NEUTRON DIFFRACTION AND TSDC ON $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ SOLID ELECTROLYTES

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The defect structure of fluorite-type $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions, which exhibit fast fluoride ion conductivity, has been investigated by quasi-elastic diffuse neutron scattering (QDNS) experiments, and thermally stimulated depolarisation current (TSDC) measurements. A comparison with model calculations reveals (212) clusters to dominate the defect structure. From 10 to 400K TSDC spectra reveal for $x < 0.05$ six relaxation peaks of dipolar nature, along with the relaxation of macroscopic space charge. Conductivity parameters calculated from the latter relaxation compare very well with those obtained from a.c. ionic conductivity studies. The low-temperature relaxation at 29.5 K is ascribed to depolarisation steps of (212) clusters. Evidence for the relaxation of a minor amount of $(\text{U}_{\text{Ba}_i}\text{F}_i)^x$ dipoles is found. A direct indication of the freedom of orientation of a (212) cluster is obtained from an initial QDNS-study on a polarised crystal.

1. INTRODUCTION

The alkaline earth fluorides have the remarkable property that large concentrations of trivalent rare-earth dopants, tetravalent UF_4 , or ThF_4 dopants can be accommodated within their structure without loss of structural integrity. The defect structure of these types of solid solutions is dominated by defect association effects, and extended defect clustering. Ion size effects play an important role.

Despite defect clustering, the concentrated solid solutions reveal an exponential increase of the isothermal ionic conductivity, which has been

attributed to fast conduction of a small number of fluoride interstitials (1,2).

Since the pioneering work of Cheetham et al. (3), and Catlow (4) many groups have studied defect clustering, and related bound ionic motion in rare-earth doped alkaline earth fluorides. Kjems et al (5), Andersen et al. (6), and Ouwerkerk et al. (7) have studied $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ with quasi-elastic diffuse neutron scattering (QDNS) experiments.

Concentrated $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals show strong anisotropic diffuse scattering which has quantitatively been explained in terms of defect clusters of the

(222)-type (Figure 1). Below 400°C ordering of up to four (222) clusters occurs (5,6).

Figure 1. A (222) cluster in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+2x}$ solid solutions.

The $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions reveal the presence of a (212) cluster (Figure 2) (6,7) without cluster-cluster correlations.

Figure 2. A (212) cluster in $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions.

A detailed study of the defect cluster relaxations by thermal depolarization, and a.c. dielectric loss experiments requires experimental temperatures well below liquid-nitrogen temperature (7,8). Because cations are virtually immobile in the fluorite lattice a (212) cluster has more freedom of

orientation than a (222) cluster, and this is the main topic of the present paper. In addition to QDNS- and thermally stimulated depolarisation current (TSDC) experiments QDNS-studies have been initiated at low-temperatures and high electric fields in order to study the defect structure of a polarised $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.10}$ crystal.

2. EXPERIMENTAL ASPECTS

Neutron scattering and TSDC experiments were performed on single crystals of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ with $7.7 \times 10^{-5} \leq x \leq 0.168$, grown by a modified Bridgman-Stockbarger technique (10). Single crystalline slabs with a surface area of about $5 \times 10^{-5} \text{ m}^2$, and a thickness of typically $1 \times 10^{-3} \text{ m}$, were inserted in a specially designed helium cryostat (11). Complete blocking of electrical current was achieved with sapphire disks.

The samples were polarised in an electric field of $3.0 \times 10^5 \text{ V/m}$. A heating rate of 0.03472 K/s was used. Details will be published elsewhere. Relaxation parameters were obtained by computer fitting the TSDC spectra to theoretical current equations.

QDNS-studies on $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ were performed on triple axes spectrometers at the DR3 reactor at Risø National Laboratory. A scan was made of the (X00)/(OYY) plane, and the result was compared with computed scattering patterns of various types of cluster arrangements. Further details have been reported elsewhere (5-7). Low temperature QDNS-studies of polarised $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.1}$ were performed in a helium flow cryostat (Thor-cryogenics).

The crystal with a length of 1.5×10^{-2} m was polarised in a d.c. electric field of 4.0×10^5 V/m at 130K, and subsequently cooled to about 5K.

3. RESULTS AND DISCUSSION

QDNS-measurements have been performed for $x = 0.02$, 0.05 , and 0.154 . The solid solutions show strong anisotropic diffuse scattering between Bragg peaks at room temperature. The scattering was elastic within the experimental resolution of 0.8 meV. The results for the (X00)/(0YY) scattering plane of the sample with $x = 0.05$ are displayed as contour plots in Figure 3.

Figure 3. Contour map of the quasi-elastic diffuse scattering for $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.1}$ at room temperature. Intensities are on an arbitrary scale.

Similar patterns were obtained for the other solid solutions, and the intensity distributions of the scattering measurements compare very well with the results reported by Andersen et al. (6). Improvement of cluster model calculations as published by Andersen (6) has been obtained by moving relaxed fluoride interstitials away from the body diagonal, and fluoride interstitials away from the (110) diagonal. Detailed defect

coordinates of (212) clusters in $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ are presented in Table I.

TABLE I

DEFECT COORDINATES OF (212) CLUSTERS IN $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$. COORDINATES ARE IN UNIT CELL UNITS RELATIVE TO THE CENTER OF THE CLUSTER.

ION	POSITIONS (X,Y,Z)		
$\text{U}_{\text{Ba}}^{**}$	0.25	0.25	0
F'_i	0.17	-0.22	0
F'_i	-0.22	0.17	0
V_F^*	0	0	0.25
V_F^*	0	0	-0.25
F'_i	0.15	0.15	0.34
F'_i	0.15	0.15	-0.34

TSDC spectra of two different $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions are presented in Figure 4. The most prominent feature is a relaxation peak at 29.5K, which is present in both

Figure 4. TSDC spectra of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ solid solutions.

dilute and concentrated solid solutions. The depolarisation current peak depends on the relaxation parameters E (reorientation energy), τ_0 (inverse of the characteristic jump frequency factor), N_D (number of dipoles per m^3), and μ (dipole moment). When a sample is polarised at a temperature T_p , and a linear heating rate b is maintained the current density is given by Eq. (1) (11),

$$J(T) = \frac{N_D \mu^2 E_p}{3kT_p \tau_0} \exp\left(\frac{-E}{kT}\right) \exp\left[-\frac{1}{b\tau_0} \int_0^T \exp\left(\frac{-E}{kT'}\right) dT'\right] \quad (1)$$

where E_p is the polarisation field, and k the Boltzmann constant. This equation has been used to fit the TSDC spectra. A reasonable fit is obtained only for the lowest dopant level ($x = 7.7 \times 10^{-5}$). At higher values peak broadening occurs. A refined approximation to the TSDC equation, taking into account peak broadening by assuming a Gaussian distribution of width σ is given by Eq. (2) (12).

$$J(T) = \frac{N_D \mu^2 E_p}{3kT_p \tau_0} \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right) \exp\left(\frac{-E}{kT}\right) \times \exp\left[-\frac{1}{b\tau_0} \int_0^T \exp\left(\frac{-E}{kT'}\right) dT'\right] dE \quad (2)$$

Figure 5 presents computed results.

Figure 5. Results of computer fitting a TSDC peak of $Ba_{0.97}U_{0.03}F_{2.06}$ to Eq. (1) (a), and to Eq. (2) (b).

Relaxation parameters are $E = 0.0896$ eV, $\sigma = 0.0047$ eV, $\tau_0 = 8.0 \times 10^{-14}$ s, $t_{\max} = 29.7$ K, and

$$(N_D \mu^2 E_p / (3kT_p)) = 4.88 \times 10^{-12}. \text{ All spectra could be analysed using Eq. 2.}$$

The relaxation peak at 29.5K, which occurs in the TSDC spectrum of all solid solutions $7.7 \times 10^{-5} < x < 0.168$, is ascribed to a (212) cluster. Because this cluster contains only one dopant ion it is formed whenever a $(U_{Ba} \cdot 2F_i)^*$ associate is formed. An important factor to note for the interpretation of the TSDC spectra is the immobility of the dopant cations in the fluorite lattice. A (212) cluster, therefore, will have more freedom of orientation than a (222) cluster. In a (212) cluster the two fluoride interstitials can connect a U^{4+} ion with a Ba^{2+} ion in twelve different directions. All directions yield equivalent (212) clusters. On the contrary a (222) cluster is fixed in one position because of the connected La^{3+} ions. Only the relaxed ions above and below the plane of the cluster have the ability to reorient.

In $Ba_{1-x}U_xF_{2+2x}$ a reorientation process, dependent on the direction of the polarising field is proposed. The single crystalline slabs used in the TSDC measurements are cleaved along the (111) plane. Hence a polarising field along the $(\bar{1}\bar{1}\bar{1})$ direction can be used. A polarised state of a (212) cluster with a dipole moment opposing the electric field will, therefore, be the most favourable configuration. For instance, a trimer with a dipole moment in the (111) direction can be formed in a single step from (212) clusters with a dipole moment in the (110), (101),

and (011) direction. To polarise a (212) cluster with its dipole moment in the (0 $\bar{1}\bar{1}$) direction to a trimer with its dipole moment in the (111) direction takes three steps: (212)(0 $\bar{1}\bar{1}$) $\xrightarrow{a}$ (212)(10 $\bar{1}$) $\xrightarrow{b}$ (212)(110) $\xrightarrow{c}$ (trimer)(111). The depolarisation steps are shown in Figure 6. The trimer comprises a U^{4+} ion, three fluoride

Figure 6. Reorientation steps: trimer (111) $\rightarrow$ (212)(110) $\rightarrow$ (212)(10 $\bar{1}$) $\rightarrow$ (212)(0 $\bar{1}\bar{1}$)

interstitials, and one fluoride ion vacancy, i.e. only one relaxed fluoride lattice ion, and has recently been proposed to occur in $Ca_{1-x}U_xF_{2+2x}$ (13). It is assumed that steps a and b, i.e. (212) cluster reorientations cause the peak at 29.5K. In order to obtain evidence for the present model, a low-temperature QDNS-study of a polarised $Ba_{0.95}U_{0.05}F_{2.10}$ crystal has been performed.

The scattering patterns are not identical, and are also different from

the unpolarised crystal (7).

While the precise computer modeling is not yet available, it is tempting to correlate the significant changes in the scattering patterns to the (212) cluster- and (212) $\rightarrow$ trimer reorientations described above.

The TSDC spectra reveal six small relaxation peaks in addition to the large peak at 29.5K. It was reported that during crystal growth reduction of a minor fraction of U^{4+} to U^{3+} is likely to occur (9). With trivalent uranium nn- and nnn-associates $(U_{Ba}F_i)^x$ are formed. The depolarisation energies of the peaks at 119K (0.379 eV), and 155K (0.508 eV) were found to be concordant with data reported by Murin and Glumov (14) for nn- and nnn-associates in $Ba_{1-x}U_xF_{2+2x}$ solid solutions. Since they are U^{4+} concentration independent, the other small peaks are to be related with residual impurities, the nature of which has yet to be established.

The space charge relaxation has been studied as a function of x . The variation of T_{max} with x is very similar to the variation of the ionic conductivity activation enthalpy ΔH_0 with x . The relaxation of macroscopic space charge is related to the ionic conductivity via Eq. (3) (15).

$$\frac{\Delta H_0}{kT_{max}} = \frac{\sigma_0}{b\epsilon\epsilon_0} \exp\left(-\frac{\Delta H_0}{kT_{max}}\right) + 1 \quad (3)$$

where σ_0 represents the pre-exponential factor in the Arrhenius equation for the ionic conductivity, ϵ_0 the permittivity of free space, and ϵ the dielectric constant. Eq. (3) has been used to calculate enthalpy data

($\Delta H_{\sigma, \text{TSDC}}$) from T_{max} data at low temperatures. These enthalpy data compare very well with ΔH_{σ} data from a.c. ionic conductivity at high temperatures (16). The results are presented in Figure 7.

Figure 7. The $\Delta H_{\sigma, \text{TSDC}}$, as calculated from TSDC data compared with $\Delta H_{\sigma, \text{cond}}$ from ionic conductivity measurements.

The agreement is very satisfactory, indicating that the relaxation of macroscopic space charge, and ionic conductivity are governed by the same mechanism, for which the Enhanced Ionic Motion model has been developed (1).

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