UNIVERSIDADE DE SÃO PAULO

INSTITUTO DE FÍSICA
CAIXA POSTAL 20516
01498-970 SÃO PAULO - SP
BRASIL

PUBLICAÇÕES

IFUSP/P-1022

EMPIRICAL MODEL FOR THE THERMOLUMINESCENCE OF LiF (Mg,Cu)

A.M. Fausto, A.W. Mol and **E. Okuno**
Instituto de Física, Universidade de São Paulo

Novembro/1992

EMPIRICAL MODEL FOR THE THERMOLUMINESCENCE OF LiF(Mg, Cu)

A. M. Fausto, A.W. Mol and E. Okuno
Laboratório de Dosimetria
Instituto de Física
Universidade de São Paulo
Caixa Postal 20516
01498-970 São Paulo, SP, BRASIL

Abstract — The influence of the impurities Mg and/or Cu as well as its concentrations on the thermoluminescent (TL) sensitivity of LiF have been investigated. The effects of the thermal treatments on the TL response and on the glow curve structure were also analyzed. Experimental results showed that the basic pattern of the glow curves and the TL sensitivity are strongly determined by the thermal treatment and by the relative proportion of the concentration of each dopant. From the experimental data, an empirical model to predict the TL response of LiF as a function of Mg and Cu concentrations was developed. From this analysis it was possible to conclude that the Mg is the main impurity associated with TL centres and that the Cu plays the role of a killer. The present approach defines an optimum range of dopant concentrations for the TL sensitivity of LiF.

INTRODUCTION

Since the report, by Nakajima *et al*[1], of a new highly sensitive thermoluminescent (TL) lithium fluoride phosphor (LiF), primarily doped with Mg and Cu and plus some of the following possible dopants P, Si, and B, several papers[2–5] have reported results on the research of these new materials. However, despite such an effort, the basic processes that govern the interactions among the main dopants themselves and the crystal are still unknown. One major difficulty found in these new materials has been the establishment of a suitable thermal treatment that assure high sensitivity, a single stable thermoluminescent peak and the reproducibility of the glow curve including the sensitivity for the reuse[6], after each cycle of annealing, irradiation and readout. The reasons for such a high dependence of the TL sensitivity and of the glow-curve shape on the thermal treatment are unknown at present but this fact is a limiting factor for the use of these new phosphors in routine dosimetry.

This work is inserted in the context of a general effort to understand and characterize the TL processes involved in such materials. Samples used in this work were doped with Mg and/or Cu and they were submitted to the three basic thermal treatments. The mutual interaction between both impurities and the phosphor itself was also investigated in order to establish a possible basic understanding of the interaction processes.

EXPERIMENTAL METHOD

The LiF (Mg, Cu) samples used in this work were manufactured by Nemoto Ltd. Co. from Japan, and they were kindly supplied by Dr. T. Nakajima from Physics Division of National Institute of Radiological Sciences, Japan. All the fourteen samples with different dopant concentrations are identified in a matrix showed in Table 1. The dopant levels, given in mol%, are nominal values provided by the manufacturer. All the samples were in powder form with the grain size range from 74 to 149 μm.

Table 1. LiF samples with Mg and Cu concentrations.

Mg (mol%) ↓ \ Cu (mol%) →	0.00	0.03	0.06	0.12
0.0	S_{00}	S_{01}	S_{02}	S_{03}
0.1	S_{10}	S_{11}	S_{12}	—
0.2	S_{20}	S_{21}	S_{22}	S_{23}
0.4	S_{30}	—	S_{32}	S_{33}

Three different thermal treatments, all in air, before irradiation with gamma rays were examined: 230°C for 10 minutes, 400°C for 1h, and 400°C for 1h followed by 100°C for 2h. After each thermal treatment the sample was quickly cooled to room temperature, spreading it over a Cu plate. The temperature of the oven was controlled within ±5°C and light exposure of the samples after thermal treatment was carefully avoided.

All pre-annealed phosphors were exposed to 0.26 mC/kg (1R) of ^{137}Cs gamma (γ) rays. A conventional TL reader with a linear heating rate of 3.7°C/s was used for TL measurements. An optical filter KG-1 from Schott, with the band pass from 300 to 900 nm, was placed between the sample and the EMI 9789 photo multiplier tube. TL readouts were performed heating the (31.0±0.1) mg of powder in a N_2 gas atmosphere at a flow rate of 0.5 l/min.

TLD-100 ribbons (3x3x1 mm³) from Harshaw Chem. Co. were also used as a reference for all the processes along this work. Under the mentioned exposition to γ rays and heating rate, the intensity of the dosimetric peak 5 was about (5.0±0.3) arbitrary units (a.u.) at an average temperature of (214 ± 8)°C.

RESULTS

Thermal treatments

Figure 1 shows three glow curves of sample S_{21} (0.2 mol% of Mg and 0.03 mol% of Cu) under the mentioned thermal treatments. This sample was chosen to illustrate the common behaviour observed in all samples doped with Mg and Mg+Cu, and because of its high TL sensitivity. After the annealing of (230°C—10 minutes) recommended by the manufacturer[7], a glow curve with three peaks is observed. After the second treatment of (400°C—1h), suggested by Shandra *et al*[8], the glow curve exhibits only one single TL peak at (215±11)°C, in agreement with their results, but with low intensity. The third researched treatment was (400°C—1h, followed by 100°C—2h), the same treatment used in routine monitoring for TLD-100, after which intense TL peaks 4 and 5 appear. Also in case of LiF (Mg, Cu), this treatment produced the best result: its glow curve showed an intense single peak at (242±4)°C, as can be see in Figure 1.

The effect of the third thermal treatment on the crystal sensitivity was studied for four samples: S_{12}, S_{21}, S_{23}, S_{30}. As no measurable sensitivity loss was detected in two successive cycles (annealing, γ exposure and readout), this was the thermal treatment elected for all the samples in this work.

Glow curves of undoped sample and those of doped with Cu only under the last quoted thermal treatment are shown in Figure 2. TL intensity of these samples is very low and the peaks appear in the lower region of temperature, when compared to the curves of Figure 1. A general decrease of the TL sensitivity, as can be seen in Figure 2, with the increase of the Cu concentration suggests the "killer" role of the TL centres carried out by Cu. On the other hand, the rise of a single TL peak at 242°C can be associated to the presence of Mg and to the thermal treatment at 400°C for 1h plus 100°C for 2h, before irradiation, as shown in Figures 1, 3, 4, 5 and 6. Therefore, it is possible to conclude from the comparison of the curves of these Figures with those of Figure 2 that the structure of

TL glow curves is determined not only by the thermal treatment but also by the associations of both dopants presents in the crystal.

Table 2 summarizes the average (at least 15 measurements) heights of the peak at 242°C for the 14 samples of LiF annealed at 400°C for 1h followed by 100°C for 2h and irradiated with 0.26 mC/kg (1R) of ^{137}Cs gamma (γ) rays.

Table 2. Relative heights (TL sensitivity) of the peak at 242°C from LiF samples doped with different Mg and/or Cu concentrations. Samples were pre-annealed at (400°C—1h plus 100°C—2h) and exposed to 0.26 mC/kg of γ rays.

Mg (mol%) ↓ / Cu (mol%) →	0.00	0.03	0.06	0.12
0.0	S_{00} (0.6±0.3) a.u.	S_{01} very low sensit	S_{02} very low sensit	S_{03} very low sensit
0.1	S_{10} (34 ± 3) a.u.	S_{11} (20 ± 2) a.u.	S_{12} (7 ± 1) a.u.	———
0.2	S_{20} (3 ± 1) a.u.	S_{21} (23 ± 2) a.u.	S_{22} (9±3) a.u.	S_{23} (4 ± 1) a.u.
0.4	S_{30} (0.5±0.3) a.u.	———	S_{32} (1.0±0.5) a.u.	S_{33} (12 ± 2) a.u.

Empirical Model

From the hypothesis that the TL centers are, under the selected thermal treatment, closely related, an empirical mathematical expression that fits the TL responses of the second column of Table 2, as a function of the Mg concentration only, was initially derived. The result of this fitting is shown in figure 7, where the full black circles represent these peak heights. TL peak heights of all other samples doped with Mg and Cu could also be interpreted through the same empirical curve, if we admit a possible competition between the Mg and Cu centres, considering the "net concentration" (K_{Net}) of Mg (free of Cu), that in its turn would be associated with the TL centers. This interpretation follows from the killer role played by the Cu in the TL of LiF(Cu) samples as previously mentioned. From these considerations we derived another "practical" analytical expression, instead of a numerical solution from the differential rate equations, that take into account such a relationship between the Mg (K_{Mg})and Cu (K_{Cu}) concentrations.

The theoretical curve of Figure 7 suggests the existence of a net Mg concentration range (0.07 — 0.09 mol%) in which the TL response should be a maximum (~ 40 a.u.), being approximately 8 times greater than that of LiF (TLD-100) ribbons for the quoted γ dose. Out of this range the TL signal decreases quickly, meaning that the TL centers virtually desapeared. As a consequence, the crystal sensitivity decreases drastically. This behaviour gives evidence that of the whole nominal concentration of Mg only a small fraction contributes effectively to the crystal sensitivity and that the excess would yet be prejudicial to the TL sensitivity.

Figure 8 shows the empirical relations among the K_{Mg} and K_{Cu} concentrations versus K_{Net} and the TL sensitivity. We observe the existence of a range of maximum TL sensitivity, associated to the selected thermal treatment, which could be achieved from several weighted combinations of K_{Mg} and K_{Cu}. However, some of them would be more adequate concerning the control of the amount of dopants introduced into the crystal (the accuracy of the doping processes), and the reliability of the TL response. For instance, the admissible range of variation, ±28% of nominal doping concentration, around 0.14 mol% of Mg (for K_{Cu}=0.01) would yet produce only a small 5% of total fluctuation in TL crystal response. If we consider another Mg doping level, this tolerance would be lower, e.g., ~ 5% for 0.32 mol% of Mg (for K_{Cu}=0.06) at the same TL response fluctuation. Furthermore, the possible variation of Cu concentration (from segregation in the crystal) must be considered too for the concise calculation of the tolerance on TL sensitivity in actual doping processes. We ought to remark that the possibilities of prevision, settled in the figure 8, are confined in the ranges covered by the available samples and the suggested thermal treatment. Extrapolations out of these ranges might be possible, although there is no experimental warranty for successful results.

DISCUSSION

We could interpret the previous results, and support the empirical model, on the base of a possible kinetic formation of TL centers, assuming the clustering effect as responsible by the behaviour of the 242°C glow peak. On such physical base, the Mg_Li_{vac} dipoles are metastable defects, formed mainly under the annealing of (400°C—1h). On the other hand, under the annealing of (100°C–2h), they are clustered to form more-stable complexes as dimers, trimers and higher order Mg clusters. The TL effect might be attributed to trimers[9] . Therefore, from the initial condition (Mg concentration in the crystal) and an adequate thermal treatment (temperature × time), the quantity of cluster population (responsible for TL centers) could be optimized, thereby improving the TL response of the crystal.

If we assume that the trimers are responsible for the TL centres, the 100°C annealing seems to favour their formation from the aggregation of Mg_Li_{vac} dipoles. However, the ideal time interval of annealing is still an open question. The determination of this time should take into account the quantity of impurities and the time evolution of clustering.

Assuming the association of Cu with the Mg clusters and that the interaction Cu/trimer can destruct the TL centres, then the net result of Cu interactions is to subtract a variable amount of Mg from the whole concentration. This amount would be proportional to the quantity and complexity of the clusters associated with Cu. Then, the phosphor would behave as a "lower" doped crystal with Mg than it really is, and its TL response can be explained by the same analytical descripition previously established for LiF doped only with Mg.

If we consider that the probability and the true nature of interactions among the Cu and the Mg complexes are unknown and that they happen under a dynamic process, it becomes clear that is very difficult to deal with this class of problems in a non empirical base. Nevertheless, concerning the Cu interaction, some remarkable previsions are supplied by the model, as the occurrency of a plateau in the parametric curves (K_{Cu}= constant). On such plateaus the corresponding TL sensitivities practically remain constant, indicating that an apparent disadvantage role of Cu (to be a killer) turns to be an usefull doping element. Such new Cu property comes directly from the dynamic aspect (non linear) of the Cu/(Mg clusters) associations. The existency of such possibilities challenge us to find a new thermal treatment where the plateau occurs for the maximum TL sensitivity, proportioning a large range of variability for the doping impurities with no sensible TL response loss.

CONCLUSION

Among the researched thermal treatments, the annealing of 400°C—1h plus 100°C—2h seems to be the most adequate, proportioning only one highly sensible TL peak at a convenient temperature range of (242±4)°C, for the available LiF(Mg, Cu) samples. It was verified that after two successive cycles (thermal treatment above referred, irradiation, and readout) the TL response of these samples showed no measurable loss of sensitivity.

From the experimental data it is possible to conclude that the Mg is the main dopant associated with the crystal TL sensitivity, and that the Cu acts as killer of the TL centers. However, this Cu feature has an useful application when we consider the dynamic characteristic of the Cu/TL centers interaction which provides a practical method to reduce the fluctuations in TL sensitivity among samples of variable doping concentrations. The best proportions of dopants, which provide the maximum TL sensitivity, can now be estimated, in view of the empirical model established from the experimental data analysis. This model predicts for LiF(Mg, Cu) crystals optimum doping concentration ranges and a maximum TL sensitivity of ~ 8 times that from the TLD-100 ribbons for the same γ radiation exposure.

ACKNOWLEDGEMENTS

We are grateful to Dr. T. Nakajima for encouragement and discussions. We thank him and Nemoto and Co. Ltd., Japan, for LiF samples supplied to us.

REFERENCES

1. Nakajima, T., Murayama, Y., Matsuzawa, T. and Koyano, A. *Development of a New Highly Sensitive LiF Thermoluminescent and its Applications.* Nucl. Instrum. Methods **157,** 155-162 (1978).

2. DeWerd, L. A., Cameron, J. R., Wu Da-Ke., Papni, T. and Das, I. J. *Characteristics of a New Dosemeter Material; LiF (Mg,Cu,P).* Radiat. Prot. Dosim. **6**, 350-352 (1984).

3. Shoushan, W., Guolong, C., Fang, W., Yuanfang. Li., Ziying, Z. and Jianhuan, Z. *Newly Developed Highly Sensitive LiF (Mg,Cu,P) TL Chips with High Signal-to-Noise Ratio.* Radiat. Prot. Dosim. **14**, 223-27 (1986).

4. Bhuwan Chandra, Pradhan, A. S., Lakshmanan, A. R., and Bhatt, R. C. *Dosimetric Characteristics of Thermoluminescent LiF (Mg,Cu,P) Phosphor.* Bull. Radiat. Prot. IARP (India) **6**.(3/4),89 (1983). Also in Radiat. Prot. Dosim. **8**, 217 (1984).

5. Driscoll, C. M. H., McWhan, A. F., O'Hagan, J. B., Dodson, J., Mundy, S. J. and Todd. C. D. *The Characteristics of New LiF Preparations and Sensitised LiF.* Radiat. Prot. Dosim. **17**, 367-371 (1986).

6. Cameron, J. R., Suntharalingam, N. and Kenney. G. N. *Thermoluminescence Dosimetry.* (The University of Wisconsin Press) Madison, WI (1968).

7. Horowitz, Y.. New *Thermoluminescence Materials.* Radiat. Prot. Dosim. 30, 2 (1990).

8. Shandra, B., Pradhan, A., S., Lakshmanan, A. R. and Bhatt, R. C.. *Dosimetric Characteristics of Thermoluminescence LiF(Mg,Cu,P) Phosphor.* Radiat. Prot. Dosim. 6, 89 (1983).

9. Yuan, X. L. and McKeever, S. W. S.. *Impurity Clustering Effects in Magnesium-Doped Fluoride.* Phys. Stat. Sol. (a) 108, 545 (1988).

10. McKeever, S. W. S. and Lilley, E. *Evidence For Thimer Formation During Dipole Clustering In Mg Doped LiF.* J. Phys. Chem. Sol. Vol. 43, nº 9, pp. 885-893 (1982).

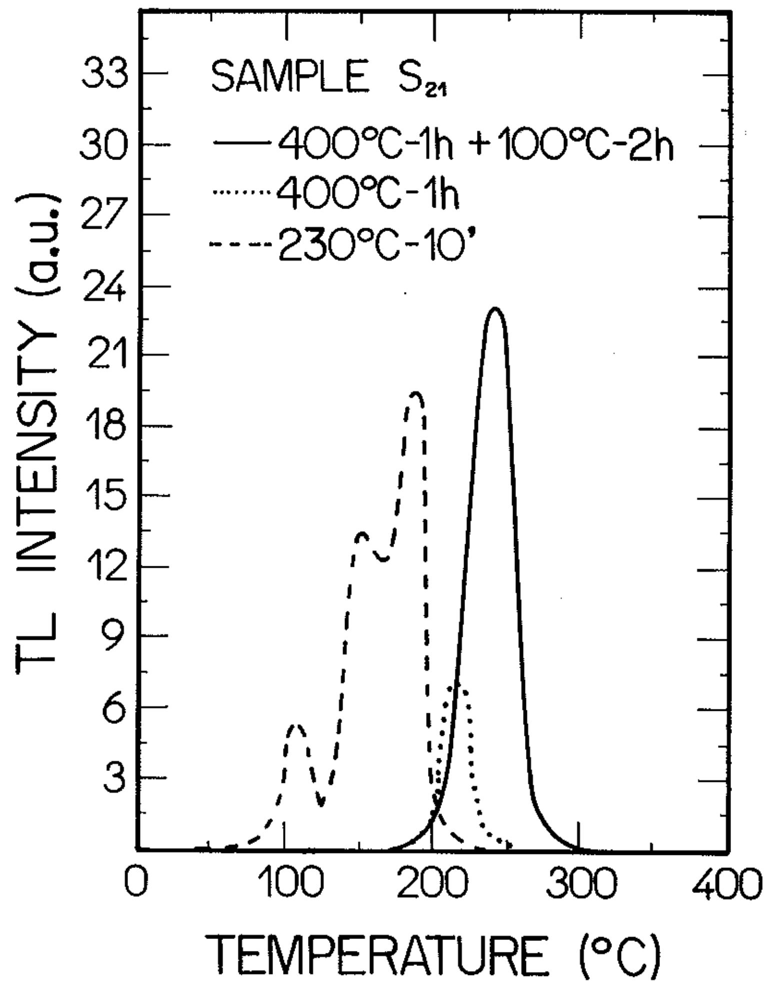

Figure 1. Glow curves of S_{21} sample (0.2 mol% of Mg and 0.03 mol% of Cu). Annealed at: 230°C—10 minutes, 400°C—1h and 400°C—1h plus 100°C—2h.

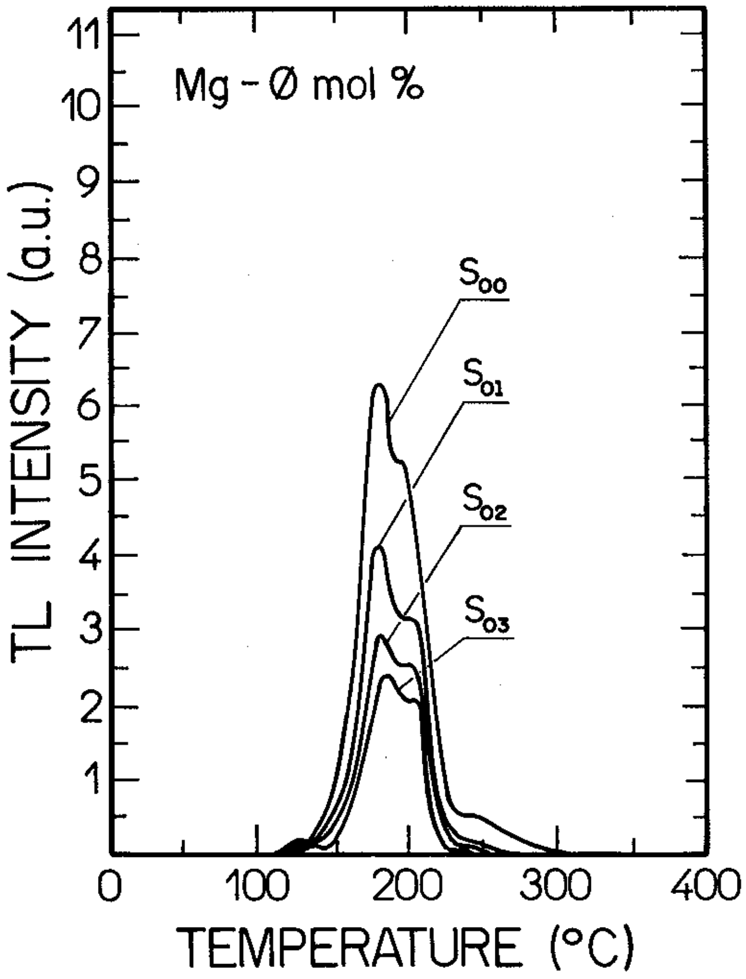

Figure 2. Glow curves of S_{00}, S_{01}, S_{02} and S_{03}. samples. Annealed at 400°C—1h plus 100°C—2h exposed to gamma rays (0.26 mC/kg).

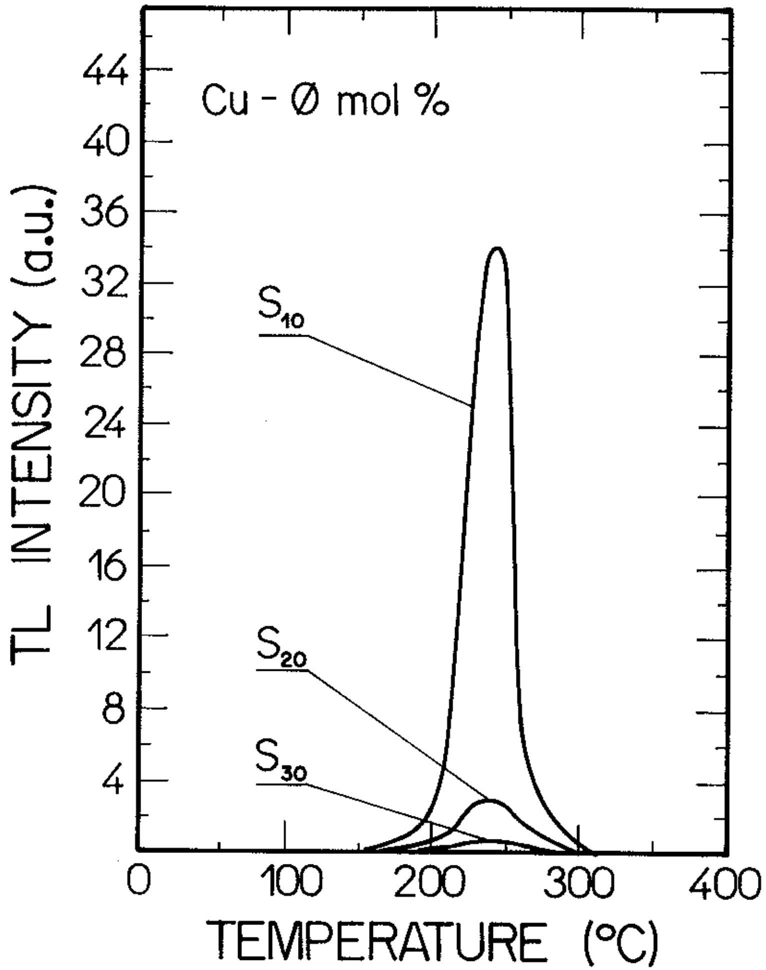

Figure 3. Glow curves of S_{10}, S_{20} and S_{30}, samples. Annealed at 400°C—1h plus 100°C—2h exposed to gamma rays (0.26 mC/kg).

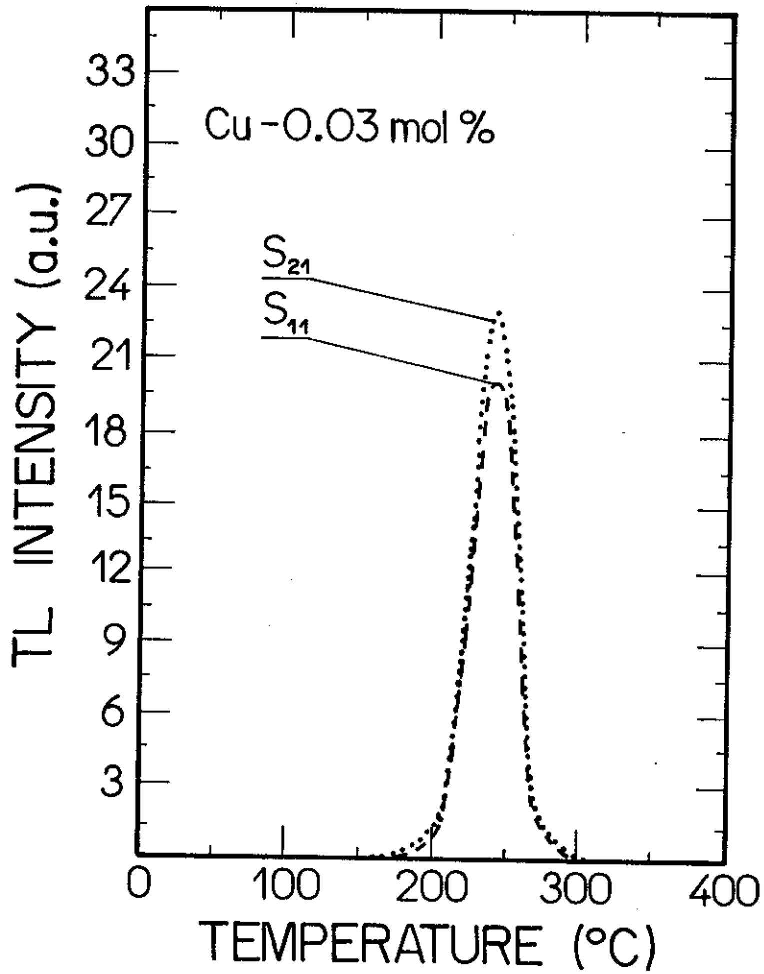

Figure 4. Glow curves of S_{11} and S_{21} samples. Annealed at 400°C—1h plus 100°C—2h exposed to gamma rays (0.26 mC/kg).

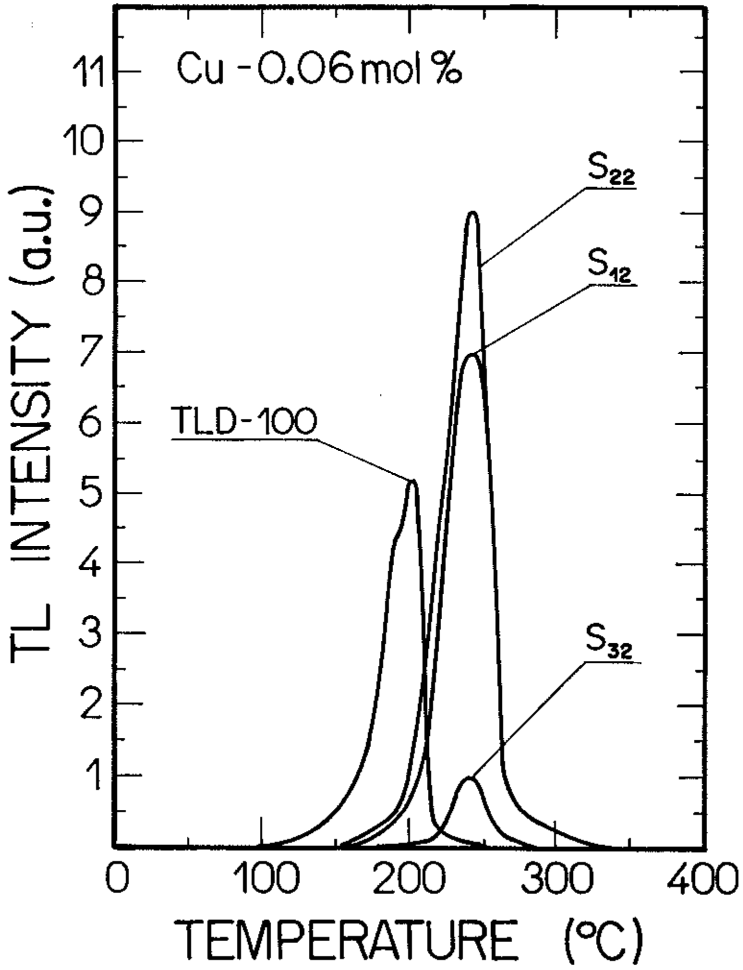

Figure 5. Glow curves of S_{12}, S_{22}, S_{32} samples and LiF TLD(100). Annealed at 400°C —1h plus 100°C—2h exposed to gamma rays (0.26 mC/kg).

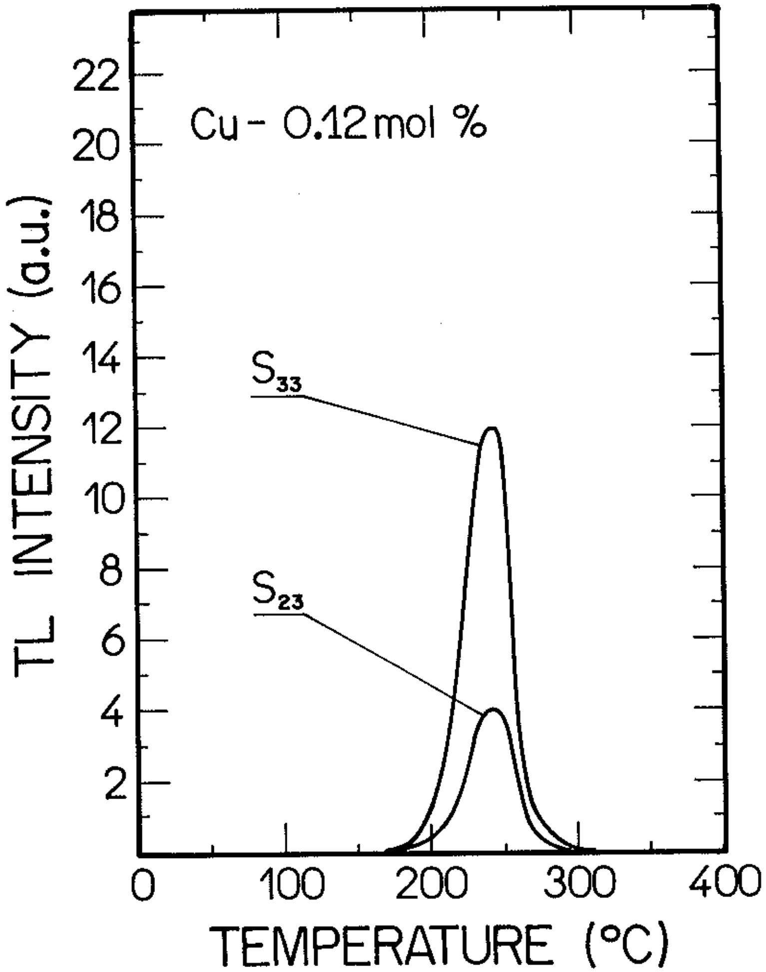

Figure 6. Glow curves of S_{23} and S_{33} samples. Annealed at 400°C—1h plus 100°C— 2h exposed to gamma rays (0.26 mC/kg).

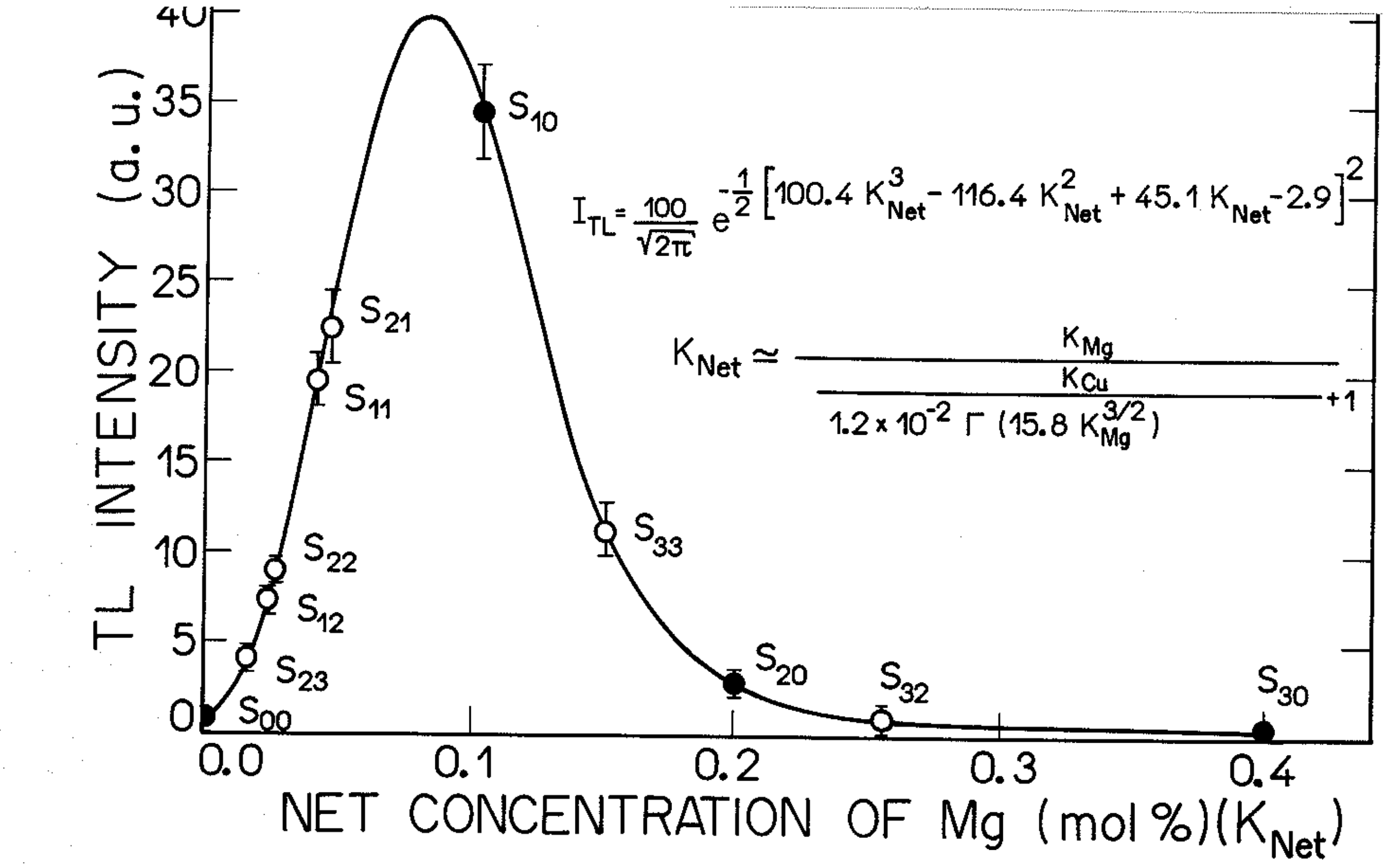

Figure 7. TL peaks at (242±4)°C of LiF samples fitted with an empirical curve.

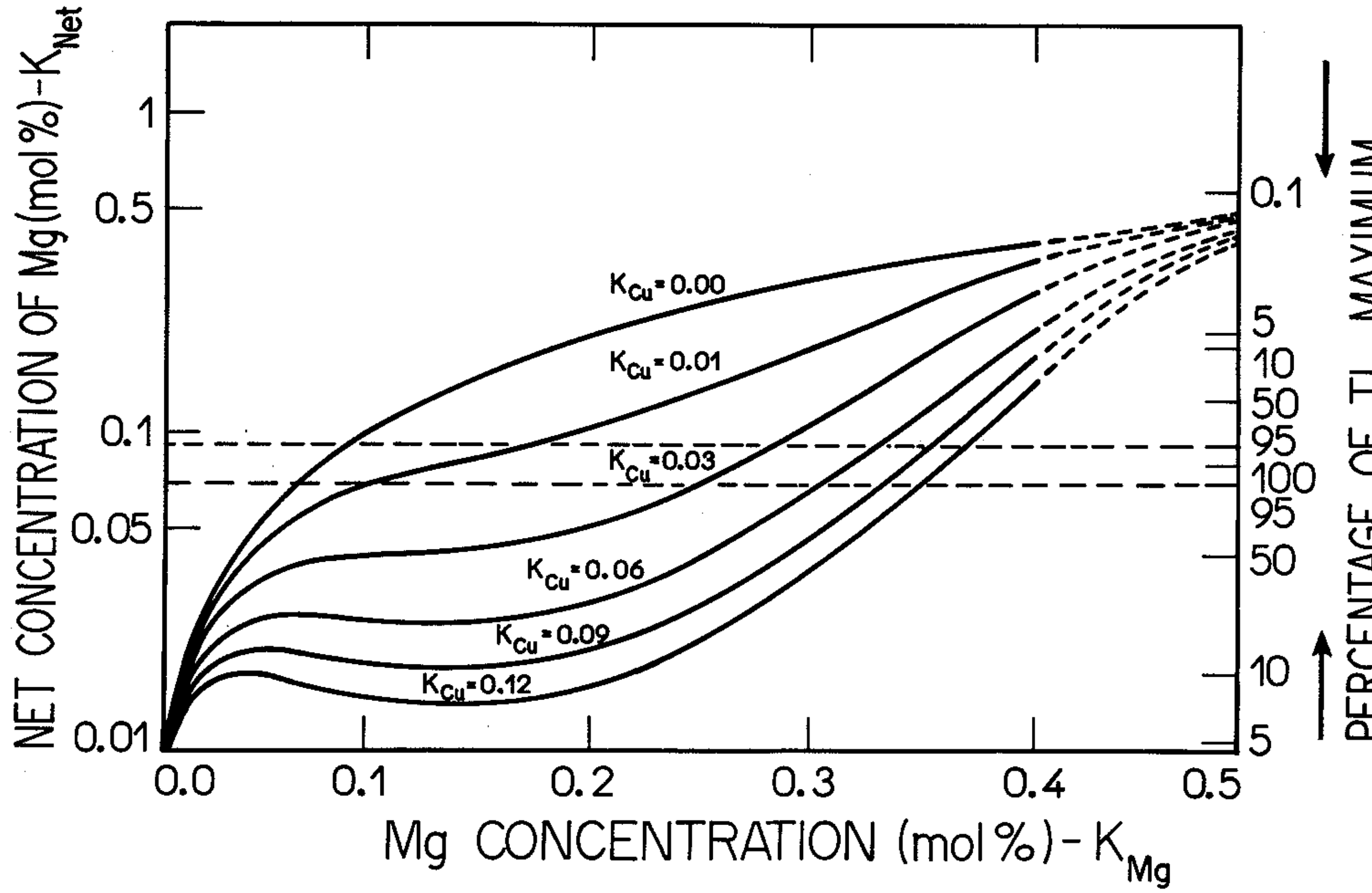

Figure 8: Relations among K_{Net} and the TL sensitivity versus K_{Mg} for K_{Cu} as a variable parameter.