminescence spectra at 1.6 K of unintentionally doped $Mg_xZn_{1-x}Te$ in the near band edge region are shown in Fig. 1. For $x = 0$ (ZnTe), the principal band edge (PBE) line at 2.376 eV was identified as being due to the annihilation of an exciton bound to a neutral lithium-acceptor present as a residual impurity [10, 11]. One or two LO-phonon replicas of this line could be observed at lower energies. Another near band edge line at 2.362 eV was attributed by Rodot [12] to a free-to-bound (FB) transition

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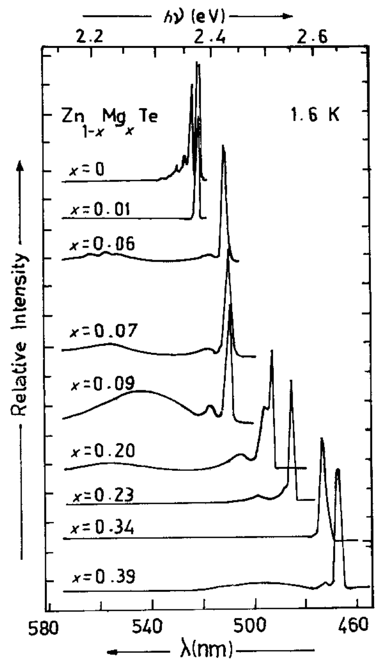

Figure 1 Photoluminescence spectra of $Zn_{1-x}Mg_xTe$ alloys at 1.6 K.

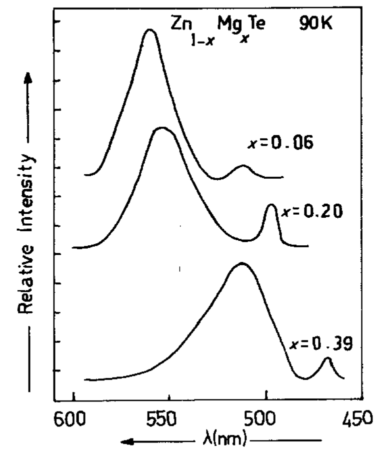

Figure 3 Photoluminescence spectra of $Zn_{1-x}Mg_xTe$ alloys at 90 K.

involving an unidentified donor. Other lower energy peaks could also be observed in the energy range 2.360 to 2.324 eV. They were attributed to FB- or pair-transitions involving residual or native impurities [11–13].

Fig. 1 shows that alloying ZnTe with magnesium leads to a spectrum in which the so-called PBE-line is dominant. Deep-lying emission bands are sometimes observed but their intensities were generally lower than that of the PBE-line at 1.6 K.

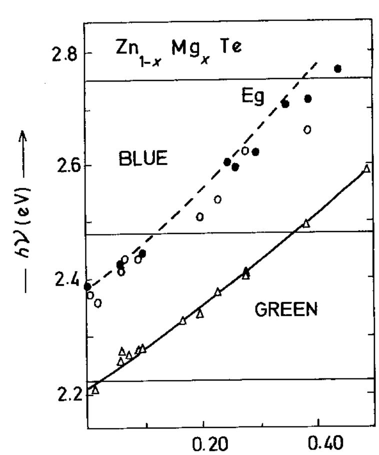

Figure 2 ○, energy of the PBE-peak at 1.6 K. △, threshold energy of the transmission at 300 K. Open points: our results; solid circles: [8]; dashed line: energy gap after [5].

In Fig. 2, the energy of the PBE-peak observed in our samples and in similar samples studied by Somogyi *et al.* [8] is compared with the fundamental energy gap E_g [5], in the composition range $0 < x < 0.48$. The observed dispersion of the points (particularly for $x \gtrsim 0.1$) cannot be explained by experimental uncertainties in the determination of $h\nu_p$ (energy of the PBE-peak) or the composition x. A possible explanation of this dispersion will be discussed later (Section 4).

The band edge spectrum at 90 K is shown in Fig. 3 for some samples. The low-energy emission band is centred at about 0.21 ± 0.01 eV from the higher energy peak for all the studied samples. The interpretation of these peaks requires further investigation. On the other hand, no luminescence could be observed at room temperature with the 20 mW excitation power of the argon laser.

In order to study the effect of lithium doping on the luminescence, an attempt has been made to incorporate lithium by diffusion at high temperature. A sample with 20% MgTe content was placed in a vacuum-sealed quartz ampoule at 950° C for 24 h while a lithium phase was condensed on its surface using $LiNO_3$ salt. Fig. 4 shows a SIMS profile of lithium and magnesium concentrations after doping. Below a surface layer estimated to be about 2 μm, the concentration of lithium is shown to be nearly constant (within ± 2%) indicating homogeneous distribution of lithium in the bulk. The magnesium homogeneity, on the other hand, is unaffected by the high-temperature treatment. This is confirmed by measuring the absolute value of x at different points on the sample surface

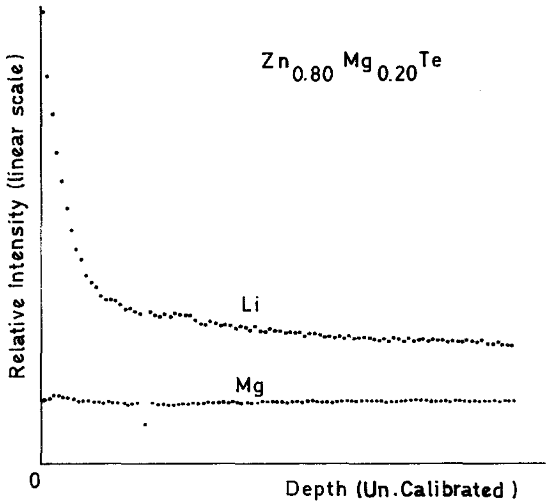

Figure 4 SIMS profiles of lithium and magnesium in $Zn_{0.80}Mg_{0.20}Te$ after doping.

before and after diffusion using microprobe analysis. No detectable change in the average value, or the homogeneity of magnesium concentration (within ± 0.5%) could be observed.

Fig. 5 illustrates the effect of lithium doping on the luminescence spectrum at 1.6 K. The observed spectrum of the sample after doping is similar to that observed on some heavily doped lithium-diffused ZnTe:Li crystals [14]. At room temperature, a broad band edge luminescence peak ($\Delta E \simeq$ 60 meV) similar to the so-called B-peak observed on ZnTe:Li [12, 14] could be detected using the 20 mW excitation power of the argon laser.

3.2. Optical properties

The room temperature optical transmission, T, and reflectivity, R, have been measured as a function of wavelength in the range $0.4 < \lambda < 2.5\,\mu m$. The energy gap, E_g, was calculated from the threshold wavelength, λ_t, of the transmission using the relation $E_g = c/\lambda_t$, c being the velocity of light. The composition dependence of E_g is shown in Fig. 2 (triangles). λ_t has also been measured as a function of temperature for the composition $x =$ 0.28. The calculated values of E_g are shown as a function of temperature in Fig. 6. The temperature coefficient of E_g above 100 K is found to be

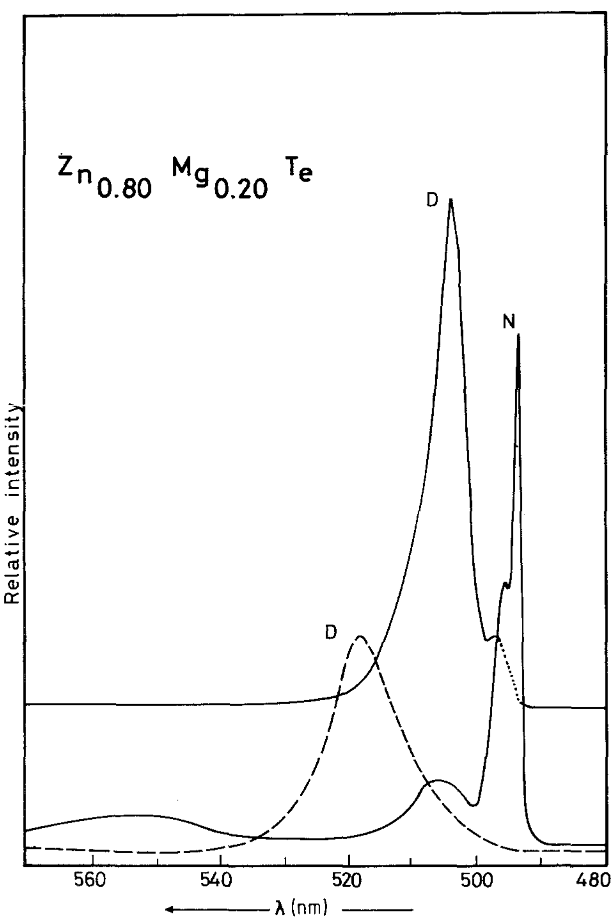

Figure 5 Photoluminescence spectrum of $Zn_{0.80}Mg_{0.20}Te$ before (N) and after (D) lithium-doping. Solid line, 1.6 K; dashed line, 300 K.

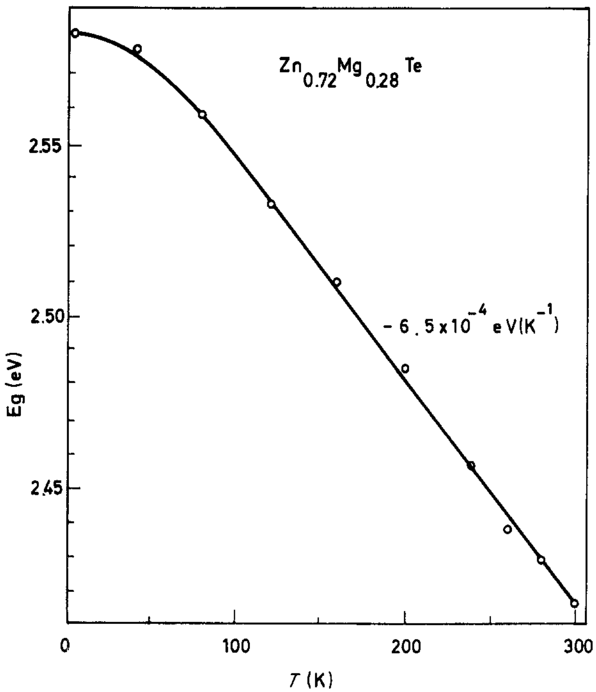

Figure 6 Temperature dependence of the energy gap, E_g, for $Zn_{0.72}Mg_{0.28}Te$.

-6.5×10^{-4} eV deg^{-1} in fair agreement with the previously reported values (-4.3×10^{-4} to -8.5×10^{-4} eV deg^{-1}) [5, 15].

The absorption coefficient, α, was calculated using the relation

$$T = \frac{(1-R)^2 \exp - \alpha d}{1-R^2 \exp - \alpha d} \qquad (1)$$

where d is the sample thickness ($d = 0.7$ to 1 mm).

The energy dependence of α for different compositions is shown in Fig. 7. For a given value of α in the steep rising edge, the shift in energy with composition is consistent with the obtained dependence of E_g with x in Fig. 2.

4. Discussion

4.1. Density of states tails in $Mg_xZn_{1-x}Te$ alloys

It has been recently reported that zinc and magnesium atoms in $Mg_xZn_{1-x}Te$ alloys are approximately randomly distributed over substitutional sites [7]. This alloying effect produces tails in the density of states which extends inside the forbidden gap at the band edge region [16]. Tailing in the density of states may also be produced as a result of the random distribution of impurities.

The interband absorption in the region of band tails can be studied using optical measurements in the low absorption coefficient range $\alpha \lesssim 10^2$ cm^{-1} (Fig. 7). Assuming an exponential dependence of the density of states as a function of energy in the so-formed band tail, the absorption coefficient is given approximately by [17–20]

$$\alpha = \alpha_0 \exp h\nu/\eta \qquad (2)$$

where η is the depth of the band tail measured relative to the undeformed band.

Fig. 8 shows the dependence of log α on $h\nu$ for

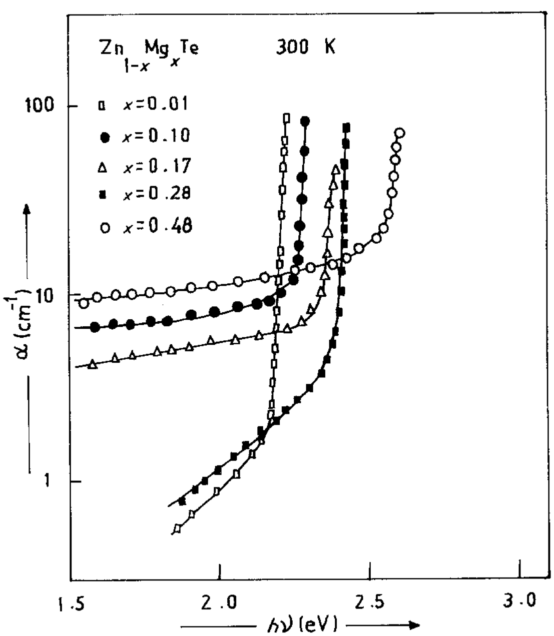

Figure 7 Energy dependence of the absorption coefficient at 300 K for $Zn_{1-x}Mg_xTe$ alloys.

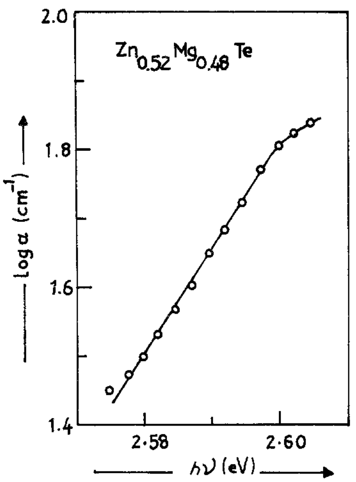

Figure 8 Energy dependence of the absorption coefficient at 300 K for $Zn_{0.52}Mg_{0.48}Te$.

a typical sample. The relation is fairly well represented by a straight line in agreement with Equation 2. The values of η deduced from the slope of similar plots for different compositions are given in Table I. They fall in the range of previously reported values for II–VI compounds (10 to 40 meV) [14].

It is clear from Table I that η shows no systematic variation with x, a behaviour which cannot be explained by alloying effect only. This suggests that the contribution of impurities in band tailing is significant in our samples. It has been reported that above $x = 0.1$, the bound exciton lines of modulated reflectivity spectra show a sudden broadening, while the room temperature hole concentration decreases drastically [7, 8]. It was assumed that donor-type impurities or defects play an important role in $Mg_xZn_{1-x}Te$ alloys. The random distribution of such impurities is expected to produce band tails which extend more or less deeply inside the forbidden gap depending on the residual doping level.

The effect of band tails on the position of luminescence lines is well known. Therefore, band tailing may be invoked in order to interpret the observed dispersion in $h\nu_p$ against x points. This dispersion may be a result of the presence of variable concentrations of residual impurities in the samples which lead to different values of η. However, it is not known whether or not the same type of residual defect is dominant in the entire range of x from 0 to 0.48. Therefore, the possibility of a change in the nature of the PBE lines as x increases cannot be excluded.

TABLE I Experimentally determined values of η (Equation 2) for $Mg_xZn_{1-x}Te$ alloys

x	η (meV)
0.01	14
0.10	14
0.17	26
0.28	11
0.48	29

4.2. Lithium-diffused $Mg_xZn_{1-x}Te$ alloys

One of the central problems in the field of LEDs is the choice of the proper dopant which should:

1. enhance the quantum efficiency of the material;
2. reduce the room-temperature resistivity of the material in order to avoid series resistance effects in the device.

In ZnTe ($x = 0$), these conditions were found to be fulfilled by the impurities Li and P which act as shallow acceptors when incorporated in substitutional sites (Li_{Zn} and P_{Te}) [11, 14, 21, 22]. At doping levels of the order of 5×10^{18} cm^{-3}, the quantum efficiency reaches 0.1% and the resistivity reaches values as low as 10^{-1} Ωcm at room temperature. However, recent investigations on MgZnTe:P doped in the melt showed that phosphorus has a complex behaviour in this alloy [8]. Several types of defects are believed to be formed. Some of these defects (e.g. associates with interstitials) are undesirable for LED applications since they act as deep centres and therefore reduce the band edge emission used for applications.

It was believed that the incorporation of the impurity by diffusion at relatively low temperatures would favour the formation of substitutional defects and reduce the concentration of other types of defects, particularly interstitials and their associates. Lithium was used in this investigation since it is known to have a higher diffusion coefficient than phosphorous in II–VI compounds. The results show that it is possible to obtain homogeneously doped lithium-diffused MgZnTe crystals without altering the composition x. The concentration of lithium could not be determined due to lack of calibration of the SIMS analyser, but the luminescence spectrum after doping indicates a high lithium concentration (by comparison with ZnTe [14]). Also, the quantum efficiency of the material is enhanced after doping. This is evident from the fact that the lithium diffused crystal shows a luminescence peak at room temperature while, under the same experimental conditions, no luminescence was detectable from undoped crystals.

The two no-phonon peaks observed in the 1.6 K spectrum of lithium-diffused $Mg_{0.28}Zn_{0.72}Te$ are similar to those previously reported for ZnTe:Li [14, 23, 24]. In the latter case, the low-energy (LE) and high-energy (HE) peaks were attributed to free-to-bound recombinations involving substitutional and interstitial lithium, respectively. If we adopt the same interpretation for the alloy, the high value of intensity ratio, I_{LE}/I_{HE}, may indicate a high ratio of substitutional/interstitial defect concentration as expected in diffusion experiments. Thus, lithium diffused MgZnTe alloys seem to possess interesting properties for applications. The good homogeneity of lithium concentration should allow the close investigation of the bulk properties and, therefore, the evaluation of this material as a possible candidate for LED applications. Electrical and optical measurements covering a wide range of x are at present being conducted.

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