

Laser active F-aggregate colour centres in LiF monocrystals doped by divalent impurity cations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 7005

(<http://iopscience.iop.org/0953-8984/11/36/316>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.220

The article was downloaded on 15/05/2010 at 17:16

Please note that [terms and conditions apply](#).

Laser active F-aggregate colour centres in LiF monocrystals doped by divalent impurity cations

V M Khulugurov[†], V N Salomatov[‡], A Vassilikou-Dova[§], V I Baryshnikov[†],
I M Kalogeras[§], S Grigorakakis[§], S K Makarov[‡] and A A Mikhailenko[†]

[†] Irkutsk State University, Institute of Applied Physics, 20 Gagarin Boulevard, 664003 Irkutsk, Russia

[‡] Irkutsk State Institute of Transport Engineers, 15 Tchernyshevsky Street, 664074 Irkutsk, Russia

[§] University of Athens, Department of Physics, Solid State Physics Section, Panepistimiopolis, 157 84 Zografos, Greece

Received 7 May 1999, in final form 16 June 1999

Abstract. F-aggregate colour centres in LiF crystals with divalent impurities ($M = \text{Ni, Co, Be, Mg}$) are investigated by optical and thermally stimulated depolarization current (TSDC) spectroscopy methods. The F_2^+ centres accumulation in the LiF:M^{2+} crystals is similar to the F_2^+ centres accumulation in undoped LiF. Accumulation of F_2^+ -like colour centres was observed only in the LiF:Mg^{2+} crystals at the first stage of low temperature irradiation with radiation doses exceeding 10^7 R. F_2^+ -like centres are not formed in LiF with Ni, Be and Co impurity ions. The difference between the properties of the magnesium on one hand and the nickel, beryllium or cobalt doped crystals on the other is discussed in terms of the Hayes–Nickols mechanism with extra anion vacancy generation in the case of the LiF:Mg^{2+} crystal. The absence of the mechanism in LiF:Ni^{2+} and LiF:Be^{2+} is connected to the reduction of the impurity Ni^{2+} and Be^{2+} ion valence state and in LiF:Co^{2+} to the small concentration of single $\text{Co}^{2+}V_c^-$ dipoles as a result of extensive dipole aggregation. The destruction of the F_2^+ and F_2^+ -like centres takes place in LiF:Mg^{2+} crystals at the second stage of aggregation, at which other F-aggregated centres are formed, with the impurity–vacancy (IV) dipoles included in their composition. The two-band structure of the TSDC curve of irradiated LiF:Mg^{2+} , with relaxation parameters close to those of single IV dipole reorientation bands, is in accordance with the above mechanism of aggregation. The creation mechanisms and models of laser active colour centres (F_2^+ -like and $F_3\text{Mg}^{2+}V_c^-$ ‘red’ colour centres) are discussed.

1. Introduction

It is known that in LiF crystals, under ionizing radiation, F, F_2^+ and other complicated F aggregate colour centres are formed, as a result of an exciton mechanism and the displacement of anion vacancies (V_a^+). The introduction of impurity anions or divalent impurity cations into the LiF crystal brings about a considerable change in the optical properties that are closely related to the aforementioned centres. As an example, Mikhailenko *et al* [1] have studied colour centres (CCs) in LiF:Mg^{2+} crystals with absorption and emission maxima at 18 520 and 12 000 cm^{-1} , respectively. Crystals with F-aggregate colour centres have been used for tuning laser-active media [2], and the model explaining their activity involves the F_2^+ centre and an impurity–vacancy (IV) dipole [1]. In contrast to the typical F_2^+ centres in undoped LiF crystals, the disintegration time of similar formations in LiF:Mg^{2+} is approximately 50 hours, at room temperature (RT), as a direct consequence of the stabilization effect due to the presence of the IV dipole. The concentration of the $F_2^+\text{Mg}^{2+}V_c^-$ centres may reach

significant values ($> 10^{18} \text{ cm}^{-3}$), which are comparable to those of the F_2^+ centres. In addition, $F_2^+V_c^-$ centres, stable at RT, are formed in LiF with the introduction of divalent impurities following γ -irradiation. $F_2^+V_c^-$ centres were identified in LiF:Mg, LiF:Ni and LiF:Ti [3], with concentration considerably less than that of the F_2^+ and $F_2^+Mg^{2+}V_c^-$ centres. In addition, 'red' colour centres (RCCs), stable at room temperature, are formed in LiF:Mg under neutron, electron, x- and γ -irradiation at 77–250 K, followed by annealing at 360–410 K. The RCC absorption and emission spectral maxima are at 17 857 and 14 925 cm^{-1} , respectively. Crystals with RCCs ($F_3Mg^{2+}V_c^-$) were used for tuning laser operation as well [4, 5].

Despite the abundance of publications devoted to LiF crystals doped with divalent impurities, creation processes and models of laser-active CCs remain in dispute. The subject of the present paper is the determination of the laser-active CC creation mechanisms and a definition of the RCC structural model. In conjunction with the traditional optical methods, the application of thermostimulated current spectroscopy methods is widely recognized as an efficient means for the determination of critical charge trapping parameters in ionic crystals [6, 7]. The thermally stimulated depolarization current (TSDC) is a sensitive technique frequently used in performing a rapid characterization of materials through their dielectrically active relaxation phenomena. The commonest mechanisms include the orientational polarization of permanent molecular or ionic dipoles, translational or space charge polarization due to intrinsic free charges (ions, electrons), interfacial polarizations in polycrystalline materials and homocharge injection from the electrodes [8].

2. Experimental details

LiF crystals with Mg^{2+} , Co^{2+} , Ni^{2+} , Be^{2+} as well as undoped LiF and mixed LiF:Mg,OH crystals were used in the present study. Undoped LiF and LiF:Mg crystals were grown by the Stockburger method in inert atmosphere, with various MgF_2 contents (0.001 to 0.1 wt%) in the preparation of the magnesium doped crystals. LiF:Ni and LiF:Co were grown by the Czochralsky method in inert atmosphere with 0.2 wt% NiF_2 or CoF_2 content, respectively. In agreement with earlier optical investigations [9, 10], the unirradiated LiF:Ni and LiF:Co crystals have shown characteristic absorption spectra due to optical transitions of the divalent impurity ions in the 6000–50 000 cm^{-1} optical range. LiF:Be crystals were grown at the Crystal Growth Laboratory, University of Utah, by doping LiF with 5×10^{-3} mole fraction of BeF_2 in the melt. Unirradiated LiF:Be is transparent in the visible range and shows weak absorption in the 28 570–50 000 cm^{-1} region and a weak emission band at 24 390 cm^{-1} , after nitrogen laser beam excitation (at 28 818 cm^{-1}). The latter, weak, optical effects, are most likely due to small concentrations of oxygen containing impurities. LiF:Mg,OH was grown by the Stockburger method in air with 0.05 wt% MgF_2 . The identification of the OH^- impurities was performed by infrared (IR) spectroscopy, which revealed the presence of metal–hydroxyl complexes only in the mixed LiF:Mg,OH crystal, with characteristic vibration frequencies $\nu_1 = 3570 \text{ cm}^{-1}$ and $\nu_2 = 3610 \text{ cm}^{-1}$ [11]. The concentration of metal impurities in the initial raw materials was determined to be less than 10^{-4} wt%.

Irradiation of the crystals, with typical dimensions ($7 \times 7 \times 3$) mm^3 , was performed by a miniature electron accelerator (beam with energy 0.15 MeV, pulse duration 1 ns and current density 0.5 kA cm^{-2}), at RT, and by γ - or x-rays in the 80–300 K temperature range. Absorption spectra in UV and visible range were measured by the Specord M40 or SF-20 instruments, at liquid nitrogen temperature (LNT) or RT. Luminescence spectra were measured using a halogen lamp and a double prismatic monochromator DMP-4 for excitation, a diffraction monochromator MDP-23 and a photomultiplier PMP-83 with measuring range extending down to 9090 cm^{-1} .

The application of the TSDC technique in dielectrics consists of monitoring the restoration of the non-polarized state of the material as a function of its instant temperature (T). The thermoelectret is generated by applying an electric field, E_p , for time t_p , at a suitable temperature, T_p . The electric stimulus causes an alignment of permanent or induced dipoles as well as a drift of real charges (homo- or heterocharges). By rapidly cooling the sample, at T_0 , the orientation of the dipoles may be frozen in and charges may be trapped. These mechanisms decay in a short time when heated up to higher temperatures with a constant heating rate, h , or upon aging. The recovery of the system is monitored by measuring the depolarization current as a function of temperature, $I(T)$. For a single relaxation mechanism the asymmetric current density band, $J_D(T)$, is described by [8]

$$J_D(T) = \frac{P_0}{\tau_0} \exp\left(-\frac{E}{k_\beta T}\right) \exp\left[-\frac{1}{h\tau_0} \int_{T_0}^T \exp\left(-\frac{E}{k_\beta T'}\right) dT'\right] \quad (1)$$

where P_0 is the saturation polarization, k_β the Boltzmann constant, E the activation energy and τ_0 the inverse frequency factor, i.e., the pre-exponential factor of the Arrhenius equation that describes the temperature dependant relaxation time [7, 8]

$$\tau(T) = \tau_0 \exp\left(\frac{E}{k_\beta T}\right). \quad (2)$$

For the determination of the relaxation parameters (E , τ_0) of each dielectrically active mechanism we have employed different techniques. In the case where only the initial part of a depolarization current peak is recorded, the activation energy can be calculated from the slope, E/k_β , of the logarithmic plot of $\ln I(T)$ against T^{-1} (referred to as the initial rise method) [7]. For the fully developed and recorded current bands, the relaxation time $\tau(T)$ and the corresponding parameters are determined directly from the whole-curve graphical integration method [7]. Highly overlapping relaxation bands were analysed with the use of an especially developed curve-fitting program.

Thermostimulated depolarization currents were measured for LiF:Mg crystals, irradiated by ^{60}Co γ -rays at 195 K and stored at RT for at least two months after irradiation. Two LiF:Mg crystals, with approximate dimensions $(1.3 \times 5 \times 5) \text{ mm}^3$, were used in the TSDC experiments. To recover the initial defect concentration, prior to dipole aggregation due to aging, one of the samples was annealed at 873 K (and following the first at 973 K) and subsequently quenched on a copper plate. Both samples were silver painted and placed in an especially designed vacuum cell, in order to perform the polarization stage and the subsequent thermally stimulated depolarization current recordings in the extended spectral range 10 to 340 K. The complete TSDC experimental setup has been presented in a previous publication [12]. Further experiments with irradiated LiF:Ni and LiF:Mg,OH crystals are in progress.

3. Results

Figure 1 demonstrates characteristic curves for the accumulation of the F_2^+ centres emission bands in single crystals of LiF, LiF:Ni, LiF:Co, LiF:Be and LiF:Mg. The crystals were annealed for 1 hour at 873 K (except for LiF:Co) and then quenched at a copper plate to create the maximum IV dipole concentration. Irradiation was performed by γ - or x-rays at low temperatures, in the range 80 to 195 K, at which the ionic processes are frozen. After the low temperature irradiation the crystals were heated quickly to RT and the emission of the F_2^+ ($10\,990 \text{ cm}^{-1}$) or $\text{F}_2^+\text{M}^{2+}\text{V}_c^-$ ($12\,000 \text{ cm}^{-1}$) centres was measured ($\text{M}^{2+} = \text{impurity cation}$). The recorded emission intensities are proportional to the centres concentrations. Curves 1 to 4 (figure 1) demonstrate the F_2^+ centres accumulation versus the aging time at RT, in the LiF,

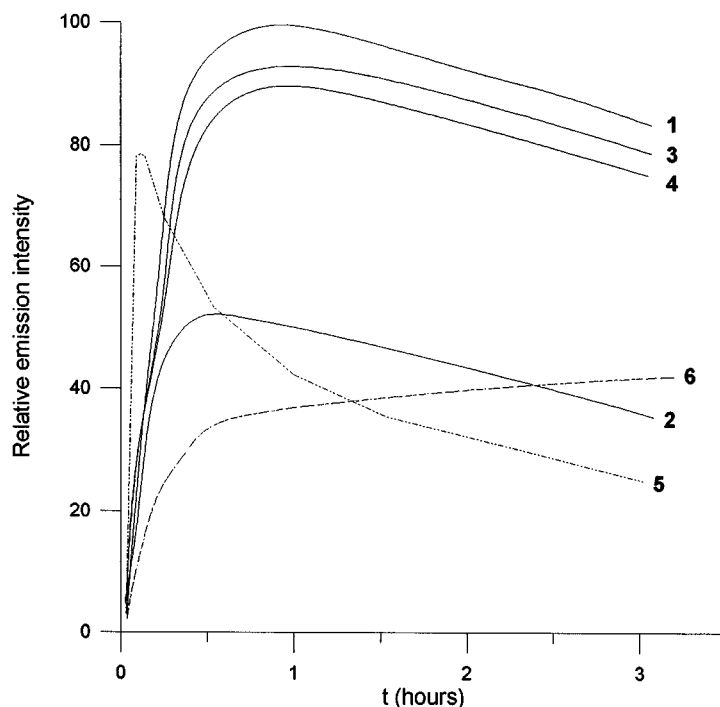


Figure 1. Representative plots of the growth of the F_2^+ centres concentrations, at RT, after low temperature irradiation in undoped LiF (curve 1), LiF:Ni (2), LiF:Co (3), LiF:Be (4), LiF:Mg (5) and the $F_2^+Mg^{2+}V_c^-$ centres in LiF:Mg (6). Excitation: $15\,625\text{ cm}^{-1}$ for the F_2^+ and $17\,860\text{ cm}^{-1}$ for the $F_2^+Mg^{2+}V_c^-$ centres.

LiF:Ni, LiF:Co and LiF:Be crystals, respectively. From the shape of these curves it is apparent that in LiF doped with Ni^{2+} , Co^{2+} and Be^{2+} the accumulation of F_2^+ centres follows the same law as in undoped LiF. In the LiF:Mg crystals the F_2^+ centres accumulation plot exhibits a much steeper rise (curve 5, figure 1), while the optical emission data indicate the formation of perturbed F_2^+ centres with other time accumulation characteristics. According to Mikhalenko *et al* [1] the model of these centres should include F_2^+ centres and IV dipoles ($F_2^+Mg^{2+}V_c^-$ centres). Nonetheless, even if the preceding model is not the only one applicable for the explanation of the observed behaviour, the centres responsible for the departure of curve 5 from the other curves depicted in figure 1 are likely to be F_2^+ -like centres. The growth of F_2^+ -like centres in LiF:Mg is described by curve 6. It should be pointed out that no F_2^+ -like centres were observed in the LiF:Ni, LiF:Co and LiF:Be crystals reported in the present investigation.

Experiments related to the creation of red colour centres have shown that the given type of centres is only formed in the LiF:Mg and LiF:Mg,OH crystals. Nevertheless, with the same magnesium concentrations, the RCC concentration in LiF:Mg,OH is one order of magnitude less than that created in the LiF:Mg crystals. In LiF:Ni, LiF:Co and LiF:Be, no RCCs were created. Increased accumulation of RCCs is observed in the annealed, at 873 K, and subsequently quenched crystals, in which single $Mg^{2+}V_c^-$ formations exist, at temperatures of irradiation in the range 77–250 K. The concentration of the RCCs in crystals irradiated at RT is by one order less than that developing in the same crystals after low temperature irradiation. Their concentration reaches a maximum value after low temperature irradiation, followed by

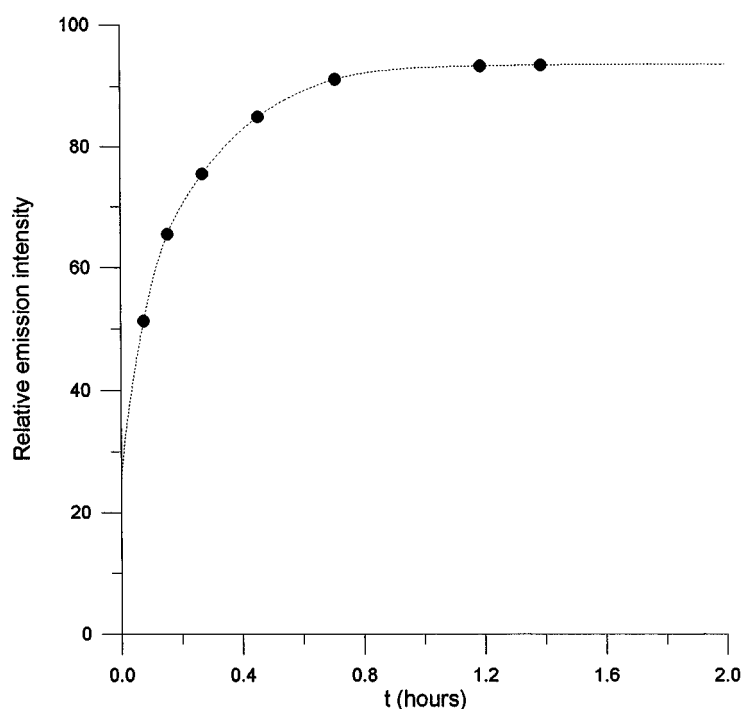


Figure 2. Growth of the RCC concentration in irradiated LiF:Mg versus the aging time of the crystal at constant temperature (363 K). Excitation: $17\,860\text{ cm}^{-1}$.

aging at RT for one month, or heating at 360 to 410 K for 1–2 hours. Figure 2 shows the variation of the RCC accumulation versus the time of aging at 363 K.

Figure 3 demonstrates the absorption spectra of undoped LiF and LiF:Mg crystals (0.05 wt%). The samples were γ -irradiated by ^{60}Co (with a dose of 2×10^8 R at 195 K), stored at room temperature for two months, annealed at 873 K and quenched before measurement. Due to the high F band optical density of the LiF:Mg crystal, irradiated by the 2×10^8 R dose, the use of crystals with thickness less than 0.1 mm is imperative in order to measure F-centres absorption. For this reason, in the present study we have used crystals irradiated by electron beams of smaller dose. Figure 4 shows the absorption spectra of the same samples, in which the irradiation process was performed by 15 pulses of accelerated electrons at 300 K. According to electron microscopy measurements the thickness of the coloured layer, for energy of electrons 0.15 MeV, does not exceed 0.1 mm. The total time of irradiation by power electron pulses was 7.5 minutes, with intervals between pulses of approximately 30 s. In this case the total dose of irradiation was a little less than by γ -irradiation, while the interval time is comparable to the lifetime of the anion vacancies (10–60 s). The experimental conditions were chosen so as to reach high levels of F and F_2 centres concentrations and decrease the efficiency of the mechanisms leading to the formation of other F-aggregate colour centres. It should be pointed out that this procedure is equivalent to low temperature irradiation, at low rates of radiation [13].

The absorption spectra in figures 3 and 4, in the range $20\,000\text{--}45\,000\text{ cm}^{-1}$, are due to F and mainly F_2 centres. F centres concentration in the Mg^{2+} doped crystals is approximately 1.5 times that in the undoped LiF. It is known that the elementary F band is well described

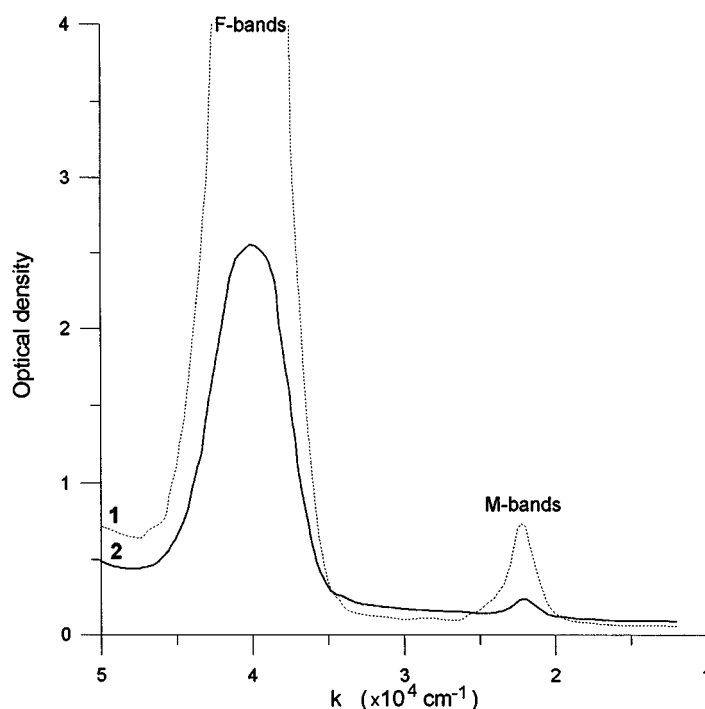


Figure 3. Optical absorption of γ -irradiated (at 195 K) LiF:Mg (curve 1, sample thickness $d = 0.125$ mm) and LiF crystals (curve 2, $d = 0.100$ mm).

by the Gauss function [14], while the M band fits to a Lorentz function [15]. Analysis of the curves for F absorption by means of Gauss functions gives practically identical results for LiF and LiF:Mg crystals, regardless of the type of experiment (i.e. low temperature irradiation by γ -rays or room temperature electron-beam irradiation). In both crystals additional absorption bands are observed, which give a significant contribution to the F band (at $40\,000\text{ cm}^{-1}$), as we can see from $44\,444\text{ cm}^{-1}$ and in the short-wave area thereafter and the weak absorption with $k < 34\,500\text{ cm}^{-1}$ (figures 3 and 4). In the range of the M bands such analysis allows us to reveal an additional band with a maximum at $24\,530\text{ cm}^{-1}$, which is absent in undoped LiF (figure 5). Growth of this band in LiF:Mg occurs simultaneously with the reduction of the R_2 band [16] with a maximum at $26\,316\text{ cm}^{-1}$. This band is due to R_2 optical transitions in non-perturbed F_3 centres. The sequence of steps for the formation of the F_3 colour centres is



The F_3 band is detectable in the absorption spectrum of the LiF:Mg crystal irradiated by electron beams at RT, when the number of electron pulses exceeds 300. In the absorption spectrum measured 1 hour after the irradiation the R_2 band decreases and the $24\,530\text{ cm}^{-1}$ band appears. Besides that, an absorption band in the range of $17\,857\text{ cm}^{-1}$ with the zero-phonon line $16\,639\text{ cm}^{-1}$ [17] is observed, in which the luminescence maximum is excited at $14\,925\text{ cm}^{-1}$, stimulated by $F_3Mg^{2+}V_c^-$ colour centres [4, 5, 18]. Therefore, the analysis and comparison of absorption spectra of LiF and LiF:Mg crystals, irradiated in equal terms, permits the conclusion that in LiF:Mg, and in contrast to the undoped LiF, we record two additional absorption bands, stimulated by magnesium centres. At the present stage we cannot

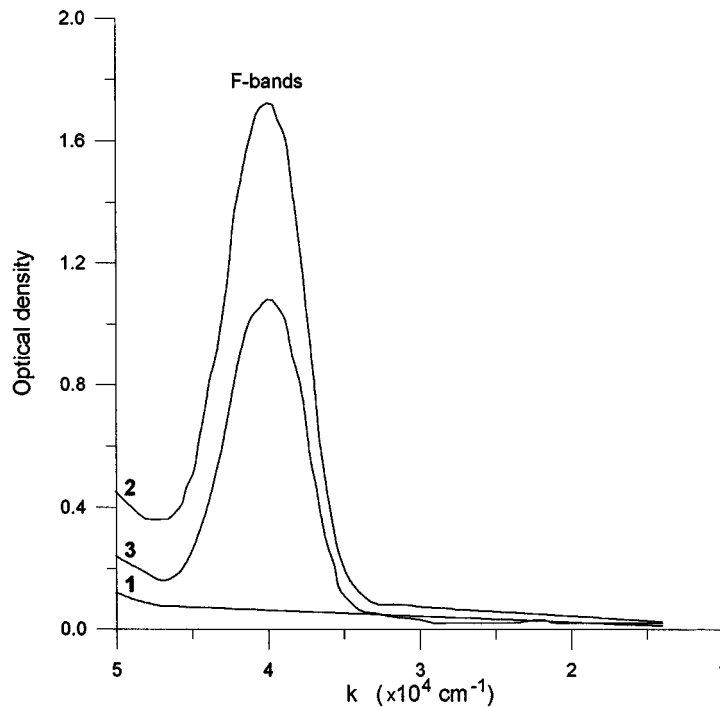


Figure 4. Optical absorption of unirradiated LiF (curve 1), electron-irradiated (at RT) LiF (curve 2) and LiF:Mg crystals (curve 3).

exclude the possibility that in the short-wave range of the F band, other bands, stimulated by Mg^{2+} -centres, are also present.

Figure 6 presents the TSDC curves for an LiF:Mg crystal, irradiated and aged (at RT) for a time period exceeding two months. The main features in this curve are the appearance of a strong thermocurrent band (denoted as band A) in the range 250–320 K and the complete absence of relaxation mechanisms in the lower temperature range. The application of an especially designed TSD current curve fitting program has revealed that band A is a complex one, with two dielectric relaxations with current peaks at $T_{m1} = 278$ K and $T_{m2} = 298$ K (bands A_1 and A_2 , respectively; inset of figure 6). In the latter experiment we employed a lower polarization temperature, $T_p = 290$ K, in order to decrease the interference of the mechanisms activating at higher temperatures. The corresponding energy barriers and inverse frequency factors were calculated as $E_1 = 0.60$ eV, $\tau_{01} = 1.4 \times 10^{-9}$ s and $E_2 = 0.62$ eV, $\tau_{02} = 5.0 \times 10^{-9}$ s, respectively. Due to the close proximity of the above pairs of relaxation parameters, a tentative attribution of peak A might consider it as the dielectric manifestation of the rotational mobility of a single kind of dipole, with a slight differentiation in the environment of a fraction of the dipolar population. A careful simulation of the observed rising current signals (band A_3) at the high temperature spectral range resulted in an activation energy $E_3 \sim (0.30 \pm 0.04)$ eV, characteristic of the relaxation mechanism involved.

In earlier TSDC studies of LiF:Mg monocrystals, the presence of electric $\text{Mg}^{2+}\text{V}_c^-$ dipoles has been identified through the appearance of a distinct current band, attributed to an IV dipole reorientation relaxation mechanism [19,20]. The typical thermostimulated depolarization current spectrum of irradiated LiF:Mg, recorded after annealing at 873 K

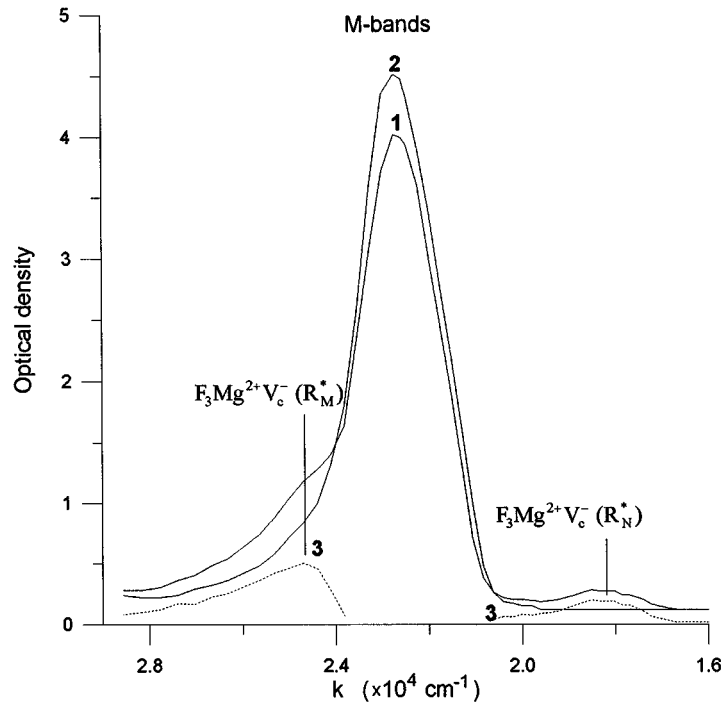


Figure 5. Optical absorption of γ -irradiated LiF:Mg (curve 1, sample thickness $d = 0.7$ mm, 0.05 wt%) and LiF crystals (curve 2, $d = 2.8$ mm), measured at 80 K. Curve 3 demonstrates the difference between the normalized curves 1 and 2.

(figure 7), demonstrates a single relaxation current band, A_4 , with peak maximum at $T_{m4} = 207$ K and the following relaxation parameters: $E_4 = 0.55$ eV and $\tau_{04} = 0.45 \times 10^{-12}$ s. The curve presented in figure 7 is similar to that received from the crystal annealed at 973 K. In both cases the corresponding mechanism involves the thermally induced (re)orientation of $Mg^{2+}V_c^-$ dipoles. The above relaxation parameters are close to those found by Katsika and Grammatikakis [19] for unirradiated LiF:Mg, i.e. $T_{m4} = 212$ K, $E_4 = 0.56$ eV and $\tau_{04} = 1.42 \times 10^{-12}$ s. The observed inconsistency between the temperatures of peak maximum is due to the difference in the heating rates ($h = 12$ degrees min^{-1} in [19] and 5 degrees min^{-1} in this study). In addition to the peak, intense rising currents (band A_5) are observed in the high temperature side of the spectrum. The corresponding relaxation mechanism is characterized by an activation energy of $E_5 = (0.60 \pm 0.05)$ eV. Taking under consideration the magnitude of the energy barrier, the spectral positioning of the current signals and the character of the defect structure in irradiated LiF:Mg, their presence could be associated with the cation vacancies released from the isolated $Mg^{2+}V_c^-$ dipoles, which appear after annealing. An analogous current rise has been observed by Hayes and Wilkens [21], during their conductivity measurements of unirradiated LiF:Ni crystals. The value of 0.65 eV for the activation energy for the V_c^- migration process in LiF, as reported by Seitz [22], is in good agreement with E_5 . It is worth noticing, (a) the absence of any distinct relaxation peak in the range of band A, and, (b) the fact that the activation energies of the mechanisms associated with the high temperature current rises in figures 6 and 7 obey the inequality $E_5 > E_3$. The high temperature bands, A_3 and A_5 , are expected to peak at temperatures exceeding 320 K, well above the investigated

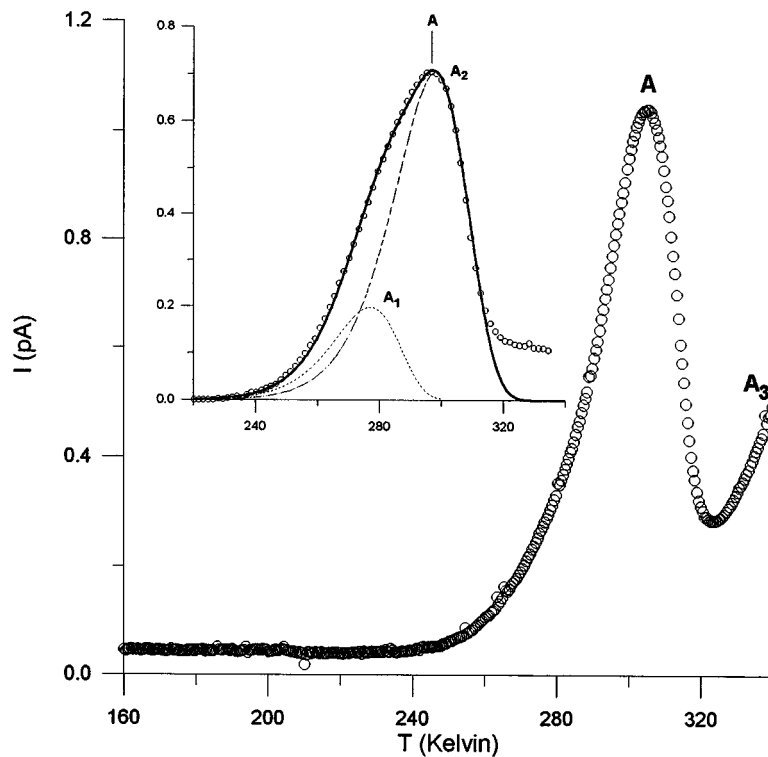


Figure 6. Part of the TSDC spectrum of irradiated and aged LiF:Mg (0.05 wt%). The aging time exceeds two months. The inset presents the decomposition of band A into two single current peaks (A_1 and A_2) with the envelope (thick line) being an accurate reproduction of the experimental points.

temperature range. However, the current rises recorded from each mechanism are sufficient for the determination of the corresponding activation energies with the initial rise method (section 2).

From the available reports pertaining to the dielectric relaxation mechanisms in unirradiated doped LiF crystals we note the TSDC studies in LiF:Be, with respect to the kinetics of the IV dipole aggregation [20, 23], and the compilation of the energy parameters of the 'free' and 'bound' cation vacancies in several LiF : M^{2+} crystals ($M^{2+} = \text{Be}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Mg}^{2+}, \text{Sr}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Ca}^{2+}$ and Ti^{2+}) presented by Grammatikakis *et al* [24].

4. Discussion

4.1. Mechanism of the formation of $F_2^+ \text{Mg}^{2+} V_c^-$ centres

Taking under consideration the experimental results reported in the preceding section for the LiF crystals doped with the divalent impurities Ni^{2+} , Be^{2+} and Co^{2+} , we attempt a close examination of the validity of the mechanism by which $F_2^+ \text{Mg}^{2+} V_c^-$ centres are formed in LiF:Mg, as proposed by Mikhaleiko *et al* [1]. The model for this mechanism was initially based on the concept of the involvement of ionic processes in the formation of F aggregate centres, proposed by Luty and Haertel [25, 26] and Delbecq [27], and experimentally checked

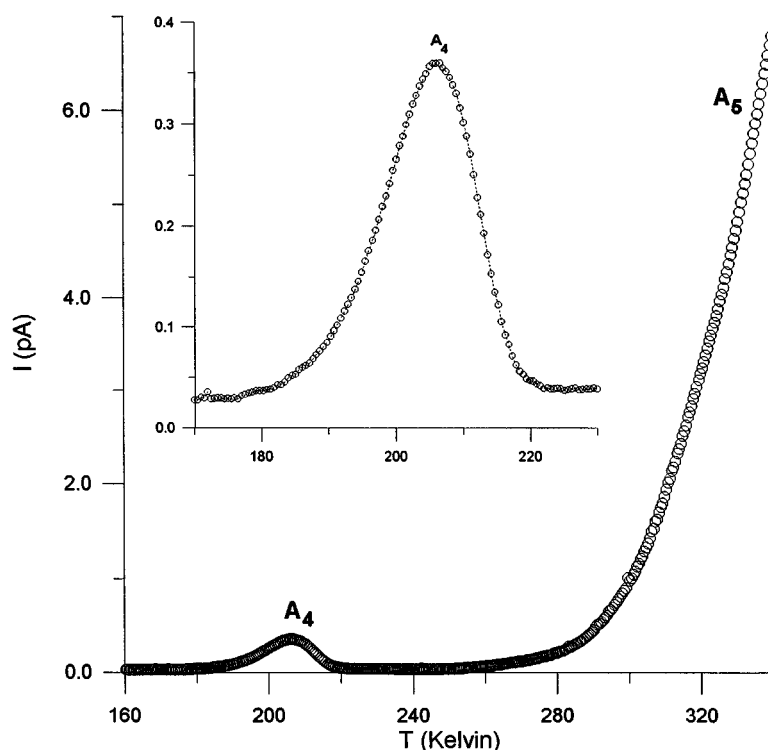


Figure 7. Part of the TSDC spectrum of irradiated and aged LiF:Mg (0.05 wt%), recorded after annealing of the crystal at 873 K for 1 hour. The inset shows the expanded temperature region 170–230 K with the single IV relaxation mechanism (band A₄).

on LiF crystals [16, 28]. In particular, the F_2^+ centres are formed by the reaction



with an anion vacancy being the mobile component responsible for the formation of F-aggregate centres. Moreover, the model is based on the mechanism suggested by Hayes and Nickols [29, 30] involving the generation of anion vacancies through the formation of hole centres. Supplementary anion vacancies lead to an increase of the number of F centres, compared to their concentration in pure LiF crystals [21], prompting the formation of F_2^+ -like centres in accordance with [1]. The F and Hayes–Nickols centres (i.e. a molecule X_2 occupying nearest anion and cation vacancies in the $\langle 100 \rangle$ direction) are created during low temperature irradiation. When the temperature reaches 250 K anion vacancies associate with the F centres, with the formation of F_2^+ and F_2^{+} -like centres. Thus, Hayes–Nickols mechanism realization is necessary to create $F_2^+Mg^{2+}V_c^-$ centres. The absence of this mechanism in the investigated LiF:Ni, LiF:Be and LiF:Co crystals can be justified as a result of the following observations. In the event that under the ionizing radiation the divalent impurity ion reduces to the monovalent form, the creation of Hayes–Nickols centres becomes difficult [30]. The main factors controlling the reduction of the divalent metal are the value of its second ionization potential, I_f , and the nature of the host alkali halide crystal [31]. The upper threshold value for LiF was determined by Bosi and Nimis [31] to be $I_f = 17.2$ eV. In accordance with the above criterion, Ni^{2+} (with $I_f = 18.15$ eV) and Be^{2+} ($I_f = 18.21$ eV) show a strong

tendency for reduction to the monovalent form, while the Mg^{2+} ($I_f = 15.04$ eV) and Co^{2+} ions ($I_f = 17.05$ eV) do not trap electrons directly. The electron spin resonance (ESR) spectra of the divalent ions Ni^{2+} and Co^{2+} have been studied in the LiF crystal before irradiation [21, 30]. After irradiation of LiF by x-rays at room temperature Ni^+ ions have been found in LiF:Ni. However, after irradiation, the LiF:Co crystal does not demonstrate an ESR signal due to monovalent cobalt species [21,30]. Thus, irradiation cannot produce Hayes–Nickols centres, and therefore $\text{F}_2^+\text{M}^{2+}\text{V}_c^-$ centres, in the LiF:Ni and LiF:Be crystals. The above situation has been confirmed by our results on the kinetics of the formation of F_2^+ and F_2^+ -like centres (figure 1). Although the preceding presentation indicates that these centres should be created in LiF crystals doped with magnesium and cobalt, in this study we recorded their presence only in the LiF:Mg crystal. A plausible explanation for the absence of $\text{F}_2^+\text{Co}^{2+}\text{V}_c^-$ centres in LiF:Co can be put forward as follows. Hayes recorded the ESR spectrum of isolated Co^{2+} -vacancy complexes shortly after the LiF:Co crystal growth procedure. However, with the crystal stored for one week at room temperature, the Co^{2+} ions form aggregates [30]. The heating process and the subsequent quenching restores the isolated divalent impurity–vacancy dipoles. In the present investigation, we have used LiF:Co crystals with cobalt concentration (0.2 wt%) that is considerably higher than that used in the melt by Hayes (0.01 mol% in [30]). In addition the crystals were kept at RT for a long period (aging time $t_{ag} > 1$ year), during which we have not recorded variations in the optical spectrum as a result of aggregation. It is possible that changes appear in the thin structure of the higher resolution optical spectrum at low measuring temperatures. When the LiF:Co crystal was annealed at 873 K or 973 K for one hour, two intense absorption bands with wavelength maxima at 34 483 and 24 038 cm^{-1} appeared in the spectrum. The halfwidth of the 24 038 cm^{-1} absorption band exceeds 1.4 eV. We have also observed the absorption in the LiF:Co crystal, irradiated and then annealed at 873 or 973 K. It seems rational to relate this phenomenon to the strong aggregation of Co^{2+} -vacancy dipoles with a simultaneous formation of a CoF_2 phase. As a result, the absence of $\text{F}_2^+\text{Co}^{2+}\text{V}_c^-$ centres in the irradiated LiF:Co crystals is probably caused by the lack of single Co^{2+} -cation vacancy dipoles.

The reason for the difference between defect formation mechanisms in LiF:Mg and LiF crystals with the other divalent impurities may be as follows. One may suppose that the $\text{Mg}^{2+}\text{V}_c^-$ centre in LiF attains a local one-electron state with energy higher than the valence band electron energies, in analogy to the local one-electron state in KCl:Eu^{2+} [32, 33]. In this case the hole trapping with Hayes–Nickols centres formation should be more probable [34] and $\text{F}_2^+\text{Mg}^{2+}\text{V}_c^-$ centres formation in LiF:Mg should occur in accordance with the mechanism suggested in [1].

4.2. Mechanism of the formation and model of 'red' colour centres

Earlier reports [2] indicate that the time interval required for the destruction of $\text{F}_2^+\text{Mg}^{2+}\text{V}_c^-$ centres, at RT, is about 50 hours, a period that is nearly twice the destruction time of F_2^+ centres in pure LiF crystals (~ 24 hours, [16]). The $\text{Mg}^{2+}\text{V}_c^-$ dipoles stabilize the F_2^+ centres; notwithstanding, with the destruction of the F_2^+ -like centres the released $\text{Mg}^{2+}\text{V}_c^-$ dipoles gain a considerable degree of freedom. These dipoles can thus migrate in the crystal and be trapped by F-aggregate centres with a simultaneous formation of other complex F-aggregate centres. The above process can stimulate the creation of $\text{F}_3\text{Mg}^{2+}\text{V}_c^-$ centres ('red' colour centres) [5, 18]. The lower concentration of RCCs in LiF:Mg,OH is in accordance with the suggested formation mechanisms, since the concentration of the single $\text{Mg}^{2+}\text{V}_c^-$ dipoles in the LiF:Mg,OH crystal is highly reduced when compared to the LiF:Mg crystal, due to the complexes formed by the Mg^{2+} and hydroxyl ions [11].

The two additional absorption bands in LiF:Mg, located at 24 530 and 17 857 cm^{-1} , are due to the magnesium impurity (figure 5) and appear simultaneously after low temperature irradiation and storage of the crystal at RT. Ivanov *et al* [35] have studied the luminescence polarization of irradiated LiF:Mg crystals at LNT and discovered that the polarization of the luminescence peak with a maximum at 14 925 cm^{-1} (after excitation in the range 25 650–26 300 cm^{-1}) is the same as the polarization of the luminescence excited at 18 180 cm^{-1} . Consequently, the 24 530 cm^{-1} band, close to the excitation range 25 650–26 300 cm^{-1} , as reported by Khulugurov *et al* [5], may be due to one of the transitions (R_M^*) in the perturbed F_3 centres ($F_3\text{Mg}^{2+}\text{V}_c^-$ complex centres). Another transition is the R_N^* (17 857 cm^{-1}) in the same centre. As can be seen from the optical spectra presented in figures 3–5, and the corresponding spectral shape analysis, two kinds of centres, the models of which include $\text{Mg}^{2+}\text{V}_c^-$ dipoles, are observed in the LiF:Mg crystals after irradiation at 195 K. At the same time, the complex TSDC spectrum of the irradiated LiF:Mg crystal shows two highly overlapping dipolar-type relaxation bands (bands A_1 and A_2 , figure 6) with activation energies close to those of the single IV dipole (band A_4 , figure 7). The impurity–cation vacancy dipolar current band is not present in the irradiated and aged crystal, indicating the absence of single $\text{Mg}^{2+}\text{V}_c^-$ dipoles. This phenomenon could be explained on the basis of two models: either the formation of IV dipole aggregates, dimer and preferably trimer clusters [36, 37], or the appearance of complex dipolar formations between IV dipoles and F-aggregate centres. The first explanation appears less probable if one considers that the activation energy for dipole disorientation of the IV dipole aggregates is expected to be significantly higher than ~ 0.60 eV (e.g. $E = 0.85 \pm 0.05$ eV for the corresponding relaxation of trimers in unirradiated LiF:Mg [36]). In the above context, the TSD current band A may be attributed to the reorientation of the $\text{Mg}^{2+}\text{V}_c^-$ dipole population in the vicinity of the F_3 centre. The rising high temperature current signals, with the low activation energy (~ 0.3 eV), could thus be ascribed to a conduction process involving the removal of a cation vacancy from the complex $F_3\text{Mg}^{2+}\text{V}_c^-$ centre.

The model of the RCC as an $F_3\text{Mg}^{2+}$ centre with the symmetry axis in the $\langle 111 \rangle$ direction has been suggested by Abramov *et al* [18], while the presence of a cation vacancy in the centre composition has been established by Khulugurov *et al* ($F_3\text{Mg}^{2+}\text{V}_c^-$ model, [5]). The results of the present investigation allow us to determine the RCC model in a more accurate and detailed manner. If the symmetry axis of the $F_3\text{Mg}^{2+}\text{V}_c^-$ centre corresponds to the C_3 axis in the crystal [18] it is necessary to assume that the cation vacancy is placed on this axis, which is directed perpendicular to the plane of the F_3 centre. Thus, we must take for granted that the model of the RCC is an F_3 centre placed between the impurity cation and the cation vacancy. In the annealed sample the distance between Mg^{2+} and the energetically favoured position of the associated V_c^- equals $d_1 = \alpha\sqrt{2}$ (figure 8(a)), while in the RCC the IV dipole length should be $d_2 = 2\alpha\sqrt{3}$ (figure 8(b)), where α is the nearest neighbours distance in the host face-centred cubic lithium fluoride crystal. Based on the classical model of point charges in a dielectric medium, the difference between bonding energies of cation vacancy in the single impurity–vacancy $\text{Mg}^{2+}\text{V}_c^-$ dipole (irradiated–annealed crystal) and the $F_3\text{Mg}^{2+}\text{V}_c^-$ centre (irradiated crystal) should be

$$\Delta E = \frac{e^2}{\epsilon\alpha} \left(\frac{1}{\sqrt{2}} - \frac{1}{2\sqrt{3}} \right) = 0.37 \text{ eV} \quad (5)$$

where e is the electron charge and ϵ the static dielectric permittivity of the crystal ($\epsilon = 9.01$). As result, the activation energy E_3 of the rising high temperature thermostimulated current signals in the irradiated and aged LiF:Mg crystal (figure 6) is expected to be lower in comparison to the energy value E_5 calculated for the same band after annealing (figure 7). Quantitatively this situation is obviously realized by the thermostimulated depolarization current results that

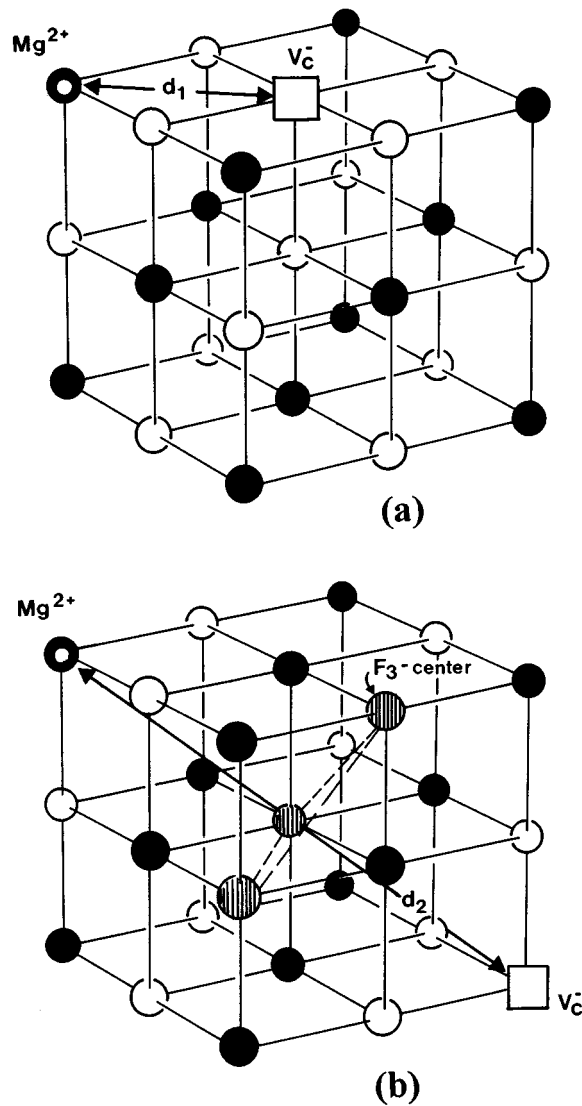


Figure 8. (a) Part of the LiF fcc lattice demonstrating the IV dipole formed by the divalent impurity ion and the 'bound' cation vacancy V_c^- in one of the 12 equivalent nearest neighbour positions. (b) Proposed structure of the red colour centre in $LiF: Mg^{2+}$ ($F_3Mg^{2+}V_c^-$).

determine an energy difference of $\Delta E = E_5 - E_3 \approx 0.30$ eV. Consequently, provided that the high temperature rising currents at figure 6 are stimulated by cation vacancies dissociating from the RCC, the $F_3Mg^{2+}V_c^-$ model with the distance $2\alpha\sqrt{3}$ between impurity ion and cation vacancy is in qualitative agreement with the experimental results obtained by the TSDC dielectric method.

Apart from the previous energetic considerations attention has to be paid to the change in the total polarization stored in the two crystals, expressed by peak area S , after using equal polarization (T_p , t_p , E_p) and quenching conditions. A direct comparison of figures 6 and 7 reveals that the total area of relaxation band A (S_A), in the irradiated and aged LiF:Mg

crystal, is higher than that covered by the single IV peak in the annealed sample (S_{IV}), with $S_A/S_{IV} \sim 4.6$. The difference is directly related to the magnitude of the polarization stored in the LiF:Mg in each experiment. The saturation polarization of a dielectric mechanism at $T = T_p$ (P_0 , equation (1)), is given by the Langevin function [7]

$$S = P_e(T_p) \approx \frac{sN_d\mu^2\kappa E_p}{kT_p} \quad (6)$$

where s is a geometrical factor, N_d the dipole concentration, μ the electric dipole moment and κE_p the local electric field responsible for dipole orientation. Here, S is predominantly controlled by the magnitude of the square dipole moment, $\mu = ed$, and consequently the square of the charge distance, d , in the corresponding dipolar formations. In conjunction with the RCC model, the polarization ratio is expected to be $S_A/S_{IV} \approx d_2^2/d_1^2 = 6.0$, in good agreement with the TSDC value of 4.6. The difference can be explained taking into consideration the small difference in the polarizing fields used in the experiments.

5. Conclusions

The results of the investigation of F aggregate centres in LiF crystals with divalent impurities by optical and TSDC methods can be summarized as follows:

- The accumulation of F_2^+ -like colour centres is observed in LiF:Mg crystals at the first stage of low temperature irradiation, with irradiation doses exceeding 10^7 R. Under similar conditions, F_2^+ -like centres are not formed in LiF:Ni, LiF:Be and LiF:Co crystals. The F_2^+ centres accumulation in these crystals is similar to the F_2^+ centres accumulation in undoped LiF crystals.
- The difference between the properties of the LiF:Mg crystals and LiF with Ni^{2+} , Be^{2+} and Co^{2+} impurities should be connected to the Hayes–Nickols mechanism with extra anion vacancy generation in the case of the LiF:Mg crystal. The absence of this mechanism in LiF:Ni and LiF:Be is connected to the reduction of the Ni^{2+} and Be^{2+} impurity ion valence state and in LiF:Co to the small concentration of single $Co^{2+}V_c^-$ dipoles as a result of dipole aggregation.
- The destruction of the F_2^+ and F_2^+ -like centres occurs in LiF:Mg crystals at the second stage of aggregation. The $Mg^{2+}V_c^-$ dipoles become free and other F-aggregated centres are formed. The IV dipoles are included in the composition of these colour centres. The two-band structure of the TSDC curve, with band parameters close to parameters of bands caused by single IV dipole reorientation, is in accordance with this aggregation mechanism.
- One kind of F-aggregated colour centre is the RCC and possibly the type of centres absorbing in the range of $44\,444\text{ cm}^{-1}$. The TSDC results are supportive of the suggested model for the RCCs, as complex $F_3Mg^{2+}V_c^-$ centres.

Acknowledgment

This work was supported by the NATO Linkage Grant HTECH.LG 971377.

References

- [1] Mikhalenko A A, Khulugurov V M, Dmitrieva E I and Salomatov V N 1989 *Phys. Status Solidi* b **155** 359
- [2] Bystrimovich S A, Karpushko F V, Mikhalenko A A, Morosov B P, Porukevich S A, Utkin I A and Khulugurov V M 1989 *Proc. 5th Int. Conf. on Tunable Lasers* part 1, p 93 (Irkutsk)

- [3] Lobanov B D, Maksimova N T, Khulugurov V M and Parfianovich I A 1980 *J. Appl. Spectrosc.* **32** 1079
- [4] Akhvediani Z G, Ivanov N A, Mikhaleiko A A, Khulugurov V M and Shkadarevich A P 1985 *Pis. Zh. Tekh. Fiz.* **11** 187
- [5] Khulugurov V M, Mikhaleiko A A and Novikov G K 1998 *Laser Phys.* **8** 1
- [6] Laverge C and Lacabanne C 1993 *IEEE Electr. Insul. Magn.* **9** 5
- [7] Vanderschueren J and Gasiot J 1980 *Field-Induced Thermally Stimulated Currents (Topics in Applied Physics)* ed G M Sessler (Berlin: Springer) p 144
- [8] Kalogeras I M and Vassilikou-Dova A 1996 *Cryst. Res. Technol.* **31** 693
Kalogeras I M and Vassilikou-Dova A 1998 *Defect and Diffusion Forum* **164** 1
- [9] Ivanov N A, Inshakov D V, Oleynikov E A, Khulugurov V M and Chernyshov A I 1991 *J. Appl. Spectrosc.* **54** 331
- [10] Low W 1958 *Phys. Rev.* **109** 256
- [11] Stoebe T G 1967 *J. Phys. Chem. Solids* **28** 1375
- [12] Vassilikou-Dova A, Kalogeras I M, Macalik B and Londos C A 1999 *J. Appl. Phys.* **84** 352
- [13] Baryshnikov V I and Kolesnikova T A 1998 *Fiz. Tverd. Tela* **40** 1030
- [14] Markham J J and Konitzer J D 1958 *J. Chem. Phys.* **29** 673
Markham J J and Konitzer J D 1959 *J. Chem. Phys.* **30** 328
- [15] Davitashvili T S H, Politov N G and Jvania M F 1969 *Spektrosk. Tverd. Tela* **4** 100
- [16] Nahum J 1967 *Phys. Rev.* **138** 3
- [17] Hughes A E and Runciman W A 1965 *Proc. Phys. Soc.* **86** 615
- [18] Abramov A I, Arkhangel'skaya V A et al 1990 *Opt. Spektrosk.* **68** 615
- [19] Katsika V and Grammatikakis J 1990 *J. Phys. Chem. Solids* **51** 1089
- [20] Vassilikou A B 1988 *J. Phys. Chem. Solids* **49** 855
- [21] Hayes W and Wilkens J 1964 *Proc. R. Soc. A* **281** 340
- [22] Seitz F 1954 *Rev. Mod. Phys.* **26** 7
- [23] Vassilikou-Dova A B, Grammatikakis J G and Londos C A 1986 *J. Phys. Chem. Solids* **47** 727
- [24] Grammatikakis J, Londos C A, Katsika V and Bogris N 1989 *J. Phys. Chem. Solids* **50** 845
- [25] Luty F 1968 *F_A Centers in Alkali Halides (Physics of the Color Centers)* ed B Fowler (New York: Academic) p 181
- [26] Haertel H and Luty F 1964 *Z. Phys.* **177** 369
Haertel H and Luty F 1964 *Z. Phys.* **182** 111
- [27] Delbecq C J 1963 *Z. Phys.* **171** 560
- [28] Farge S, Lambert M and Smoluchowski R 1966 *Solid State Commun.* **4** 333
- [29] Hayes W and Nickols G 1960 *Phys. Rev.* **117** 993
- [30] Hayes W 1962 *J. Appl. Phys.* **33** 329
- [31] Bosi L and Nimis M 1985 *Phys. Status Solidi b* **131** K 111
- [32] Salomatov V N and Kristoffel N N 1974 *Izv. Acad. Nauk, Ser. Fiz.* **38** 1238
- [33] Parfianovich I A, Metsik V M, Salomatov V N and Shuraleva E I 1974 *Opt. Spektrosk.* **35** 876
- [34] Salomatov V N and Shuraleva E I 1978 *Izv. Vuz'ov, Fiz.* **4** 139
- [35] Ivanov N A, Penzina E E and Zilsov S A 1999 *Phys. Status Solidi b* **213** 210
- [36] Strutt J E and Lilley E 1981 *J. Phys. Chem. Solids* **42** 827
- [37] McKeever S W S and Lilley E 1982 *J. Phys. Chem. Solids* **43** 885