

# TSDC AND NEUTRON SCATTERING 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

M. OUWERKERK, F.F. VELDKAMP, N.H. ANDERSEN\* and J. SCHOONMAN\*\*

Solid State Department, Physics Laboratory, Utrecht University,  
P.O. Box 80.000, 3508 TA Utrecht, The Netherlands.

\* Physics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark.

\*\* Present address: Laboratory of Inorganic and Physical Chemistry,  
Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands.

A study was made of the dynamical behaviour of bound interstitial fluoride ions in disordered  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  and  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions with Thermally Stimulated Depolarisation Current measurements and neutron scattering measurements, and a combination of both techniques. From 10 K to 400 K the TSDC spectra showed four reorientation peaks to be present in  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ , and six in  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ , along with the relaxation of the macroscopic space charge. The position of a space charge peak shifted to lower temperatures with increasing solute content. The dipolar realaxations were concentration invariant. In  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  neutral associates, L-shaped- and (222)-clusters occur. The present study reveals (212)-clusters to be present in  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ . The relations between ion dynamics and defect structures are discussed.

## INTRODUCTION

The alkaline-earth fluorides with the fluorite structure (i.e.  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$ ) show a remarkable increase in ionic conductivity upon doping with  $\text{LaF}_3$  (1) and  $\text{UF}_4$  (2).

In order to obtain a better understanding of the  $\text{UF}_4$ -concentration dependence of the ionic conductivity, a study was made of the defect structure of  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions with  $7.7 \times 10^{-5} \leq x \leq 0.169$ . Especially the arrangement of the excess interstitial fluoride ions around the  $\text{U}^{4+}$  dopant ions, the local distortions of the fluorite lattice, and the dynamical behaviour of the bound interstitials are the main subjects of this investigation. In addition it is shown that defect cluster relaxations in  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  and  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions show up in the TSDC spectra well below liquid

nitrogen temperature. Due to lattice distortions around dopant ions, the migrational enthalpy of the conducting interstitial fluoride ions is lowered considerably, causing fast relaxations, and an exponential increase of the ionic conductivity of this type of fluorite solid solutions.

Use was made of three methods of investigation: Thermally Stimulated Depolarisation Current measurements (TSDC), neutron scattering, and a novel technique, comprising a combination of both TSDC and neutron scattering.

The defect structure of alkaline-earth fluorides doped with trivalent rare earth fluorides has been the subject of many investigations (refs. 3-6). This paper presents the first attempt to characterise the defect structure of  $\text{BaF}_2$  containing the tetravalent dopant  $\text{U}^{4+}$ , as well as cluster relaxations below 77 K.

## EXPERIMENTAL ASPECTS

The growth of the  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  (1) and  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  (7) crystals has been reported before.

Single crystals, approximately  $1.0 \times 10^{-3}\text{m}$  thick, and  $1.0 \times 10^{-2}\text{m}$  in diameter, cleft along the (111) plane, were polarised in a dc electrical field of  $3.0 \times 10^5\text{V/m}$ , and subsequently cooled to 10 K. At this temperature the field was switched off, and a Cary 401 electrometer was shunted into the circuit. When the dielectric current had stabilised below  $10^{-15}\text{A}$ , the temperature was increased linearly. This increase caused depolarisation currents to flow, which were dependent on the depolarisation energy. With the TSDC technique it is, therefore, possible to determine the depolarisation energies for the different types of dipoles in the solid solution.

Neutron scattering measurements were carried out with the TAS6 triple axis spectrometer at the Risø National Laboratory in Denmark. With this technique it is possible to measure diffuse scattering in the regions between the Bragg peaks, which is caused by the presence of defect clusters in the crystal. Single crystals of  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions with  $x = 0.02, 0.05$  and  $0.154$  of irregular shape, and with a volume between  $3.0 \times 10^{-7}\text{m}^3$  and  $3.0 \times 10^{-6}\text{m}^3$  were used. A scan was made of the (X00/OYY) plane, and the result was compared with computer calculated scattering patterns of various types of cluster arrangements. These measurements were carried out at room temperature.

At liquid helium temperature we scanned the (X00/OYY) plane of a  $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.10}$  crystal, which was cleft along the (111) plane, and polarised in an electrical field of  $4.0 \times 10^5\text{V/m}$  at 120 K, and subsequently cooled to 4.2 K. By studying a crystal under these conditions it is possible to determine the structure of polarised defect clusters, and estimate the extent of the polarisation.

## RESULTS

The results of the TSDC measurements for two different solid solutions of  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  and  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  are shown in Figures 1 and 2 respectively. The large high-temperature space-

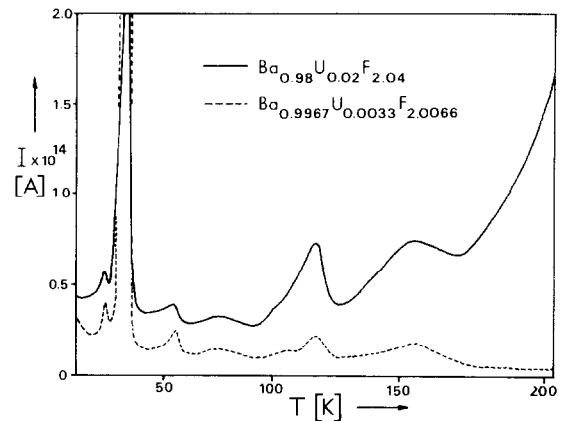


Figure 1 : TSDC spectra of  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions with  $x = 0.0033$ , and  $0.02$ .

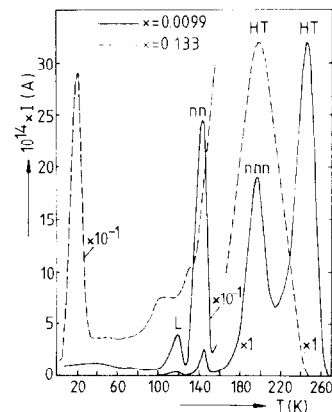


Figure 2 : TSDC spectra of  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  solid solutions with  $x = 0.0099$ , and  $0.133$ .

charge peak in these solid solutions is due to diffusion of free charge carriers. The maximum temperature of this peak decreases with dopant concentration (viz. Figure 3). In as much as the relaxation peaks are not masked by the space-charge peak they have been found for every dopant concentration; this is shown in Figure 4.

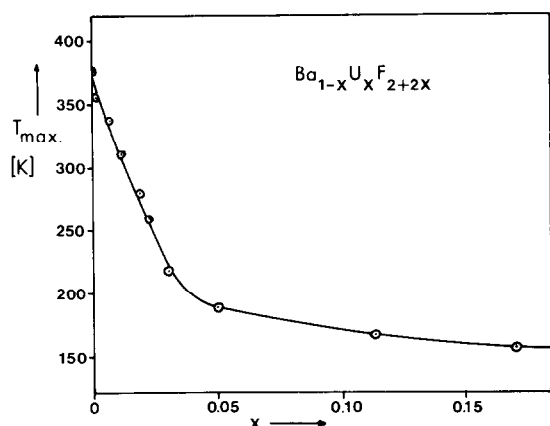


Figure 3 : The maximum temperature of the space-charge peak vs.  $x$  for  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ .

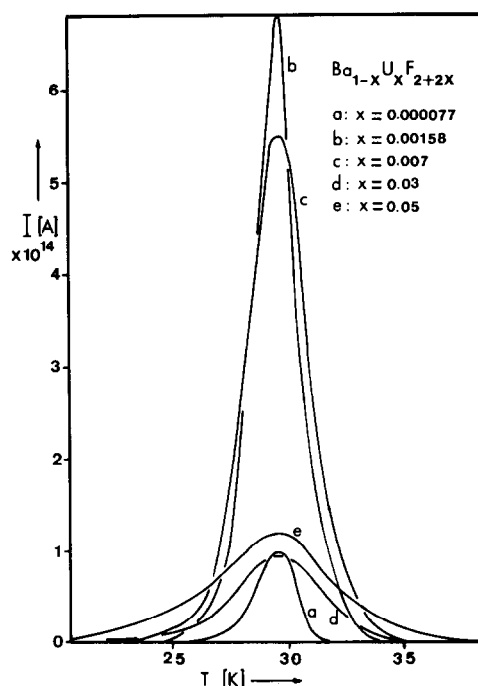


Figure 4 : The dipole reorientation peak at 29.5 K for different dopant concentrations.

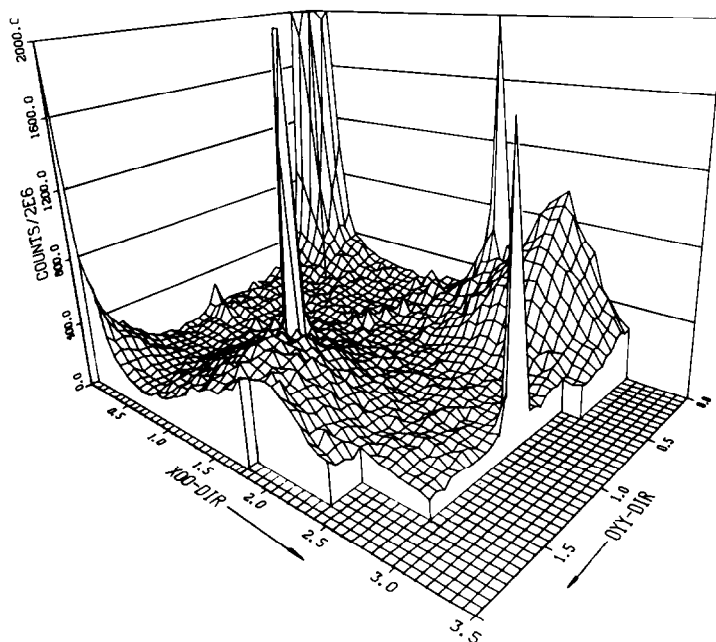


Figure 5 : A diffuse neutron scattering scan of the (X00/OYY) plane for  $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.10}$ .

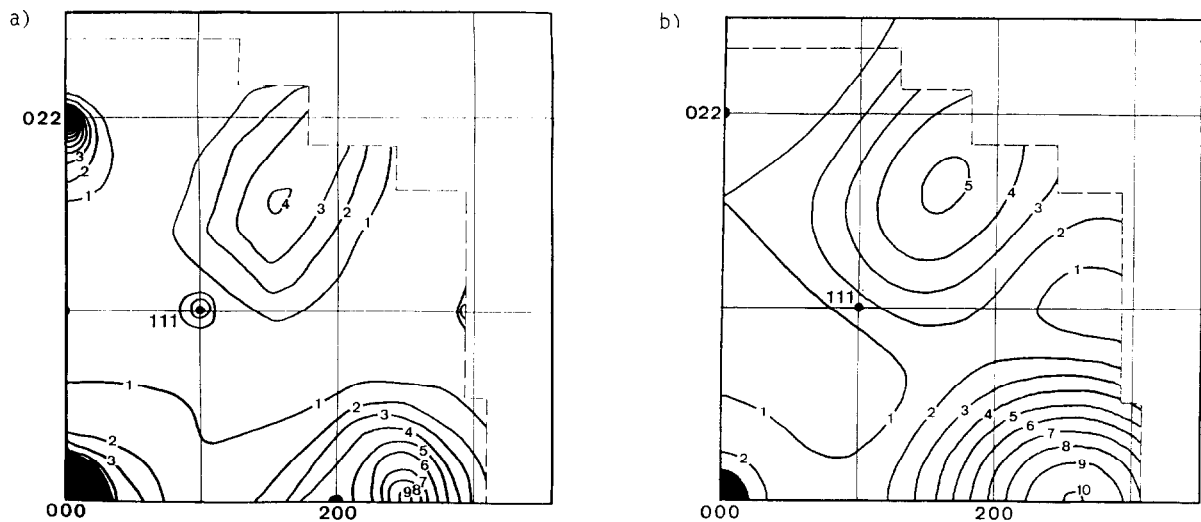


Figure 6 : A contour mapping of a neutron scattering scan of the (X00/0YY) plane of  $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.10}$  a) compared with a computer calculated pattern of a (212)-cluster b).

The result of a scan of the (X00/0YY) plane of  $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.10}$  is depicted in Figure 5. A contour mapping of this result is figured along with a computer calculated contour mapping of a (212)-cluster in Figure 6. The structure of a (212)-cluster is shown in Figure 7. The results for the  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions with  $x = 0.02$  and  $0.154$  are similar to the result for  $x = 0.05$ .

The results for the polarised crystal neutron scattering measurements performed at liquid helium temperature at two different polarisation directions ( $\bar{1}\bar{1}\bar{1}$  and  $1\bar{1}\bar{1}$ ) are shown in Figure 8.

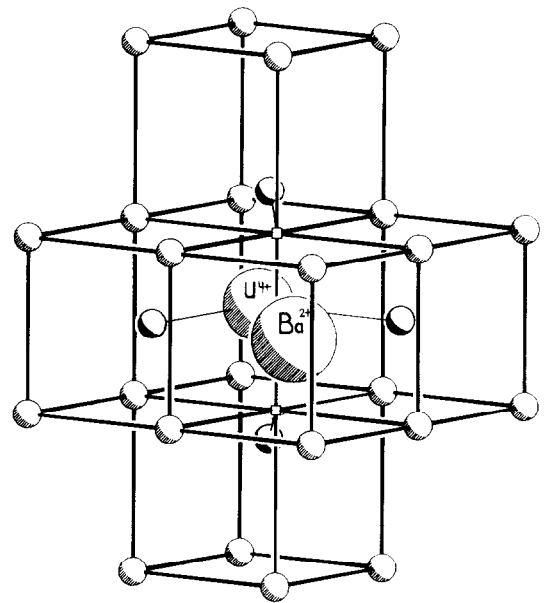


Figure 7 : A (212)-cluster in  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions.

and contain two  $\text{La}^{3+}$  ions instead of one  $\text{U}^{4+}$  ion.

The neutron scattering patterns with  $x = 0.02$ ,  $0.05$  and  $0.154$  give basically the same picture in the (X00/0YY) plane. The experimental results

## DISCUSSION

The defect structure of  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  solid solutions has been determined before. The dilute solid solutions contain simple nn and nnn  $(\text{La}_{\text{Ba}}^+\text{F}_i^-)^x$  dipoles. With increasing concentration a L-shaped  $(\text{La}_{\text{Ba}}^+2\text{F}_i^-)'$  cluster is formed. The relaxations related to these dipoles have been well documented in the literature (8). For dopant concentrations above  $x = 0.05$  the presence of (222)-clusters has been reported (6). These clusters are similar to (212)-clusters,

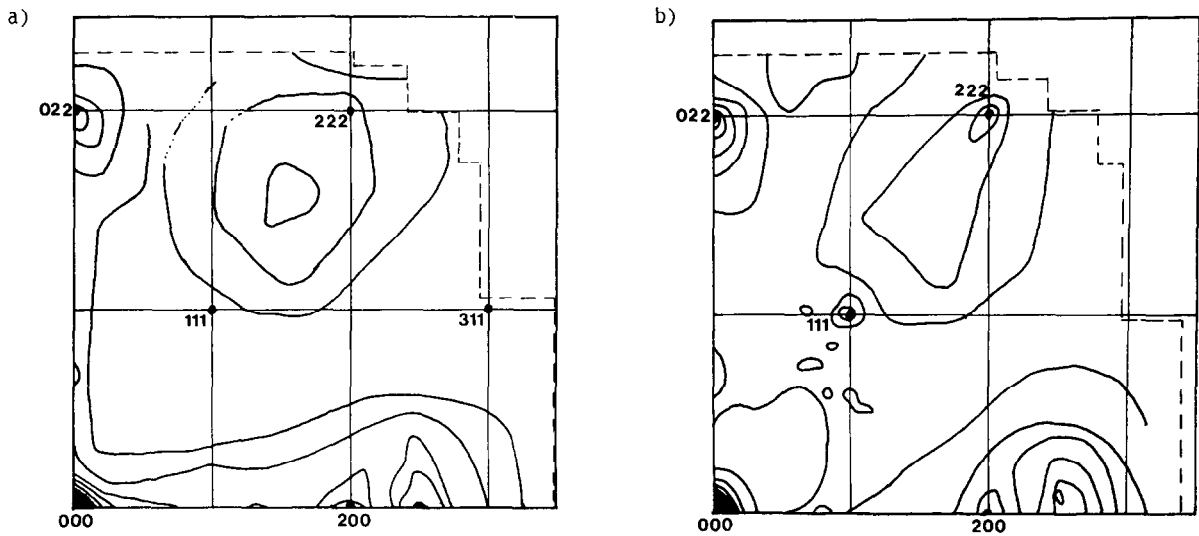


Figure 8 : Contour mappings of neutron scattering scans of the (X00/0YY) plane of a  $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.10}$  crystal, polarised in the (111) a) and the (111) b) direction.

can be fitted reasonably with a computer calculated scattering pattern of a (212)-cluster. An earlier attempt to fit the neutron scattering data of  $\text{Ba}_{0.846}\text{U}_{0.154}\text{F}_{2.308}$  with a (212)-cluster has been published before (9).

For  $\text{Ba}_{0.867}\text{La}_{0.133}\text{F}_{2.133}$  a low temperature TSDC run reveals a reorientation peak at 21 K, which shows a strong resemblance to the reorientation peak at 29.5 K for the  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions (viz. figure 4). Both peaks can be ascribed to a displacement of the relaxed fluoride ions above and below the plane of the (222)- and (212)-clusters.

An important factor to note for the interpretation of the TSDC results is the immobility of the dopant cations in the fluorite lattice. It is because of this that a (212)-cluster has much more freedom of orientation than a (222)-cluster. In a (212)-cluster the two fluoride ion interstitials can "connect" a  $\text{U}^{4+}$  ion with a  $\text{Ba}^{2+}$  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  $\text{La}^{3+}$  ions. Only the relaxed fluoride ions above and below the plane of the

cluster have the ability to reorient. This explains the large number of (212)-cluster reorientation peaks in  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  compared to only one (222)-cluster relaxation peak in  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ .

For  $\text{Ca}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions the presence of a different type of defect cluster has recently been predicted (10). This defect cluster, comprising a  $\text{U}^{4+}$  ion, three fluoride ion interstitials, and one fluoride ion vacancy is called a trimer (viz. Figure 9).

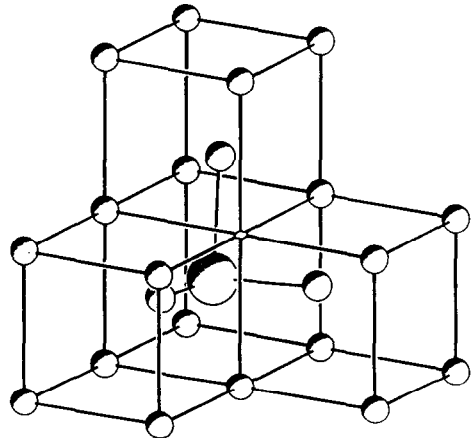


Figure 9 : a trimer in  $\text{Ca}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions.

The dipole moment of this cluster lies along the (111) direction, giving rise to the possibility that a  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  crystal containing (212)-clusters, and polarised along the (111) direction, will contain trimers pointing in the same direction, i.e. with their dipole moments opposing the electrical field direction.

In order to investigate this possibility the neutron scattering pattern in the (X00/OYY) plane was determined after polarising a  $\text{Ba}_{0.95}\text{U}_{0.05}\text{F}_{2.10}$  crystal, and cooling down to liquid helium temperature. As the results of this experiment show it was not yet possible to measure the scattering pattern in the precise direction of the electrical field. Before polarisation there are eight equivalent (111) directions. After polarisation this is no longer true. Neutron scattering patterns were recorded in the (X00/OYY) plane (containing the (111) Bragg peak), when the crystal was polarised in the  $(\bar{1}\bar{1}\bar{1})$  and  $(1\bar{1}\bar{1})$  direction. These patterns are both not equivalent to one another, and to the unpolarised scattering pattern. It is, however, clear that at the electrical field strengths used for the TSDC measurements significant changes occur in the defect structure of  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions.

More detailed measurements at different polarisation directions and electrical field strengths are needed to obtain a complete picture of the nature and extent of these changes.

## CONCLUSIONS

Both TSDC, and neutron scattering results show that the (212)-cluster is the dominant type of defect cluster in  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  solid solutions in the entire concentration range studied here ( $7.7 \times 10^{-5} \leq x \leq 0.169$ ).

To observe defect cluster relaxations in

$\text{Ba}_{1-x}\text{La}_x\text{F}_{2+2x}$  and  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  TSDC spectra need to be recorded well below liquid nitrogen temperature.

Evidence is found for a significant polarisation effect of the defect clusters when polarised in an electrical field of the same strength as used for the TSDC measurements.

More detailed studies of the scattering patterns of polarised  $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$  crystals are necessary to determine the structure of polarised defect clusters.

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