

THERMALLY STIMULATED DEPOLARIZATION CURRENT MEASUREMENTS ON $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ AND $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ SOLID SOLUTIONS

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The fluorite-type solid solutions $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ were studied with the thermally stimulated depolarization current technique. From 10 to 400 K the TSDC scans showed four dipolar reorientation peaks to be present in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, and seven in $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$; each scan also showed the relaxation peak due to macroscopic space-charge. An assignment of these peaks is made using the defect structure of the solid solutions as derived from neutron scattering results. The depolarization steps that cause low-temperature reorientation peaks at 21 K for $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and at 29.5 K for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ are ascribed to 2 2 2-clusters, and 2 1 2-clusters, respectively. A discussion of the present theories on depolarization current peaks and space charge peaks is also presented.

1. Introduction

The thermally stimulated depolarization current (TSDC) technique is a very sensitive method for the study of dipolar relaxations in ionic crystals. The technique has been widely employed to investigate and to characterize relaxations of bound interstitial fluoride ions in fluorite-type solid solutions of alkaline-earth fluorides and trivalent metal fluorides [1–4]. In dilute solid solutions simple dipoles are formed between a trivalent dopant cation and an interstitial fluoride ion in an adjacent empty cube center. The dipole with the fluoride interstitial in a nearest neighbor (nn) position has tetragonal symmetry, while the dipole with the fluoride interstitial in a next-nearest neighbor (nnn) position has trigonal symmetry. With increasing dopant content several solid solutions reveal the formation of more complex arrangements of dopant ions and fluoride ion interstitials [5]. For example a TSDC peak at 110 K for $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions has been attributed to the presence of an L-

shaped complex, comprising an nn dipole which has trapped an additional fluoride interstitial ion [6].

Dielectric loss (DL) measurements on MF_2 ($\text{M} = \text{Ca}, \text{Sr}$ and Ba) doped with MeF_3 ($\text{Me} = \text{La}–\text{Lu}$) have been performed by Andeen et al. [7]. At very low temperatures these measurements reveal dielectric loss peaks for a number of solid solutions which are ascribed to defect clusters, formed by two trivalent dopant cations, two fluoride ion interstitials, and two relaxed lattice fluoride ions, the well-known 2 2 2-clusters.

Usually TSDC measurements are performed starting at liquid nitrogen temperature (LNT). Extended and polarizable defect clusters are expected to reorient well below LNT. Therefore, we have performed TSDC measurements starting at liquid helium temperature (LHeT) to be able to study the low activation enthalpy relaxations of defect clusters in detail. A specially designed cryostat has recently become available [8].

In this paper we report detailed results on relaxa-

tions of defect clusters in the fluorite-type solid solutions $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ in the temperature range 10–400 K.

Besides the relaxation of bound interstitials, another important feature which may show up in a TSDC scan is the relaxation of macroscopic space charge. This usually large relaxation peak is caused by the diffusion of free charge carriers. For the solid solutions studied here, the position of this peak is found to shift to lower temperatures with increasing solute content. This is to be related to a decrease of the migration enthalpy of the free fluoride ion interstitials. As this migration enthalpy can be derived directly from ionic conductivity measurements [9], a comparison and a discussion of the results will be presented.

2. Experimental aspects

Single crystalline slabs of the solid solutions $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ ($x = 0.0099$ and 0.133), and $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ ($7.7 \times 10^{-5} \leq x \leq 0.168$) with a surface area of about $5 \times 10^{-5} \text{ m}^2$, and a thickness of typically $1.0 \times 10^{-3} \text{ m}$ were used in the experiments. The preparation and characterization of these crystals have been described before [10,11]. The single crystals were cleaved along the $[111]$ -plane to ensure a reproducible polarization direction and to avoid noise signals, which are commonly observed in polished samples. Randomly oriented slabs with polished surfaces were found to increase the background noise level of the TSDC measurements with about one order of magnitude. Neutron diffraction studies on the samples [12,13] were used to determine the orientation of the cleavage planes.

The single crystal slabs were inserted in a helium cryostat between polished sapphire disks with a surface area of about $1.0 \times 10^{-4} \text{ m}^2$, and a thickness of $6.0 \times 10^{-4} \text{ m}$. By doing so, complete blocking of both ionic and electric current is achieved. A detailed description of the cryostat has been published by Roos and Keijzer [8]. The samples were polarized in an electric field of $3.0 \times 10^5 \text{ V/m}$ at a constant polarization temperature T_p for about 25 min by a stable dc voltage power supply (Oltronic N176).

An increase of the polarization field E_p did not change the polarization peak sizes, indicating the ex-

tent of polarization to be almost complete.

After polarization the samples were cooled in about 40 min to liquid helium temperature. At this starting temperature T_0 , the field was switched off, and a Cary 401 electrometer was shunted into the circuit. The current level was allowed to stabilize at about $1.0 \times 10^{-15} \text{ A}$ in approximately 30 min, before starting a linear increase of the temperature. A linear heating rate is a prerequisite for the reliable determination of the kinetic parameters, and was achieved using a digital temperature controller DTC 2 (Oxford Instruments), and a linearized sweep unit (Oxford Instruments, type E). However, in the low-current modes the response time of the electrometer becomes relatively long.

Therefore, the heating rate used in our TSDC measurements (0.03472 K/s) was a carefully chosen compromise. A faster heating rate would increase peak sizes, while the slow response of the electrometer would influence the shape of the depolarization peaks. A slower heating rate would decrease the peak sizes, and hence increase the relative noise level of the measurements. During the measurements the background current level was stable at about $1 \times 10^{-15} \text{ A}$. The noise level was equal to the measuring accuracy of the Cary electrometer at about $5 \times 10^{-17} \text{ A}$.

The current-temperature scan was recorded on a Hewlett-Packard 7045B x-y recorder. Analysis of the results was performed by determining the kinetic parameters of the relaxation peaks by computer fitting the data to theoretical current equations as described in the next section.

3. Theory

The thermally stimulated depolarization current (TSDC) technique, often referred to as ionic thermal current (ITC) technique, has been introduced in 1964 by Bucci and Fieschi [14]. They derived a set of equations describing the depolarization current due to reorienting non-interacting dipoles in an ionic crystal, when heated with a linear heating rate after having been polarized, and cooled down to liquid nitrogen temperature.

A depolarization current peak was found to depend on the relaxation parameters ΔE (the activation energy for reorientation), τ_0 (the inverse of the charac-

teristic frequency factor for the jump), N_D (the number of dipoles per m^3), and μ (the dipole moment of the dipole). When a sample is polarized at a temperature T_p , and a linear heating rate b is maintained during the measurement, Bucci and Fieschi reported the current density at a temperature T to be:

$$J(T) = (N_D \mu^2 E_p / s k T_p \tau_0) \exp(-\Delta E / k T) \times \exp \left[-(b \tau_0)^{-1} \int_0^T \exp(-\Delta E / k T') dT' \right], \quad (1)$$

where E_p is the externally applied polarization field, s is a structure-dependent scaling factor ($s = 1/3$ for fluorites), and k is the Boltzmann constant.

This equation has been used to fit our experimental data in order to obtain the dipolar relaxation parameters. However, it is found that only for the lowest dopant level ($x = 7.7 \times 10^{-5}$) a reasonable fit is obtained. At higher values of x , a measured reorientation peak is much broader than the best fitted theoretical peak (see fig. 1). It has been reported by Shelley and Miller [15], and by Van Weperen et al. [16] that peak broadening with increasing dopant concentration can be ascribed to a reorientation activation enthalpy which has not a single value, but instead has a Gaussian distribution around a value ΔE_0 as a result of interactions with surrounding dipoles. The current density equation at a temperature T will then become:

$$J(T) = (N_D \mu^2 E_p / s k T_p \tau_0) \int_{-\infty}^{\infty} (2\pi)^{-1/2} \sigma^{-1} \times \exp [-(\Delta E - \Delta E_0)^2 / 2\sigma^2] \exp(-\Delta E / k T) \times \exp \left[-(b \tau_0)^{-1} \int_0^T \exp(-\Delta E / k T') dT' \right] d\Delta E, \quad (2)$$

where σ is the width of the energy distribution. Using this equation the results of our measurements could be fitted, yielding acceptable relaxation parameters. A fit result is shown in fig. 1b. However, the shape of a depolarization peak may also be influenced by a number of other parameters, such as a non-homogeneous dopant distribution throughout the sample, and a partial shielding of the external polarizing field due to the migration of free charge carriers.

The migration of the free ionic charge carriers towards the blocking electrodes causes a large TSDC peak to appear. The activation enthalpy for migration of fluoride interstitials as found in ionic conductivity measurements has been reported by Wang and Nowick [17] to be related to the maximum temperature T_m of the space-charge peak according to the following equation:

$$(\Delta H_\sigma / k T_m) = (A / b e \epsilon_0) \exp(-\Delta H_\sigma / k T_m) + 1, \quad (3)$$

where ΔH_σ is the migration enthalpy of fluoride interstitials from ionic conduction, A is the pre-exponential factor of the conductivity Arrhenius equation, b the heating rate of the TSDC measurement, and k , e , and ϵ_0 have their usual meanings. A comparison of ΔH_σ calculated from this equation with the observed values of T_m , and ΔH_σ from ionic conductivity measurements on $Ba_{1-x}U_xF_{2+2x}$ solid solutions [9] is presented in section 4.4.

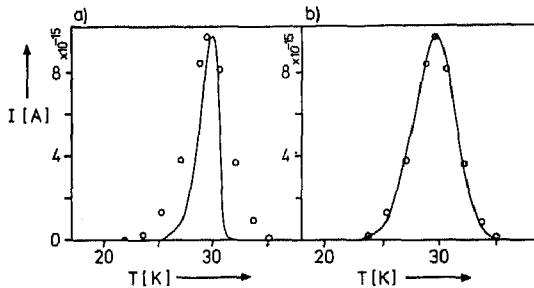


Fig. 1. The results of computer fitting of a TSDC relaxation peak of $Ba_{0.97}U_{0.03}F_{2.06}$ using a single activation energy (a) and a Gaussian distribution of activation energies (b).

4. Results and discussion

The TSDC scans of two solid solutions of $Ba_{1-x}La_xF_{2+x}$ and of $Ba_{1-x}U_xF_{2+2x}$ are shown in figs. 2 and 3, respectively. The relaxation parameters ΔE , τ_0 and σ for a number of samples are presented in table 1. The solute content of the $Ba_{1-x}La_xF_{2+x}$ samples was determined by neutron activation analysis [10], and of the $Ba_{1-x}U_xF_{2+2x}$ solid solutions by X-ray diffraction and X-ray fluorescence [11].

Table 1

Reorientation peak parameters of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ and $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions.

x	T_{max} (K)	c^a	E (eV)	σ (eV)	τ_0 (s)	$T_{\text{max,fit}}$ (K)
$\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$						
0.0001	29.7	2.75×10^{-12}	0.0896	0.0014	8.0×10^{-14}	29.7 II
0.009	29.7	2.07×10^{-11}	0.0905	0.0027	9.5×10^{-14}	29.7 II
0.03	29.7	4.88×10^{-12}	0.0896	0.0047	8.0×10^{-14}	29.7 II
0.055	29.7	9.53×10^{-12}	0.0894	0.0089	8.0×10^{-14}	29.7 II
0.009	54.3	4.25×10^{-13}	0.170	0.0021	4.2×10^{-14}	54.4 III
0.055	75.0	4.77×10^{-13}	0.220	0.0138	4.2×10^{-13}	75.5 IV
0.009	119.0	1.02×10^{-12}	0.379	0.0027	3.0×10^{-14}	119.7 VI
0.009	155.0	1.07×10^{-12}	0.508	0.0152	1.0×10^{-14}	154.3 VII
$\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$						
0.010	117.7	1.34×10^{-12}	0.2825	0.0020	1.2×10^{-10}	117.5
0.133	21.0	3.87×10^{-11}	0.0613	0.0145	1.0×10^{-13}	21.0

a) $c = (N_D \mu^2 E_p) / (3kT_p)$.

4.1. Reorientation processes

4.1.1. $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$

Single crystals of the solid solutions $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ with low solute content ($1.0 \times 10^{-4} \leq x \leq 1.0 \times 10^{-2}$) have been studied by Laredo et al. [2] using the TSDC technique. In the covered temperature range 120 to 300 K two relaxation peaks at 141 and 195 K were ascribed to the reorientation of nn-dipoles and nnn-dipoles, respectively. The size of both peaks depends strongly on the thermal history of the sample. It was, therefore, suggested that annealing of the crystals at 1250 K induced the formation of larger non-polarizable defects, thereby decreasing the concentration of nn- and nnn-dipoles. A more recent TSDC study of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions with dopant concentrations up to the solubility limit of LaF_3 (~ 50 m/o) in BaF_2 , has been reported by Wapenaar et al. [6]. This study covered the temperature range from 100 to 320 K. In $\text{Ba}_{0.9901}\text{La}_{0.0099}\text{F}_{2.0099}$, the nn- and nnn-dipole reorientation peaks have been found, along with a reorientation peak ascribed to a L-shaped $(\text{La}_{\text{Ba}}2\text{F}_i)'$ complex, comprising a nn-dipole with a scavenged fluoride ion interstitial.

The TSDC measurements presented in this paper cover the temperature range 10–400 K. For the solid solution $\text{Ba}_{0.9901}\text{La}_{0.0099}\text{F}_{2.0099}$ the TSDC scan shows all three relaxation peaks mentioned above, as well as the space-charge reorientation peak (see fig. 2).

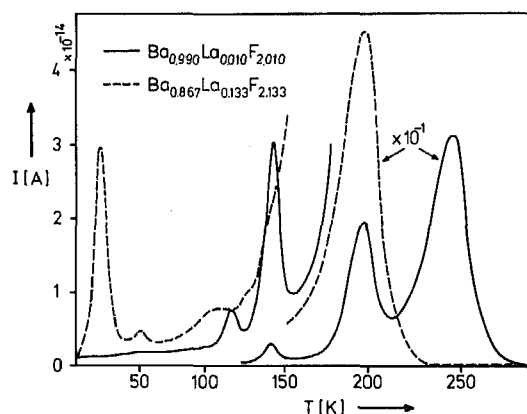


Fig. 2. TSDC scans of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions with $x = 0.0099$ and 0.133 .

An entirely different TSDC spectrum is obtained for the heavily-doped solid solution $\text{Ba}_{0.867}\text{La}_{0.133}\text{F}_{2.133}$, in which a large reorientation peak around 21 K is the most prominent feature. A different TSDC result suggests a different defect structure. A neutron scattering study of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions with $x = 0.209$ and 0.492 has been published [12]. This describes the presence of 2 2 2-clusters. The structure of a 2 2 2-cluster is shown in fig. 4. A possible reorientation mechanism in a 2 2 2-cluster has been proposed by Jacobs and Ong [3] in their TSDC-study of $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ solid solutions. By this mechanism the

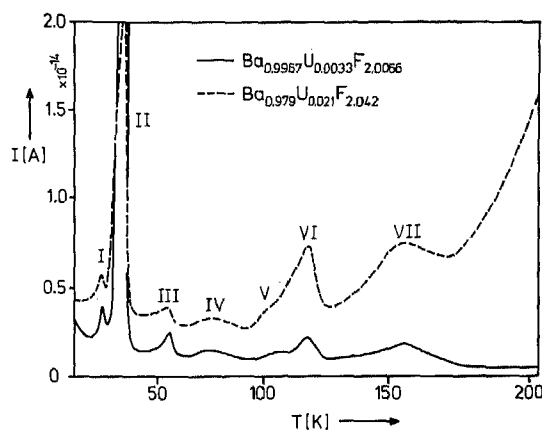


Fig. 3. TSDC scans of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions with $x = 0.0033$ and 0.02 .

polarizing step is a shift of the relaxed lattice fluoride ions above and below the plane of the cluster from a "trans" to a "cis" configuration. The depolarization step, which shows up in a TSDC measurement, will be a "cis" to "trans" relaxation. In the paper by Jacobs and Ong, the computed activation energy of this relaxation is reported to be 0.62 eV. This value seems rather high, since the depolarization path will lead a negatively charged fluoride interstitial through an effectively positive vacant anion site to an empty interstitial site (see fig. 5a).

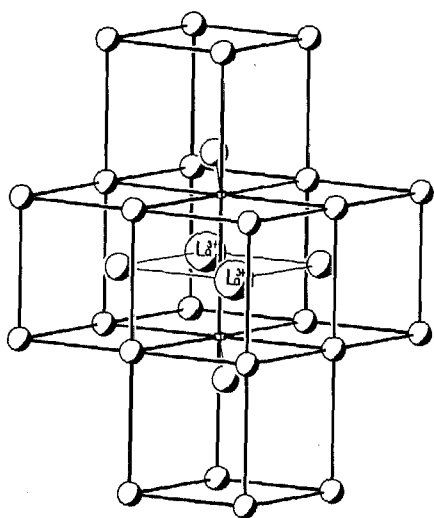
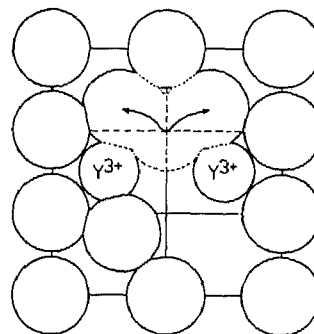


Fig. 4. A 2 2 2-cluster in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions.

(a) $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$



(b) $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$

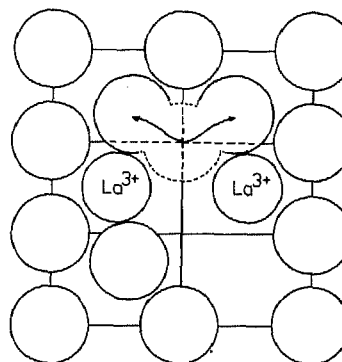


Fig. 5. A reorientation step in a 2 2 2-cluster in $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ (a) and in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ (b). Only the $[110]$ plane is shown. Open circles present F^- ions.

In the solid solutions $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ a similar (de)polarization step in a 2 2 2-cluster can proceed almost unhindered. A small activation energy is to be expected for this solid solution, because there is enough free space within the structure to perform this (de)polarization step in the 2 2 2-clusters without shifting adjacent lattice ions from their sites, in contrast with the situation in the $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ solid solutions, as is indicated in fig. 5. Therefore, the TSDC peak at 21 K, which is observed for the $\text{Ba}_{0.867}\text{La}_{0.133}\text{F}_{2.133}$ sample, is ascribed to a reorientation, as depicted in fig. 5b. The defect structure of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions with $x \leq 0.01$ comprises nn-dipoles, nnn-dipoles, and L-shaped $(\text{La}_{\text{Ba}}2\text{F}_i)'$

complexes [6]. At dopant concentrations above $x = 0.05$ the presence of 2 2 2-clusters has been reported [12]. It takes two adjacent La_{Ba} ions to form 2 2 2-clusters. Therefore, it is not likely for such clusters to be present at low dopant levels. The absence of the reorientation peak at 21 K in the TSDC scan of $\text{Ba}_{0.99}\text{La}_{0.01}\text{F}_{2.01}$ supports this view. Additional evidence for the absence of 2 2 2-clusters in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions at low dopant levels has been reported by Andeen et al. [7]. These authors performed ac dielectric loss measurements on MF_2 ($M = \text{Ca}, \text{Sr}, \text{and Ba}$) doped with MeF_3 ($\text{Me} = \text{La} - \text{Lu}$). For a number of these solid solutions, low-temperature peaks were observed, which have been ascribed to defect clusters. For $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions with low solute content, these low temperatures peaks were absent.

4.1.2. $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$

The TSDC scans of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions show a reorientation peak at 29.5 K for all compositions with $7.7 \times 10^{-5} \leq x \leq 0.168$. For $\text{Ba}_{0.832}\text{U}_{0.168}\text{F}_{2.336}$ this peak, with its maximum around 29 K, was broadened to such an extent that it was smeared out between 6 and 60 K and only a small increase in the current was observed. The presence of this peak in the TSDC scans suggests defect clusters similar to the 2 2 2-cluster to be present in the lattice. A neutron scattering study of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions reveals the defect structure to consist

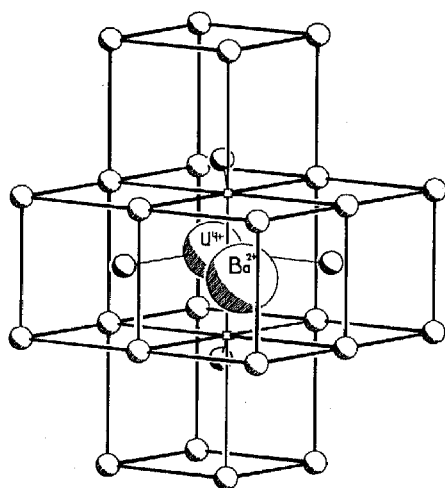


Fig. 6. A 2 1 2-cluster in $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions.

mainly of 2 1 2-clusters [13,18]. These clusters have a similar anion array as is found in the 2 2 2-clusters with one substitutional U^{4+} ion and one regular lattice Ba^{2+} ion instead of two La^{3+} ions, and the relaxed fluoride ions above and below the plane in a "cis" configuration (fig. 6).

The relaxation peak at 29.5 K in the TSDC scans is presented for a number of dopant concentrations in fig. 7. This relaxation peak occurs already in the TSDC result for $\text{Ba}_{0.999923}\text{U}_{0.000077}\text{F}_{2.000154}$. Also in this dilute solid solution the relaxation can be ascribed to 2 1 2-clusters. Because these clusters contain only one dopant cation, they can be formed even at the lowest dopant levels, provided that the neutral associate $(\text{U}_{\text{Ba}}2\text{F}_i)^{\times}$ is formed. The reorientation step, which is responsible for the TSDC peak at 29.5 K can be described with two models. The most plausible explanation seems to be a polarization of the 2 1 2-cluster by shifting both relaxed fluoride ions from the "cis" configuration above and below the U^{4+} ion to a "cis" configuration with the interstitials above and below the lattice Ba^{2+} ion, and a depolari-

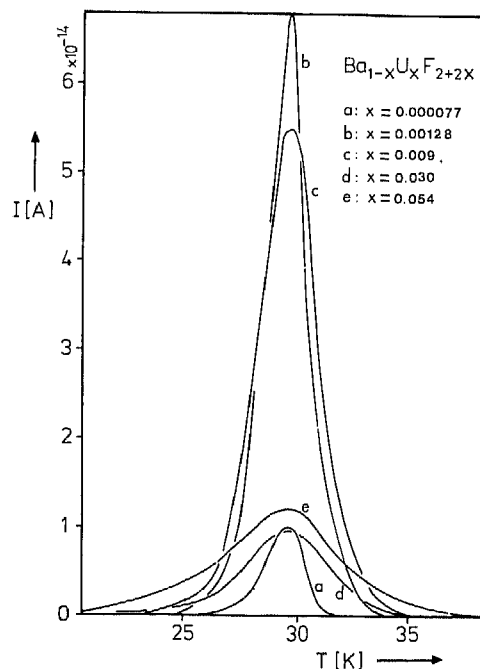


Fig. 7. The TSDC reorientation peak at 29.5 K for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions with different dopant concentrations.

zation vice versa. However, another reorientation process, dependent on the direction of the polarizing electrical field deserves careful consideration. The single crystalline slabs used for the TSDC measurements, are cleaved along the $[1\ 1\ 1]$ -plane, which introduces the possibility to use a polarizing field along the $[\bar{1}\ \bar{1}\ \bar{1}]$ direction. A polarized state of a 2 1 2-cluster with a dipole moment opposing the electrical field, i.e. in the $[1\ 1\ 1]$ direction will therefore be the most favourable configuration.

A stable defect cluster with its dipole moment in this direction has been proposed for $\text{Ca}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions [19]. This defect cluster, comprising a U^{4+} ion, three fluoride ion interstitials and one fluoride ion vacancy, i.e. only one relaxed fluoride lattice ion is called a trimer (see fig. 8). The neutron scattering data [13] reveal this cluster to be absent in our unpolarized crystals.

A trimer with a dipole moment in the $[1\ 1\ 1]$ direction can be formed from 2 1 2-clusters with a dipole moment in the $[1\ 1\ 0]$, $[1\ 0\ 1]$, and $[0\ 1\ 1]$ direction in a single step as is shown in reverse in fig. 9a for $[1\ 1\ 1] \rightarrow [1\ 1\ 0]$. This polarization step can be described as a back relaxation of one relaxed fluoride ion interstitial below the plane of the 2 1 2-cluster to its original lattice site, and a shift of the other relaxed fluoride ion interstitial above the plane towards the cube center. All three fluoride ion interstitials are reported to relax to positions between their respective cube centers and the fluoride ion vacancy. This together with the fluoride ion vacancy yields a defect

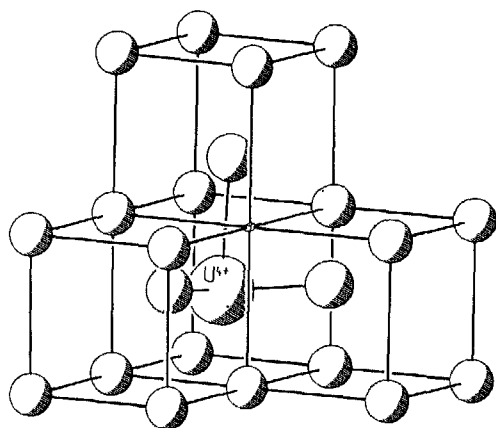


Fig. 8. A trimer in $\text{Ca}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions.

cluster with trigonal symmetry [19].

In an unpolarized $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ sample the 2 1 2-clusters are oriented in twelve different directions, with the two fluoride ion interstitials in the plane of the cluster pointing at each of the twelve Ba^{2+} ions around a cluster U^{4+} ion. The dipole moments of the clusters will be in the $[1\ 1\ 0]$, and all related directions, such as the $[0\ 1\ 1]$ direction, the $[\bar{1}\ 0\ 1]$ direction, etc. To polarize a 2 1 2-cluster with its dipole moment in the $[\bar{1}\ \bar{1}\ 0]$ direction to a trimer with its dipole moment in the $[1\ 1\ 1]$ direction takes three steps. The subsequent depolarization steps are depicted in fig. 9. The last two steps (figs. 9b and 9c) are in fact identical, and therefore they will have the same activation energy. The first step, from a trimer with its dipole moment in the $[1\ 1\ 1]$ direction to a 2 1 2-cluster with its dipole moment in the $[1\ 1\ 0]$ direction consists of only small and practically unhindered displacements of four fluoride ions. The activation energy for this reorientation will probably be very low. Therefore, it will not show up as a distinct relaxation peak in the TSDC scan of a $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ sample, because this type of depolarization of the trimer will already take place when the electrical field is switched off at liquid helium temperature. It can therefore be concluded, that if the polarized state of a 2 1 2-cluster is a trimer, the activation energy for reorientation will be less than 0.04 eV.

The reorientation peak at 29.5 K for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions has a computed activation enthalpy of 0.09 eV, and is the most prominent feature in the TSDC scan, apart from the space-charge peak. Because the steps as depicted in figs. 9b and 9c require the same activation enthalpy, they will both contribute to the depolarization current. Hence the 29.5 K peak is assigned to this type of 2 1 2-cluster reorientations. In fig. 10 a scheme of all possible polarization steps with $\Delta E = 0.09$ eV is pictured, along with the fractions of the total 2 1 2-cluster concentration involved in those steps.

The activation energy for the reorientation of an L-shaped $(\text{La}_{\text{Ba}}2\text{F}_i)'$ complex in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions is reported to be 0.354 eV [6]. For $\text{Ba}_{0.9901}\text{La}_{0.0099}\text{F}_{2.0099}$ we obtained the value 0.28 eV from a fit. This L-shaped complex was reported to induce lattice fluoride ion relaxations similar to a 2 2 2-cluster ("trans"-configuration) [6]. It is, however, plausible to take for these relaxations those de-

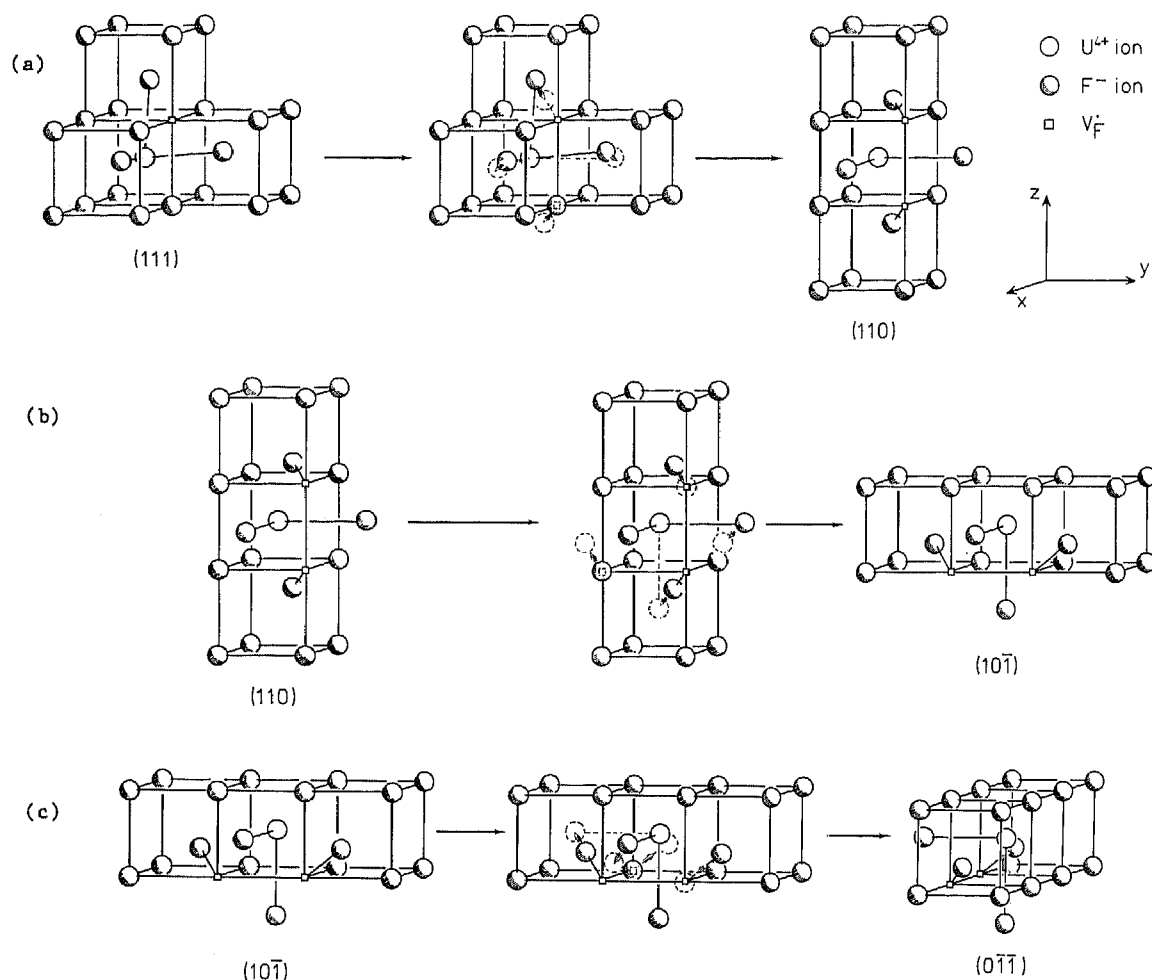


Fig. 9. The three reorientation steps which polarize a trimer, having its dipole moment in the $[111]$ direction, to a 212 -cluster with its dipole moment in the $[0\bar{1}\bar{1}]$ direction.

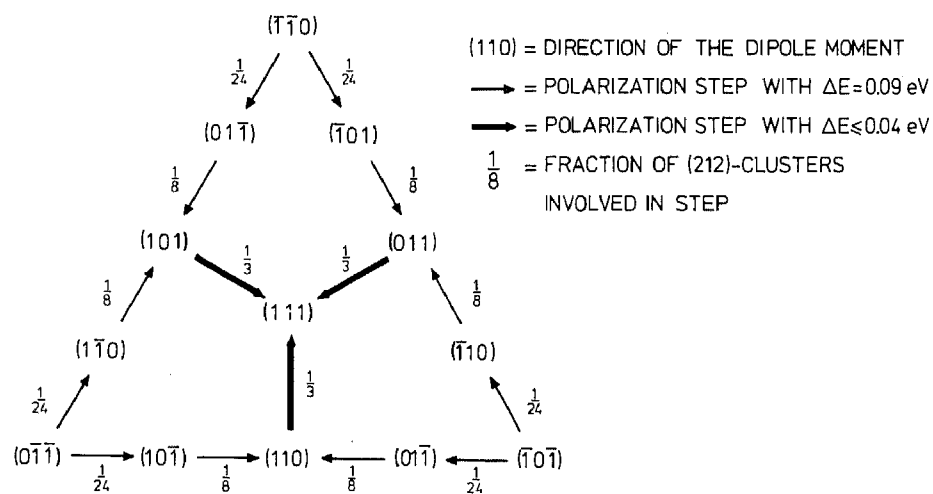


Fig. 10. A schematic representation of the polarization steps for 212 -clusters in $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions.

scribed for the "cis"-configuration of a 2 1 2-cluster, because this cluster contains also only one single dopant cation and two fluoride ion interstitials in a L-configuration. A large difference is noted between the activation enthalpies for reorientation of a L-shaped complex (0.28 eV), and of a 2 1 2-cluster (0.09 eV). Although both reorientation pathways are the same, the smaller size of the U^{4+} ion ($r = 1.00 \times 10^{-10}$ m) compared to the size of the La^{3+} ion ($r = 1.160 \times 10^{-10}$ m), the higher charge on the U^{4+} ion and the negative charge of the L-shaped $(La_{Ba}2F_i)'$ complex will most probably result in a substantial decrease of the reorientation energy (ionic radii for eight coordination were taken from ref. [20]).

In order to obtain more evidence for the present model, a neutron scattering study of a polarized $Ba_{0.95}U_{0.05}F_{2.10}$ single crystal has been performed [13]. In this experiment the crystal is polarized in an electric field of 5.0×10^5 V/m, and cooled to liquid helium temperature as in a TSDC experiment. The defect structure of this polarized solid solution is then determined by measuring the diffuse scattering between the Bragg reflections in the (X00)/(0YY)-plane. This pattern is analyzed with a computer fitting program. At present it has been established that indeed significant changes occur in the defect structure of $Ba_{0.95}U_{0.05}F_{2.10}$ upon polarizing, but further research is being performed to solve the detailed structure of the polarized 2 1 2-clusters. These investigations are hampered by uncertainty about the extent of polarization in the examined crystals. If the polarization of the samples is incomplete, computer fitting of the neutron scattering results to obtain the structure of a polarized 2 1 2-cluster is not possible. By varying the polarizing electrical field, attempts are made to determine the precise extent of polarization.

The TSDC scans of $Ba_{1-x}U_xF_{2+2x}$ solid solutions show six relaxation peaks in addition to the large peak at 29.5 K, as can be seen in fig. 2. The positions of the maxima of these peaks, as well as some fit parameters are gathered in table 1. The relaxation peak at 29.5 K has been ascribed to the reorientation of 2 1 2-clusters. The assignment of the other peaks in the TSDC scan requires some more information about possible other complexes and impurities in the $Ba_{1-x}U_xF_{2+2x}$ solid solutions.

In a recent paper the crystal growth and characterization of these solid solutions have been discussed

[11]. It was reported that during crystal growth reduction of U^{4+} ions to U^{3+} ions was likely to occur to a minor extent, unless elaborate precautions were taken. With trivalent uranium nn- and nnn-associates $(U_{Ba}F_i)^X$ can be formed. In fact the TSDC scan of a BaF_2 crystal doped with UF_3 has been measured by Murin and Glumov [4], reporting the presence of nn- and nnn-dipoles with reorientation activation enthalpies of 0.39 and 0.55 eV, respectively. The depolarization activation enthalpies of the peaks at 119 and 155 K in the present $Ba_{1-x}U_xF_{2+2x}$ solid solutions, were found to be 0.38 and 0.51 eV, respectively. The size of these peaks increases with increasing solute content, which is concordant with reduction of U^{4+} ions. Therefore, we ascribe the peaks at 119 and 155 K to nn- and nnn-dipole relaxations of $(U_{Ba}F_i)^X$ associates, respectively. The small size of these peaks suggests the concentration of U^{3+} to be of the order of parts per million.

For the small relaxation peaks numbered I, III, IV and V it can be noted from fig. 2 that the peak sizes are UF_4 -concentration independent. Therefore, they are ascribed to relaxations around other impurities in the BaF_2 host lattice. A few possibilities are the following: (i) during crystal growth [11] an oxygen contamination is bound to occur since the alkaline-earth fluorides are known to be highly reactive to oxygen when they are in the liquid state; (ii) an oxygen scavenger in the form of a few m/o lead fluoride has been introduced into the growth mixture to reduce the amount of oxygen and water contamination. It is possible that several other impurities are introduced in this way. It is clear that only impurity ions which are able to form some kind of dipoles in the lattice show up in the TSDC scan.

4.2. Peak broadening of TSDC reorientation peaks

In section 3 of this Chapter, a Gaussian distribution of (re)orientation activation enthalpies was introduced to account for peak broadening effects [16]. This distribution was used in a model for computer fitting of TSDC-reorientation peaks. This energy distribution had been proposed in analogy to observed peak broadening effects due to dipole-dipole interactions and monopole-dipole interactions with increasing dopant concentration (figs. 1 and 7).

In an extremely low-doped $BaF_2:U^{4+}$ crystal the

activation energy of the 2 1 2-cluster reorientation is determined only by the surrounding undisturbed host lattice. Therefore, the activation enthalpy is expected to be the same for all clusters in the lattice, its value being denoted ΔE_0 . With increasing solute content the reorientation of a 2 1 2-cluster will become more influenced and eventually hampered by nearby 2 1 2-clusters in the lattice. This effect will increase with increasing UF_4 concentration, because the average distance between 2 1 2-clusters decreases.

At moderate doping levels there will exist a range of possible surroundings for a 2 1 2-cluster in the lattice. Each environment will have a different effect on the reorientation activation energy. The net result will be a distribution of activation energies around a mean value $\Delta \bar{E}$. The position of the reorientation peak is concentration invariant, which means that the energy broadening takes place around the value ΔE_0 .

Although computer fitting of the TSDC results with this model yields satisfactory results, it is questionable whether the mean activation energy $\Delta \bar{E}$ will always be equal to ΔE_0 for all dopant concentrations. Also, it has been assumed in the model that the reciprocal of the characteristic jump frequency τ_0 will not have a distribution around a mean value $\bar{\tau}$. Examples of an approach using such a distribution to account for peak broadening have been published before for electrets and polymers [21].

For $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions with $x > 0.10$, the dopant concentration is high enough to cause distorted surroundings for every 2 1 2-cluster in the lattice. The polarization of a large fraction of these clusters will therefore be hindered, while the remaining part of the clusters will exhibit depolarization energies which will be strongly influenced, resulting in extensive peak broadening. Evidence for this effect is also presented in ref. [13].

At low temperatures an additional factor may influence the shape of a depolarization peak, i.e. the response time of the electrometer. For the apparatus used in our experiments (a Cary type 401), the response time was specified to be as long as one minute in the measuring range used ($0-1.0 \times 10^{-14}$ A). Especially at low temperatures the depolarization peaks are narrow, for instance the 29.5 K peak for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions with $x \leq 0.05$ has a half-width of about 4 K. With the heating rate used in our experiments (0.03472 K/s), a response time of

1 min will therefore result in a considerable error in the measured current. This error is larger on the high temperature side of the relaxation peak, because the descent of a TSDC peak is steeper than the ascent. The effect of the response time error will therefore be an effective broadening of the low-temperature TSDC peak. At higher temperatures, the peak half-widths are several times larger, and consequently the response time error will become negligible. Since this response-time error could not be taken into account in the computer fitting of the reorientation current peaks, its extent being yet unknown, a slight deviation of the fit results at the descending slope of the low-temperature peaks was tolerated.

4.3. Corrections of the presented theory

When the heating rate of a TSDC experiment was doubled, the peak maxima of all peaks shifted to higher temperatures and the peak heights were doubled, which is entirely according to the theory presented in section 3. When, however, the polarizing temperature T_p was varied, no apparent effect on a depolarization peak was observed. As this temperature T_p is incorporated in eq. (2), which describes the temperature dependence of the depolarization current resulting from reorientation of polarized 2 1 2-clusters, a clear effect on the current peak size should have been the result of a change of the polarization temperature.

If the 2 1 2-cluster reorientation which causes the current peak at 29.5 K for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions is considered, the resulting dipole moment change can be calculated using the precise positions of the ions which constitute this cluster. These positions have been determined by neutron scattering measurements [13]. The calculated dipole moment change is: $\mu = (1.72 \pm 0.02) \times 10^{-28}$ Cm. In a $\text{Ba}_{0.991}\text{U}_{0.009}\text{F}_{2.018}$ solid solution the 2 1 2-cluster concentration is $1.5 \times 10^{26} \text{ m}^{-3}$, if each U^{4+} ion is taken to form a cluster. The volume of the crystal, which was used in the experiment from which the computer fits of the reorientation peaks in table 1 were made, is $1.2 \times 10^{-8} \text{ m}^3$. In eq. (2) the peak size is dependent on a constant $c = (N_D \mu^2 E_p) / (3kT_p)$. This constant has been determined by the computer fitting, and all other factors in this constant are either known or were mentioned above.

The polarization temperature can then be calculated to be $T_p = (9.2 \pm 1.2)$ K. If either N_p or μ is taken to be smaller, because the maximum possible values were used, the calculated T_p will even decrease. In our experiments on $\text{Ba}_{0.991}\text{I}_{0.009}\text{F}_{2.018}$, the polarizing temperature T_p was varied from 50 K to 400 K, without any change in peak size. We suggest, therefore, that in eq. (2) the polarizing temperature T_p can be replaced by a constant which has a value of 9.2 K for this sample.

Finally we note a problem in obtaining the τ_0 and ΔE values. Literature data of four different sources are available for the parameters of the nnn-dipole reorientation peak in low-doped $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions [6,22–24]. If we plot $\log \tau_0$ against the reorientation enthalpy ΔE , a linear relationship is found (see fig. 11). If the reported parameters are used to compute this reorientation peak, the same result was obtained for all four sources. Although all the authors obtained a satisfactory fit result, the obtained parameters differ widely (the τ_0 values differ by more than two orders of magnitude). Because of this it is clear that in order to obtain accurate ΔE values by peak fitting, τ_0 must be known beforehand, and vice versa. If this is not the case only a linear relationship can be reported between $\log \tau_0$ and ΔE , for which

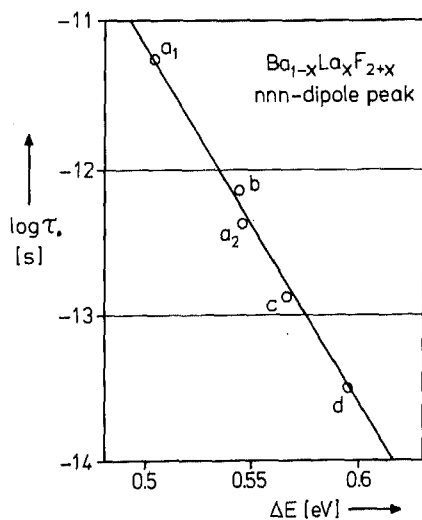


Fig. 11. The relaxation parameters $\log \tau_0$ and ΔE of the nnn-dipole peak of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ from four literature sources. a_1 and a_2 from ref. [24], b from ref. [23], c from ref. [22] and d from ref. [6].

each combination yields an accurate fit result. The values given in table 1 were selected by considering also the NMR data on these systems [25].

4.4. The space-charge depolarization peak

For all the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions studied here, a large depolarization peak was observed in the TSDC scans. This peak was positioned at higher temperatures than the dipole- or cluster-reorientation peaks. Unlike for the dipole- or cluster-reorientation peaks, the position of this peak was strongly dependent on the dopant concentration. For $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions the dependence of the temperature of the maximum of the peak (T_m) with solute content x is shown in fig. 12.

Ionic conductivity measurements on the same $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions [9] showed the activation enthalpy for fluoride ion interstitial migration to have a similar dependence on x . The large high-temperature TSDC peak is therefore ascribed to the migration of unbound fluoride ion interstitials. As has been described in section 3 of this paper, the maximum temperature T_m of this peak is related to the migration energy of fluoride ion interstitials ΔH_g . In table 2 the values of $\Delta H_{g,\text{TSDC}}$ calculated from the TSDC results according to eq. (3), are compared with $\Delta H_{g,\text{cond}}$ values derived directly from ionic conductivity measurements [9].

For the calculation of $\Delta H_{g,\text{TSDC}}$ the A values were derived from ionic conductivity measurements,

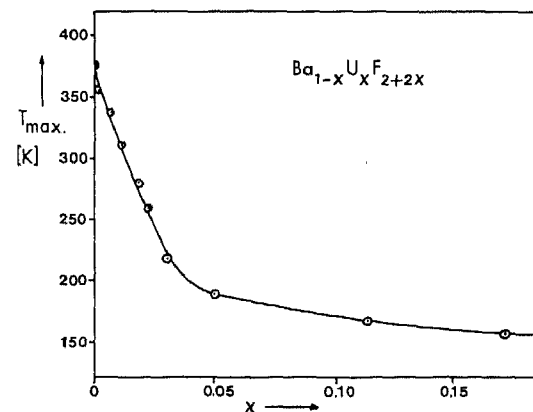


Fig. 12. The maximum temperature of the space-charge peak (T_m) versus x for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions.

Table 2
 $\Delta H_{\sigma, \text{TSDC}}$ compared with $\Delta H_{\sigma, \text{cond}}$ for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$

x	$\Delta H_{\sigma, \text{TSDC}}$ (eV)	$\Delta H_{\sigma, \text{cond}}$ (eV)
0	1.440	1.35
0.009	1.244	1.13
0.012	1.137	1.07
0.018	1.007	1.00
0.021	0.935	0.98
0.03	0.761	0.79
0.055	0.639	0.64
0.113	0.549	0.536
0.168	0.506	0.493

and for the dielectric constant ϵ the value for undoped BaF_2 at 300 K was taken, i.e. 7.36 [26]. It has been shown by Wapenaar and Schoonman [27] that ϵ increases considerably in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions with increasing dopant content. For $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions the dependence of ϵ on x is yet unknown. Therefore a similar concentration dependence of ϵ is assumed as in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, in order to get accurate $\Delta H_{\sigma, \text{TSDC}}$ values from eq. (3).

One aspect of the space-charge depolarization has so far remained undiscussed. From the size of the space-charge depolarization peak it is apparent that upon polarizing the sample, a considerable number of unbound fluoride interstitials migrate through the lattice in the direction of the positive electrode. An effective internal electric field will be generated by this migration. If this electric field due to fluoride ion interstitial migration is generated, the effective polarizing field strength E_p will be diminished. The value of E_p is incorporated in eq. (2) which describes the depolarization current of dipoles and clusters. Therefore the peak size of cluster and dipole reorientation peaks can be influenced by a space-charge polarization.

We observed, however, no change in peak size when a sample is polarized at a temperature above, or directly below the space-charge depolarization peak. It has been stated above, that an increase of the polarizing field E_p did not influence peak sizes either. Our conclusion is, therefore, that the internally generated electric field is small compared to E_p , and that $E_p - E_{\text{induced}}$ is large enough to achieve an almost complete

polarization of both dipoles and clusters in the studied samples.

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