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B. M. DITCHEK
K. R. BREEN
J. D. VENABLES
Martin Marietta Laboratories,
Baltimore,
Maryland 21227, USA

Growth of Z centres in X-irradiated LiF:Mg

The enhancement of *F* centre formation by divalent impurities in alkali halides has been studied by several workers. Most of the data on this subject are confined to alkaline earth impurities such as Ca^{2+}, Ba^{2+} and Sr^{2+} in NaCl, KCl and KBr. There are comparatively few works on the effect of doping with Mg^{2+} in LiF in spite of the fact that this material is very important for thermoluminescent dosimetry. In this letter some interesting results on this subject are reported.

A sample obtained from a crystal doped with 0.2 wt% Mg in the melt and a size of $8 \times 8 \times 2$ mm^3 was used for the study. The sample was first annealed for 1 h at 480° C, cooled to room temperature within 15 min and then thermally treated at 80° C for either 16 h (Procedure 1), 5 h (Procedure 2), or 2 h (Procedure 3). X-ray exposure after each thermal treatment was performed in steps between 0.026 and 0.52 kC kg^{-1}. After each irradiation the absorption spectrum was measured and resolved into a set of Gaussian shaped bands.

Figs 1a and b, show the influence of two different pre-irradiation annealing procedures on some selected radiation-induced optical absorption curves. As can be clearly seen, there is a strong dependence of the absorption regions on both sides of the *F* absorption band at 5 eV on the duration of the 80° C annealing. These regions are known to be connected to the different *Z* centre absorption bands, i.e. the 3.3 eV band, the Z_2 band at 4 eV and the Z_3 band at 5.5 eV [1]. According to Dryden *et al.* [2] it is considered that annealing Procedure 1 provides for a low concentration of dipoles (Fig. 1a), Procedure 2 for a medium concentration and Procedure 3 for a high concentration (Fig. 1b).

After computer analysis of all the absorption spectra, to determine the peak absorption coefficient for the different bands, the data were plotted as shown in Fig. 2. The abscissa dose *D*

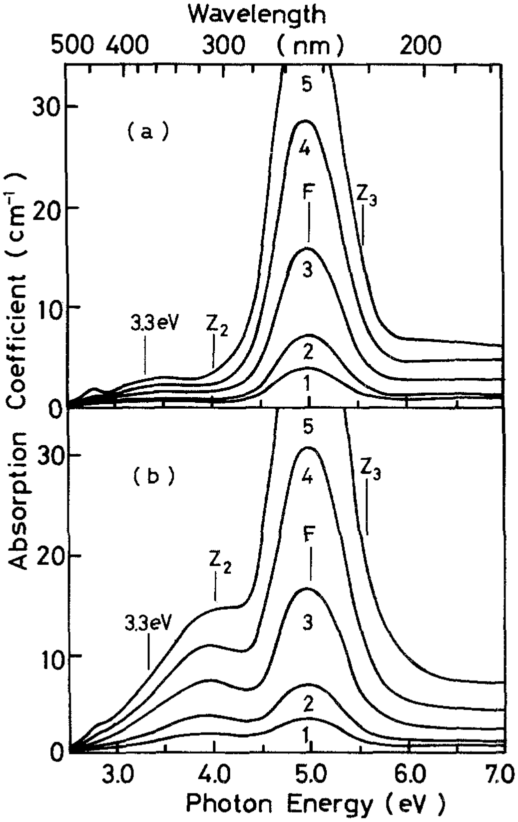

Figure 1 Absorption spectra of LiF : Mg after pre-irradiation annealing at 80° C for (a) 16 h and (b) 2 h and subsequent X-ray irradiation to different doses: (1) 0.026, (2) 0.052, (3) 0.13, (4) 0.26, (5) 0.52 kCkg^{-1}. The absorption spectra present prior to irradiation have been subtracted in all figures.

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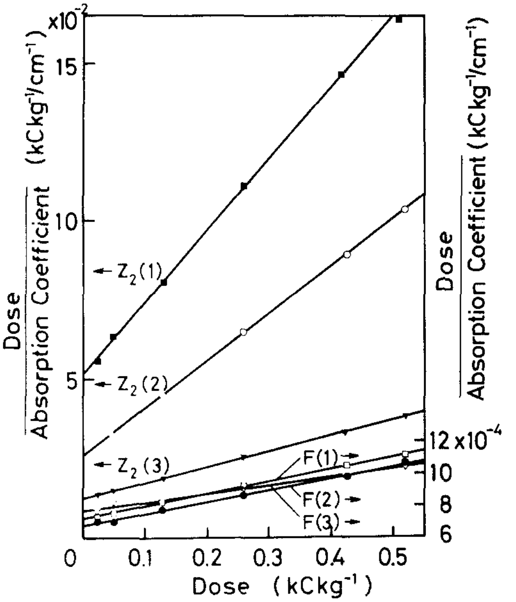

Figure 2 Dose divided by the peak absorption coefficient as a function of dose. Left scale: data for Z_2 band. Right scale: data for F band. Numbers in parenthesis correspond to different pre-irradiation annealing times at 80° C: (1) 16 h, (2) 5 h, (3) 2 h.

is divided by the absorption coefficient and this ratio is plotted as the ordinate. This has been done for the F and Z_2 centre absorption coefficients. The data for the 3.3 eV band and for the Z_3 band have not been plotted, because they were found to be proportional to the peak absorption coefficient of the Z_2 band. The three different plots for the F and Z_2 centres correspond to the three different thermal treatments. In general, all the plots obtained in Fig. 2 are straight lines over the measured dose range. It should be noted that a plot like this was first performed by Etzel and Allard for F centres in NaCl doped with Ca^{2+} [3]. The curves obtained in Fig. 2 can be described by the equation, $D/\alpha = mD + b$, where α is the peak absorption coefficient, m is the slope, b is the intercept on the D/α axis and D is the dose. From this, $d\alpha/dD = (m^2/b)(1/m - \alpha)^2$, is obtained. The new equation indicates that the basic mechanism for the formation of these centres is a second order reaction.

Hays and Nichols [4] proposed a mechanism in which an X_2^- centre (where X represents the halogen) is formed, during the irradiation, in the vicinity of a divalent cation vacancy dipole. One part of this X_2^- centre is relaxing into the bound cation vacancy thus creating one anion vacancy which is used for the production of an F centre. Later Crawford and Nelson [5] suggested that an isolated cation vacancy is involved.

If one now compares the curves in Fig. 2 with similar plots for the F centres of NaCl:Ca by Etzel and Allard [3] some striking similarities are seen. (1) All the curves are generally straight lines. (2) The curves can be described by a second order reaction. (3) The slope of the Z_2 centre curve shows a strong dependence on the dipole concentration, with decreasing dipole concentration the slope increases. The F centres in NaCl: Ca behave in the same manner. (4) The F centre curves in LiF:Mg do not show a significant dependence on the dipole concentration obtained by different thermal annealing.

Comparison of Etzel and Allard's results and the results given here shows that the Z_2 centres in LiF:Mg behave in the same way as the F centre in NaCl: Ca. That means a similar mechanism must be responsible in both cases. If a reason is sought for this analogous behaviour we have to look for some important properties which are different in LiF compared with other alkali halides: for example, the Z_2 centres in LiF are directly produced by irradiation at room temperature whereas in other alkali halides an additional optical and/or thermal F-bleaching is necessary. Another difference is that no significant early stage of F centre formation in LiF is observed [6]. It is known that there are in general two stages of F centre formation in alkali halides: the first stage being strongly dependent on, and the second stage being independent of, the impurity concentration. The absence of the first stage in LiF suggests that the mechanism proposed to explain the F centre formation in other alkali halides is not operative in LiF. From the fact that the Z_2 centre production in LiF:Mg is similar to the F centre production in other alkali halides containing divalent impurities (e.g. NaCl:Ca), it may be deduced that the conversion mechanism for the production of F centres in other alkali halides can be applied to the Z_2 centre production in LiF:Mg. Because most of the models proposed hitherto for the Z_2 centre contain one divalent impurity and at least one anion vacancy which can trap electrons, it is our opinion that the Hays–Nichols mechanism is very probable.

Although it is not possible to describe the exact mechanism for the production of Z_2 centres which reveals the second order reaction of dipoles, it is considered that the movement of divalent ions or their complexes during X-irradiation is required in order to give rise the second order reaction. With respect to this problem, it has been reported that the divalent metal aggregates as well as showing decomposition of dipoles during X-irradiation at room temperature [7], which seems to suggest the free movement of dipoles as well as impurity ions and/or vacancies when the sample is irradiated by X-rays at room temperature.

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H. -J. KOS
R. NINK
Physikalisch-Technische Bundesanstalt,
Institut Berlin

N. TAKEUCHI
Faculty of Technology,
Kanazawa University,
Kodatsuno 2-40-20,
Kanazawa (920),
Japan

Intergranular embrittlement caused by the precipitation of M_6C carbide containing silicon

It was found that a nickel alloy with the following base composition (wt%)

C	Si	Cr	W	Mo	Ti	Al	Ni
⩽0.12	⩽0.6	13	6	3	2	2	Base

becomes embrittled when the silicon content approaches its upper limit. Therefore a series of alloys with silicon contents varying from 0.22 to 1.49 wt% were prepared. After quenching first from 1190° C and then from 1050° C, these alloys were aged at 800° C for 16 h. Fig. 1 shows the room temperature impact toughness of these alloys with a minimum at 0.5–0.6 wt% Si. This abrupt degradation in the impact property at 0.4–0.6 wt% Si and its subsequent recovery at a silicon content above 0.7 wt% was considered to be somewhat abnormal and therefore a thorough metallographic examination was carried out in order to clarify the behaviour of silicon in this type of alloy.

The embrittled alloy gives typical intercrystalline fracture appearances after impact testing. Microscopic examination of polished specimens shows the presence of many tiny particles precipitated at the grain boundaries along which cracking takes place. Electron microprobe analysis shows the enrichment of silicon at the grain boundary reaching about 7 to 8 times the average silicon content of the matrix. In order to ascertain the nature of the grain boundary precipitates, an electron optical examination of the extraction replica, made directly from the intergranular fracture surface, was carried out.

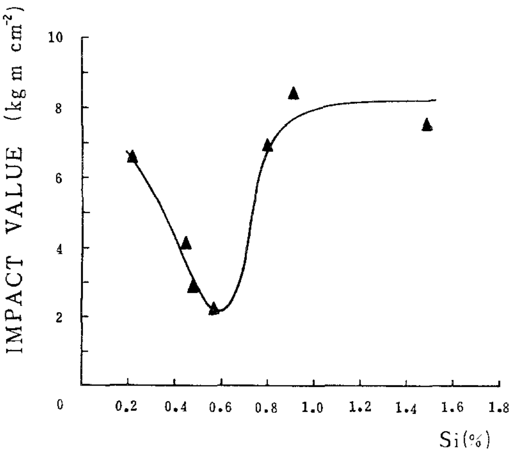

Figure 1 Variation of impact toughness with percentage silicon in a nickel alloy, measured at room temperature.

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