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TECHNICAL NOTE

METHOD TO MANUFACTURE THE THERMOLUMINESCENT DETECTOR CHIPS USING LiF CRYSTAL

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The paper presents two methods to grow the LiF single crystal impurified with Mg and Ti, used to manufacture the TL detectors in the form of chips, in IFIN-HH. The comparative analysis of the methods have shown that the chips obtained by Czochralschi (Cz) method have a homogeneity that corresponds to the parameters required by the standards in force, IEC 1066 - Thermoluminescence Dosimetry System for Personal and Environmental Monitoring, 1991, for a much larger number of detectors in a lot (as e.g. the detectors obtained by Bridgman method), and, consequently, they can be used in personnel dosimetry. LiF: Mg, Ti, Tl detectors (chips) are aimed to measure the echivalent absorbed dose in the range of $5 \cdot 10^{-5}$ - 10 Sv, generated by ionizing radiation having the energy between 15 keV and 3 MeV. The document also presents the parameters and characteristics of the detectors produced in IFIN-HH, irradiated and tested with a ^{60}Co source (Δ = 3 Ci), ^{137}Cs (Δ = 30 mCi) and at the 7 MeV electron linear accelerator in NILPRP.

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1. Introduction

"Thermoluminescence", in short "TL", is the physical phenomenon consisting in the population of some active centers, by irradiation with ionizing radiation and their subsequent depopulation by heating. With the latter process, the energy built-up in the crystal is released as light radiation.

Thermoluminescence is the shortened name of radioluminescence [1-6]. The full name of radioluminescence points out that the activation energy is given by the ionizing radiation and the stimulating energy is thermal. The materials having the characteristic of thermoluminescence are called "phosphors". Actually they are phosphors with accumulation, where the active centers are relatively stable at ambient temperatures [5]. By heating the previously irradiated phosphors they emit two kinds of luminescent radiations. For dosimetry the high energy luminescent radiation shows interest.

2. Manufacturing process

2.1. Impurifying (doping) of the LiF powder

LiF single crystal does not show thermoluminescence. LiF sensitivity at ionizing radiation is closely connected to the presence of Mg^{2+} ions as well as other impurities.

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Besides, studying the thermal absorption and the brightness curve it was noticed that the addition of tiny quantities of Ti, determines a significant increase of the thermoluminescence sensitivity of the LiF single crystal.

The doping of the LiF powder in order to get activated single crystal follows a stoichiometric calculation and pre-set receipt. High purity LiF powder is mixed with the dopant in an agate mortar. The mixture is subject to one of the procedures for drawing the single crystal. Such procedures shall be dealt with in section 3.

The LiF crystal doped with Mg and Ti and irradiated was investigated by optical absorption measurements in the wavelength range 180 nm - 450 nm. Optical absorption bands of 3.3 eV due to the Mg presence in the mash were evidenced. The absorption band is generated by the thermoluminescence centers, which produce a peak at 120 ^{o}C in the LiF brightness curve. The 4 eV band is also generated by the thermoluminescence centers. The band gives rise to a TL peak at 200 ^{o}C in the brightness curve (K. Becker). The presence of Ti in the single crystal produces the 6.2 eV absorption band. The 3.3 eV optical absorption band decreases with the increase of temperature and actually becomes zero at 120 ^{o}C. At 250 ^{o}C temperature, a complex luminescence spectrum occurs.

Such features must be taken into account when the generation conditions for the LiF thermoluminescent detectors activated with Mg and Ti are considered.

2.2. Single crystal growth methods

For phase transients enveloped in the crystal growth processes, there are 3 types of processes: -solid phase growth process (S-S); - gaseous phase growth process (G-S) and liquid phase growth to obtain: a) growth from solution; b) growth from melting.

Below it is presented the method “b” because for the other methods the technology was not accessible and the raw material did not allow many experiments.

2.2.1. The method of crystal drawing from melt

This method is used for a large range of substances [3] having a crystalline structure. The advantages of this method are: larger crystals can be obtained in a reasonable time period, without dislocations, and the existence of the possibility to control the diameter and length of the crystal during the growth process. The material used for the growth is melted in a crucible which is kept at a temperature (10-20) ^{o}C higher than the melting point, for a possible degassing. Temperature is slowly decreased close to the solidification temperature simultaneously with the grain getting close to the melt surface. Next, the grain is brought in contact with the melt, well wet, left to melt a little to eliminate the dislocation generated by processing, slowly drawn and permanently rotated. The rotation avoids the aggregation of the impurities at the growth area interface.

Two further protective actions must be taken related to the temperature distribution in the melt. The temperature distribution must be so made that the temperature at the solid-liquid interface be the lowest in the liquid in order to avoid the induced nucleation. The melt surface must be protected against foreign particles that may become centers of nucleation. Doping is a procedure to impurify a pure crystal, in our case LiF. Crystal doping is made during the crystal growth process.

The solidifying process represents the phenomenon of crystal growth from liquid phase (melt) by atom or molecule attachment on a back up existing in the melt and made of crystallizing growing grains. If the passing from the liquid condition to the solid condition is slowly accomplished, one single crystal is obtained. If during the solidifying process a large number of crystallization centers are simultaneously occurring, an aggregate of small crystals (crystallites) making-up a polycrystal is obtained. Periodicity of the crystal structure is accomplished only in crystallites having dimensions from some angströms to microscopic dimension. The solidification process from melt is associated with the formation of crystal grains and is called: "primary crystallization".

Primary crystallization is characterized by the cooling curve, T = f (t), where T is temperature and t is time.

For fine crystals, the cooling curve is is shown in Fig. 1:

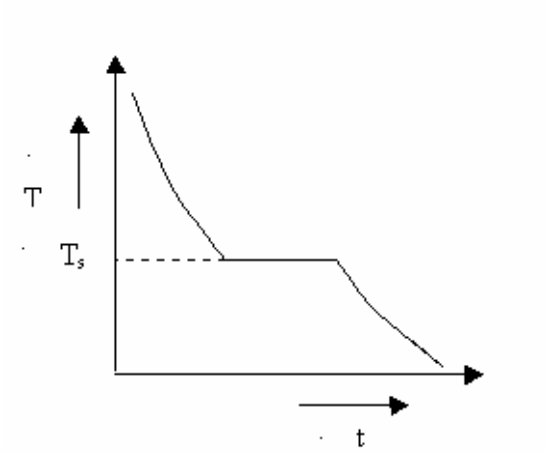

Fig. 1. Cooling curve for crystallization form melt.

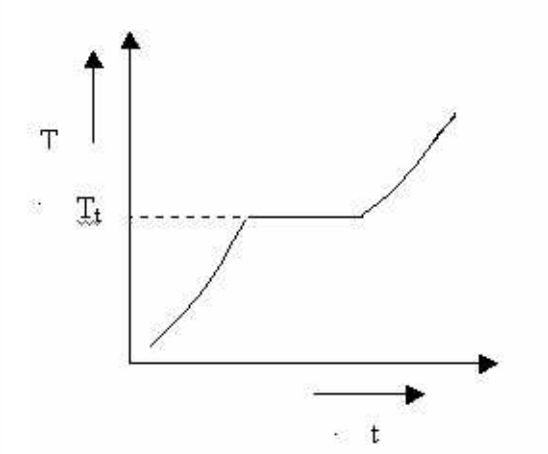

Fig. 2. Heating curve for crystallization from melt.

The reverse phenomenon (i. e. melting) is characterized by a heating curve which expresses the raise of temperature in time (see Fig. 2).

The curve shows a plateau at T_t, melting temperature. Theoretically $T_s = T_t$. In practice T_s is different of T_t .

The phenomenon emphasized in the optically controlled doping theory is the balance distribution ratio, K_o. The balance distribution ratio, K_o, is defined as the rate between the impurity concentration in the solid, C_s, and the impurity concentration in the liquid, C_m:

$$K_o = \frac{C_s}{C_m} \tag{1}$$

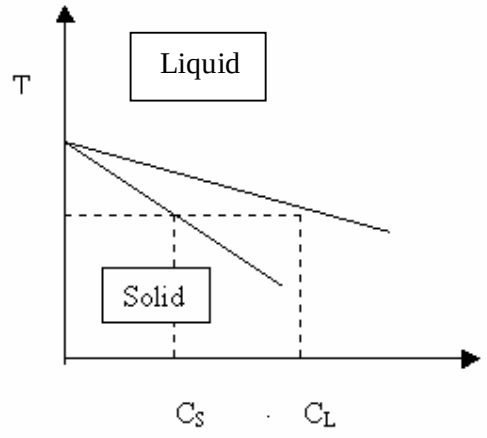

Fig. 3. Phase diagram for a binary system.

Fig. 3 presents the phase diagram for a linear system based on the substance dissolved in a solvent at a temperature very close to the solvent melting point.

When the two figures are compared, one can see that if the impurity reduces the melting point of the initial substance, then $K_o > 1$.

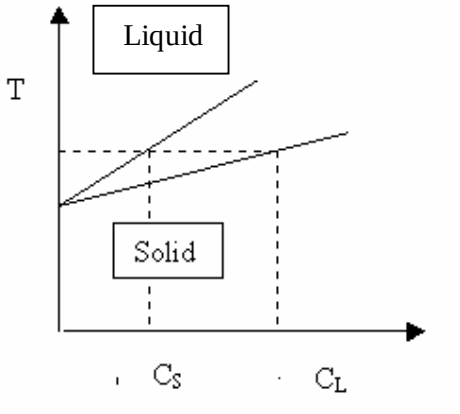

Fig. 4. The dissolved substance concentration dependence on the distance to the interface.

Fig. 4. illustrates the dependence of the dissolved substance concentration on the distance to the liquid solid interface for a system with $K_o < 1$.

The actual distribution ratio is defined by the relation:

$$K = K^* \cdot F \tag{2}$$

Here "F" is a factor, which depends on several parameters: growth speed, mixture degree, and diffusion of the substance dissolved in the liquid, the dissolved substance concentration.

Drawing of the LiF single crystal is developing in a platinum or graphite crucible, in argon atmosphere. In LiF single crystal the drawing speed is 2 mm/h.The obtained single crystal is a doped single crystal from which detectors, in the shape of chips, are cut. In order to get the LiF single crystal doped with Mg and Ti, the method of growth in liquid phase was used. Within this method, the growth of the single crystal from melt was selected and two procedures were applied: A - Bridgeman method and B - Czochralski method.

A. Bridgeman Method to grow a Mg and Ti impurified LiF single crystal from melt [3]; the melt is contained in a crucible and solidified progressively starting from one end of the crucible.

To make the Mg and Ti doped LiF single crystal detectors LiF- Merck was used and doped (impurified) as per the receipt used by Siruna Harshow [2]. After having manually mixing the components in the agate mortar for homogenizing, the substance was placed in a graphite crucible with 7 orifices of $\Phi = 7$ mm and h = 5 cm. By the above method, 7 rods of doped LiF single crystal of the above-mentioned size were obtained. To obtain the chips, three rods were machined and optically processed to $\Phi = 5$ mm. By means of a thread melting device, disks of h = 1 mm were cut and optically processed to h = 0.9 mm. The disadvantages of the method consist in the strain of the grown crystal due to the contact with the crucible and the formation of crystallization grains on the crucible wall. Out of the 50-g doped material 7 m rods of single crystal were obtained. Out of each rod 42-43 chips were cut. This paper presents, also, the results with two processed rods: rod "B" and "C".

B. Czochralski Method. In this method the LiF was first melted to reduce its volume and next it was doped following the same procedure like [3], with B method. 170 g LiF was used to obtain the LiF single crystal rod of $\Phi = 15$ mm and 1 - 60 mm. The drawing of the single crystal from the melt was developed in a graphite crucible; the drawing speed was 4-5 mm/h and the rotation speed was 3-4 rot/min. The obtained single crystal was machined and optically processed to $\Phi = 5$ mm and h = 0.9 mm. After machining and optically processing out of one 54 chips were cut from one rod.

3. Results and discussions

The TL detectors activated with Mg and Ti (chips), obtained by the two methods presented above were tested for a first characterization.

The operational characteristics subject to analysis during the experiments and their results are presented in the next sections: the shape of the brightness curve and the homogeneity of the detector lot for each rod.

3.1. Brightness Curve

The brightness curve for the chips obtained after processing, but without a thermal treatment, is presented in Fig 5.

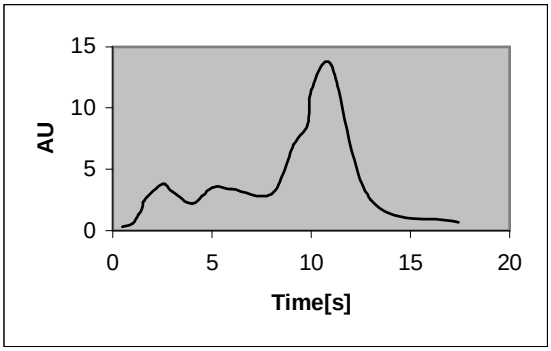

Fig. 5. Brightness curve for LiF: Mg, Ti - TLD-s (chips) after machining and optical processing.

Detectors were irradiated with a ^{70}Sr - ^{90}Y source with A = 50 mCi. Brightness curve was made by Mark IV - Model 1100 TLD connected to X-Y recorders. The heating cycle of TLD reader is situated in the range of 20 – 400 ^{o}C and the heating speed is about 15 ^{o}C/ sec. The brightness curve of LiF: Mg, Ti detectors show a main peak at 195 ^{o}C and two secondary peaks at 90 ^{o}C and 120 ^{o}C respectively. The secondary peaks represent superficial traps close to the conduction band. These traps were released and wiped - off by a thermal treatment at 400 ^{o}C for 1-5 hours followed by a 24-h treatment at 80 ^{o}C for 24 hoursand next, the resulted brightness curve is the one in Fig. 6.

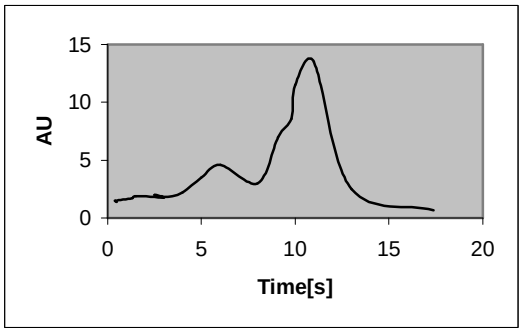

Fig. 6. Brightness curve of LiF: Mg, Ti (chips) detectors after thermal treatment.

Analyzing Fig. 6, one may notice the maintenance of the main peak at the same temperature and the decrease of the peak at 120 ^{o}C down to wiping - off; the total elimination of the 2nd secondary peak could not be obtained. To mach the brightness curve, some detectors from the middle of the rods were used considering that in the middle of a rod the distribution of the impurities is almost uniform.

3.2. Homogeneity at radiation

The homogeneity of the thermoluminescent detectors lot [CEI] represents the performance criterion according to which the value of the dosimetric response for every detector in a lot must not be different from the value of the dosimetric response of any detector in a lot, with more than 30% for a 10 mGy (1 rad) dose.

The assessment of the dosimetric response homogeneity for each detector lot was made after irradiation in a panoramic irradiation system. The source employed was a ^{137}Cs source with Λ=3.22 Ci and the dose equivalent, conventionally true: $D_{c.a.}$ = 8.3 mSv. By the panoramic irradiation, the successive irradiation error is eliminated. Each chip was numbered from 1 to 40 starting from one of the single crystal ends. The obtained results are presented in the below tables.Two lots of chips (from two rods) obtained by" B" method were irradiated and studied. They were noted by "B" and "C" and according to the chip number.

Table 1. Dosimetric response of LiF:Mg,Ti detectors (chips) obtained by B method - "B"rod, irradiated at a dose value conventionally true $D_{c.a.}$= 8.3 mSv.

No. crt	No. det.	TL response [imp.]	No. cr.	No. det.	TL response [imp.]	No. cr.	No. det.	TL response [imp.]
1	B_2	2510	18	B_{19}	4250	35	B_{36}	2530
2	B_3	2960	19	B_{20}	3650	36	B_{37}	2720
3	B_4	3160	20	B_{21}	3920	37	B_{38}	2680
4	B_5	2660	21	B_{22}	3920	38	B_{39}	2430
5	B_6	3360	22	B_{23}	3620	39	B_{40}	2490
6	B_7	3490	23	B_{24}	3660	40	B_{41}	2330
7	B_8	3260	24	B_{25}	3770	41	B_{42}	2190
8	B_9	3680	25	B_{26}	3440	42	B_{43}	2100
9	B_{10}	3850	26	B_{27}	3700	43	B_{44}	2200
10	B_{11}	3960	27	B_{28}	3260	44	B_{45}	1810
11	B_{12}	3590	28	B_{29}	3580	45	B_{46}	1940
12	B_{13}	4070	29	B_{30}	3190	46	B_{47}	2120
13	B_{14}	4010	30	B_{31}	3220	47	B_{48}	2010
14	B_{15}	4120	31	B_{32}	2920	48	B_{49}	2000
15	B_{16}	4440	32	B_{33}	2960	49	B_{50}	1620
16	B_{17}	4020	33	B_{34}	2830			
17	B_{18}	3620	34	B_{35}	2680			

with $\overline{X} = 3132 \pm 754.33(24.07\%)$, where: $\overline{X}$ -is mean value of TL response.The value of homogeneity of TL detectors response is high and must be selected.

Table 2. Dosimetric response of LiF: Mg, Ti detectors (chips) obtained by B method- "C"rod, irradiated at a dose value conventionally true $D_{c.a.}$ = 8.3 mSv

N. cr.	Nr. det.	TL response [imp.]	No. cr.	No. det.	TL response [imp.]	No cr.	No. det	TL response [imp.]
1	C_2	1188	15	C_{16}	3210	29	C_{30}	3880
2	C_3	1930	16	C_{17}	3290	30	C_{31}	4220
3	C_4	1970	17	C_{18}	3180	31	C_{32}	4140
4	C_5	2060	18	C_{19}	3390	32	C_{33}	-
5	C_6	1950	19	C_{20}	3620	33	C_{34}	3790
6	C_7	2110	20	C_{21}	3650	34	C_{35}	3790
7	C_8	2150	21	C_{22}	3720	35	C_{36}	3680
8	C_9	2290	22	C_{23}	3640	36	C_{37}	3610
9	C_{10}	2150	23	C_{24}	3830	37	C_{38}	3190
10	C_{11}	2670	24	C_{25}	3840	38	C_{39}	3060
11	C_{12}	2460	25	C_{26}	3540	39	C_{40}	3030
12	C_{13}	2620	26	C_{27}	3800	40	C_{41}	2860
13	C_{14}	2800	27	C_{28}	3870	41	C_{42}	2570
14	C_{15}	3020	28	C_{29}	3970	42	C_{43}	2400

with $\overline{X} = 3076 \pm 756.36(25\%)$, where: X-is mean value of TL response. The value of the homogeneity of TL detectors response is high and must be selected.

Table 3. Dosimetric response of LiF:Mg, Ti detectors (chips) obtained by B method-"C"rod, irradiated at a dose value conventionally true $D_{c.a.}$ = 8.3 mSv.

No. cr.	No. det.	TL response [imp.]	No. cr.	No. det.	TL response [imp.]	No. cr.	No. det.	TL response [imp.]
1	Acz_5	11100	17	Acz_{21}	11800	33	Acz_{37}	11500
2	Acz_6	12000	18	Acz_{22}	11200	34	Acz_{38}	11700
3	Acz_7	11800	19	Acz_{23}	11600	35	Acz_{39}	11800
4	Acz_8	11300	20	Acz_{24}	11700	36	Acz_{40}	11700
5	Acz_9	11500	21	Acz_{25}	12000	37	Acz_{41}	12000
6	Acz_{10}	11800	22	Acz_{26}	12200	38	Acz_{42}	11300
7	Acz_{11}	11300	23	Acz_{27}	11100	39	Acz_{43}	12000
8	Acz_{12}	11600	24	Acz_{28}	11900	40	Acz_{44}	12000
9	Acz_{13}	11800	25	Acz_{29}	11200	41	Acz_{45}	11600
10	Acz_{14}	11300	26	Acz_{30}	11800	42	Acz_{46}	11400
11	Acz_{15}	11700	27	Acz_{31}	11800	43	Acz_{47}	10700
12	Acz_{16}	11700	28	Acz_{32}	10900	44	Acz_{48}	11100
13	Acz_{17}	11700	29	Acz_{33}	11000	45	Acz_{49}	12200
14	Acz_{18}	11800	30	Acz_{34}	11100	46	Acz_{50}	11600
15	Acz_{19}	11800	31	Acz_{35}	11700	47	Acz_{51}	11400
16	Acz_{20}	11000	32	Acz_{36}	11600	48	Acz_{52}	12200

with $\overline{X} = 11583 \pm 362.8(3.1\%)$, where: $\overline{X}$ -is mean value of TL response. The value of homogeneity of TL detectors response is 14% and the detectors must not be selected.

4. Conclusions

The presented results show that the sensitivity of the chips is not constant throughout the rod length. There is only segments in the middle of the rod where the homogeneity of the dosimetric response falls in the range of the international standards [CEI]. The homogeneity of the dosimetric response is 24. 07 %, and 25 %, respectively. One can say that only the detectors from this segment can be used in dosimetric tests. For the detectors obtained by C method, the homogeneity is 3.1 %. Thus, only 2 % of the detectors are eliminated. In C method the uniform distribution of the activator in the matrix is provided. These detectors may be used in the environment and personnel dosimetry by encasing the chip in a dosimetric card, also providing the possibility of reading it by an automatic TL reader.

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