

Ionic thermocurrents and ionic conductivity of solid solutions of SrF₂ and YbF₃

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Ionic thermocurrents and ionic conductivity of solid solutions of SrF_2 and YbF_3

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We report dielectric [ionic thermocurrent (ITC)] experiments and ionic conductivity of cubic solid solutions of the type $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$. These combined experiments provide us with new information concerning the ionic conductivity mechanisms which play an important role in solid solutions $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$ (R is a trivalent rare-earth ion). From the results it will be concluded that the depolarization peak, which is associated with space charges in a polarized sample, can be connected with bulk ionic conductivity. An interesting feature of the ITC results and the ionic conductivity data is that there are major fluctuations of the dielectric properties and the ionic conductivity as a function of the concentration of Yb^{3+} impurities. These fluctuations are ascribed to clustering of Yb^{3+} impurities. Fluctuations of this type have not been observed in earlier investigations, where solid solutions $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$ were treated. It appears that clustering is important for R^{3+} ions of the final part of the series of lanthanide ions. For R^{3+} ions of the first part of the series of lanthanide ions clustering turns out to be unimportant.

I. INTRODUCTION

Recently, we have studied the dielectric properties of some solid solutions of the type $A_{1-x}\text{R}_x\text{F}_{2+x}$ (where A is an alkaline-earth ion and R is a rare-earth ion).¹⁻³ Apart from the dipole reorientation, we have paid attention to the dielectric properties of space charges which one can produce in these materials. Until now we have limited ourselves to solid solutions in which clustering at an extensive scale has not been proved to occur. These solid solutions are, for example, $\text{SrF}_2:\text{LaF}_3$, $\text{SrF}_2:\text{CeF}_3$, and $\text{SrF}_2:\text{NdF}_3$, but probably also the solid solutions $\text{BaF}_2:\text{LaF}_3$ do not show extensive clustering either. The latter system was studied in detail by den Hartog and Langevoort¹ and den Hartog, Pen, and Meuldijk.⁴ From the results obtained for the above mentioned solid solutions we were able to draw important conclusions concerning the charge transport processes in heavily doped materials. Especially, in $\text{BaF}_2:\text{LaF}_3$ we have obtained clear evidence for a percolation-type conduction process in which interstitial fluoride ions of dipolar complexes are involved.¹

In the present paper we report on dielectric relaxation experiments and ionic conductivity of solid solutions of SrF_2 and YbF_3 . The concentration x of the Yb ions was varied between 0 and 0.30. Although the maximum concentration is such that approximately one-third of the Sr sites is occupied by a trivalent impurity and in addition one-third of the

empty cubes of fluoride ions is occupied by an interstitial fluoride ion, the crystal structure of these materials is the same as that of undoped SrF_2 . Furthermore, the lattice parameter only shows slight deviations from that of pure SrF_2 . Similar observations have been made for many of the other possible solid solutions of $A\text{F}_2$ and RF_3 .^{2,4-7} Despite this similarity of the various solid solutions, it turned out during this investigation that there are significant differences between the individual materials. The system $\text{SrF}_2:\text{YbF}_3$ is completely different from the solid solutions $\text{SrF}_2:\text{LaF}_3$. In the latter, materials clustering is relatively unimportant whereas in the system $\text{SrF}_2:\text{YbF}_3$ clustering is the dominant phenomenon, which has major implications for the dielectric relaxation processes and the ionic conductivity, as will be discussed later.

The above mentioned solid solutions can be considered to be the extremes; in the system $\text{SrF}_2:\text{LaF}_3$ simple dipolar defects are present up to relatively large La^{3+} concentrations. In $\text{SrF}_2:\text{YbF}_3$ solid solutions clustering already takes place at concentrations of the order 10^{-2} – 10^{-1} mol %. In Fig. 1 we have shown schematically the two types of dipolar defects that may occur in cubic solid solutions $A_{1-x}\text{R}_x\text{F}_{2+x}$. The most important coagulates discussed in the literature.⁸⁻¹⁰ We should add, however, that apart from these clusters more and different types have been proposed.¹¹ On the other hand, we know from detailed experimental investigations carried out by Tallant, Wright, and Moore¹² and Moore and Wright¹³ that in those crystals where clustering

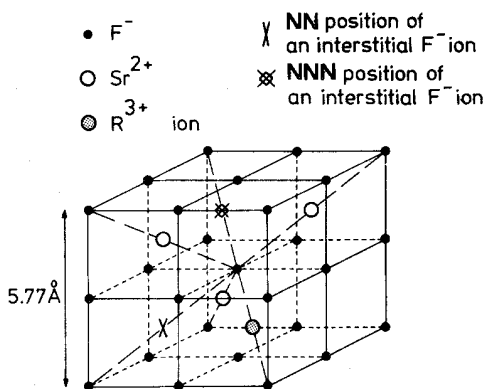


FIG. 1. Three-dimensional schematic representation of an SrF_2 crystal showing the structure of a tetragonal (NN) and a trigonal (NNN) $\text{R}^{3+}\text{-F}_i^-$ complex.

has been observed there are many different clusters. If a similar situation is found in $\text{SrF}_2\text{:YbF}_3$ it will probably be quite difficult to explain the dielectric relaxation and ionic conductivity results in a straightforward and quantitative way. The problems with the materials studied in this paper will be even more complicated than with the crystals investigated in Refs. 12 and 13 because we have crystals with Yb concentrations up to 30 mol %, whereas the crystals studied in Refs. 12 and 13 had 0–1 mol % trivalent impurities. From this it will be clear that it is possible to draw only qualitative conclusions for the concentrated materials.

We have shown in earlier papers that the ITC (ionic thermocurrents) method is a very useful technique for the investigation of dipolar relaxations and space-charge relaxations.^{1–3} In this paper we will demonstrate that combined investigations with ITC and ionic conductivity are very powerful (see also Refs. 14 and 15), and allow us, even for very complicated systems such as $\text{SrF}_2\text{:YbF}_3$, to draw conclusions concerning the mechanisms of charge transport in these crystals.

In this paper we shall employ our, recently developed, two-jump model for the dc conductivity^{1–3} in heavily doped fluorite-type crystals. We have proposed that the conduction is governed by jumps of interstitial fluoride ions, which are present in large concentrations in the systems $\text{AF}_2\text{:RF}_3$. These interstitial fluoride ions may jump from one “free” interstitial position to another free interstitial position. These jumps are referred to as free jumps. A free interstitial does not have a trivalent impurity at a nearest-neighbor (NN) or next-nearest-neighbor (NNN) substitutional lattice position. The alterna-

tive jumps contributing to the ionic conductivity are the dipolelike jumps. For these jumps at least one of the two situations—the interstitial position before the jump or the final one after the jump—corresponds with a NN or NNN dipole. The consequences of the occurrence of the two competing jump mechanisms will be discussed briefly and special attention is paid to the effect of the concentrations of dipolar defects on the conductivity of the solid solutions. In addition, the effects of clustering will complicate the results of the ITC and ionic conductivity experiments. First, there is a reduction of the number of dipolar defects due to clustering, which leads to a decrease of the number of dipolelike jumps, and second, the presence of clusters may influence the ionic conductivity because these defects are capable of trapping interstitial fluoride ions. Because for very high YbF_3 concentrations clusters probably play an important role, we define a third type of jump. This is the jump within a cluster. It is quite probable that different types of clusters exist in concentrated solid solutions $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$; consequently, there are different types of jumps within clusters. A remarkable correspondence between the behavior of the ionic conductivity in a wide range of temperatures and YbF_3 concentrations with that of the space-charge relaxation peak, observed with the ITC method, will be discussed.

II. EXPERIMENTAL PROCEDURES

The crystals investigated in this paper have been prepared in the crystal-growth facility of the Solid State Physics Laboratory in Groningen. The crystal-growth machine consists of a 25-kW high-frequency generator operating at 800 kHz and a high-vacuum vessel. The crystals were grown in highly pure carbon crucibles with an inner diameter of 8 mm and a length of 60 mm. In the setup we are able to prepare seven crystals simultaneously. The advantage of this method is that the crystals are grown under the same conditions (temperatures, atmosphere, etc.).

The starting materials are SrF_2 (Merck, “suprapur”) and YbF_3 (Ventron, 99.9% purity). In order to get rid of eventual OH^- or O^{2-} impurities we added a few mol % PbF_2 . The oxygen impurities leave the melt at high temperatures as PbO , which has a rather low boiling temperature as compared to those of SrF_2 and YbF_3 . The crystals are grown with the Bridgman method at a rate between 3 and 6 mm/h. The resulting materials are clear and crack free. After growth the crystals were cooled down to room temperature in 8 h.

The concentration of the Yb impurities in the

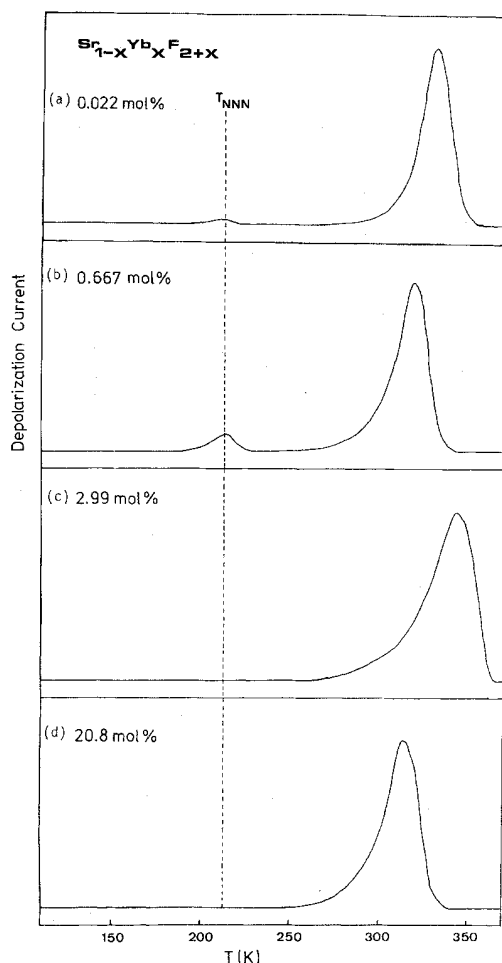


FIG. 2. Survey of the most characteristic ITC results obtained for the series of solid solutions $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$. The crystals were all polarized with an electric field of approximately 2000 V/mm; the polarization temperature was in all cases chosen well above the high-temperature (HT) band.

samples have been determined with x-ray fluorescence. This technique provides us with reliable concentrations for $x \geq 0.01$. For the concentrations lower than 0.01 we have taken the nominal values.

Cylindrical disks were cut from the as-grown crystals with a slide wire saw. The thickness of the samples was 2.0 mm; the samples were polished and the cylindrical part of the surface was cleaned by grinding it with emery paper in order to avoid short circuits caused by carbon particles from the crucible material. The samples prepared in this way were used for both ITC and ionic conductivity experiments. Preliminary conductivity results on $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$ have been reported by Schoonman

and den Hartog.¹⁶

Before the ITC experiment the sample was polarized at a temperature well above that of the depolarization peak associated with space charges. Between the electrodes and the sample a thin teflon foil was mounted to avoid ohmic contacts. A more detailed description of our ITC setup was given in our previous papers.^{1,2} For details of the conductivity measurements we refer to Wapenaar *et al.*¹⁷

III. EXPERIMENTAL RESULTS

SrF_2 crystals doped with very small concentrations Yb^{3+} ions contain predominantly NNN type $\text{Yb}^{3+}\text{-F}_i^-$ complexes. In an ITC experiment these dipolar complexes give rise to a dipole reorientation band, which is (for a heating rate $b=0.03$ K/sec) located at 210 K. In addition, we find a very strong peak at a temperature of about 330 K, which should be related with the space charges that are formed opposite to the electrodes. During depolarization the space charges diminish as a result of the mobility of the free interstitial F^- ions.

The space-charge relaxation peak shows interesting features in the concentration range $0 < x < 0.30$. In the concentration range $0 < x < 0.003$ this peak shifts to lower temperatures with increasing Yb^{3+} concentration. In the concentration range $0.003 < x < 0.05$ the space-charge relaxation peak shifts to higher temperatures and reaches values for T_{max} , which are about 15 K higher than those for very heavily doped materials. For concentrations higher than 5 mol% T_{max} decreases until for 30 mol% a value for $T_{\text{max}} \approx 315\text{--}316$ K is reached.

A survey with some characteristic results on the system $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$ has been given in Fig. 2. The variation of T_{max} for the space-charge relaxation peak is shown very clearly just as the stable position of the dipole reorientation peak at about 210 K. In Fig. 3 we have given all the data obtained for T_{max} of the space-charge relaxation peak as a function of $\log_{10} x$, and the maximum and minimum of the T_{max} value are observed very clearly.

Another parameter that gives important information about the space-charge relaxation is the width of the corresponding depolarization band as a function of the concentration. Recently, we have shown that it is possible with this information to distinguish between a one-jump mechanism (with varying activation energy E) and a two-jump mechanism. The two-jump mechanism has been described by den Hartog and Langevoort¹ and Meuldijk, Mulder, and den Hartog¹⁸; for the two-jump mechanism two different types of jumps, with different activation energies, contribute to the space-charge relaxation. The relaxation time for the two different mechanisms

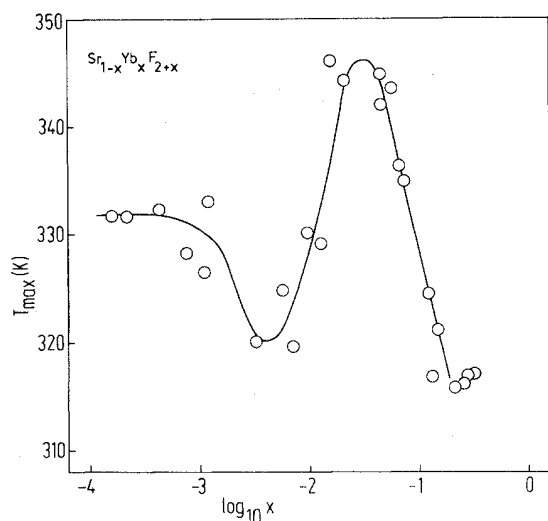


FIG. 3. Behavior of the positions of the space-charge relaxation (HT) band as a function of $\log_{10} x$ (the logarithm of the YbF_3 concentration).

can be written as

$$\tau = \tau_0 e^{E/kT} \quad (1a)$$

or

$$\frac{1}{\tau} = \frac{\alpha}{\tau_d^0} e^{-E_a^d/kT} + \frac{(1+\alpha)}{\tau_f^0} e^{-E_a/kT}, \quad (1b)$$

respectively. In Eqs. (1) τ_0 , and τ_f^0 , and τ_d^0 are the characteristic relaxation times associated with the "one-jump" conduction process, jumps of free interstitial fluoride ions, and jumps of NNN dipoles, respectively. E , E_a , and E_a^d are the activation energies of the one-jump conduction process, the jumps of free interstitial fluoride ions, and the jumps of NNN dipoles, respectively. k is the Boltzmann constant. The observed relation between the width of the space-charge relaxation band and the concentration has been given in Fig. 4. It shows a maximum at about 2–3 mol %. This behavior indicates that a jump mechanism as described by Eq. (1b) is operative. The variations of the linewidth as a function of the concentration can be reproduced by varying the parameter α , which is the probability of a dipolelike jump to contribute to the space-charge relaxation process (see Ref. 1). In general, one calculates in the range of small values of α (low concentrations) an increasing width of the ITC band with increasing values of α ; for intermediate values of α (the corresponding concentration is a few mol %) a maximum bandwidth is obtained; for large values of

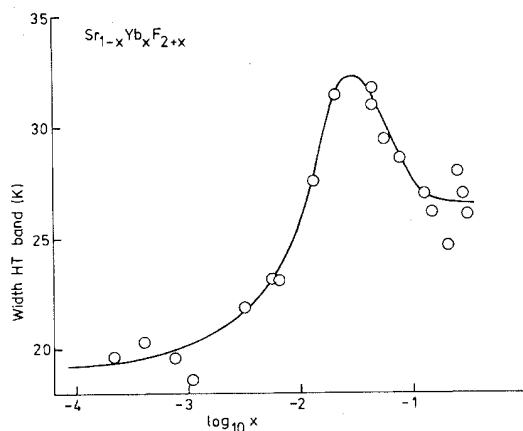


FIG. 4. Behavior of the halfwidth of the space-charge relaxation band as a function of $\log_{10} x$.

α the width of the ITC peak decreases until a constant value is obtained. This behavior agrees with what has been observed experimentally (see Fig. 4). We have found that the two-jump model [Eq. (1b)] can be employed to explain the results on $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$ in detail.^{1,18} The question whether this approximation is also applicable in exactly the same way to the system $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$, with significant clustering, will be discussed later in this paper.

It is now of interest to pay some attention to the behavior of the dipole relaxation peak as a function of the Yb^{3+} concentrations the dipole reorientation peak associated with the bound charge compensators (NNN dipoles) increases in intensity. The position of the peak remains the same in a wide concentration range. The width of the dipole reorientation peak increases slightly with the concentration. For concentrations higher than 0.3 mol % the intensity of the dipole reorientation peak decreases with increasing concentration (see Fig. 5). A comparison of these results and the ones on the T_{\max} values given in Fig. 3 shows that as long as the number of NNN dipoles increases the space-charge relaxation band shifts to lower temperatures. In the concentration region where the number of NNN dipoles decreases the space-charge relaxation band shifts to higher temperatures.

We note that the NNN dipole reorientation peak and the space-charge relaxation band are the only two peaks we have observed in the temperature range 77–400 K. We have not found any additional peaks at any concentration.

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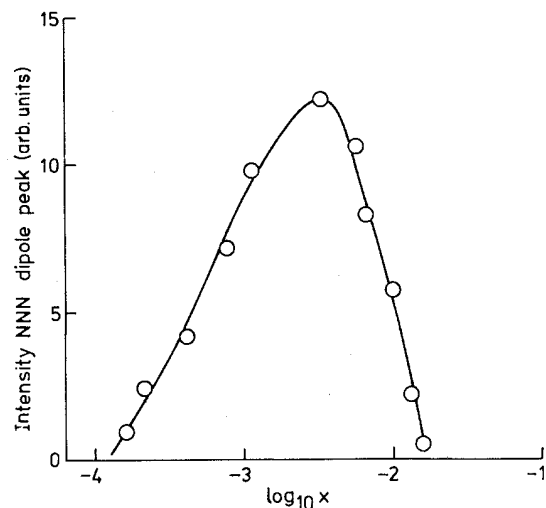


FIG. 5. Behavior of the intensity of the NNN dipole reorientation peak as a function of $\log_{10} x$.

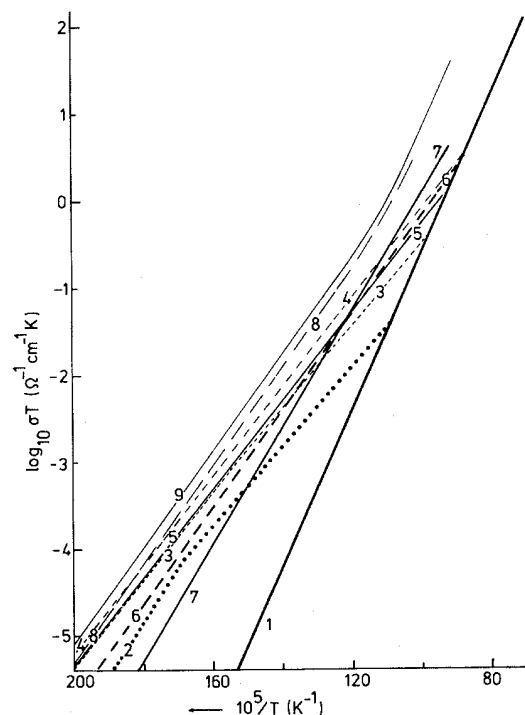


FIG. 6. Ionic conductivity results of 9 SrF_2 samples doped with varying amounts of YbF_3 . The different lines are associated with the following YbF_3 concentrations: 1, pure SrF_2 ; 2, 0.022 mol % YbF_3 ; 3, 0.11 mol % YbF_3 ; 4, 0.327 mol % YbF_3 ; 5, 0.669 mol % YbF_3 ; 6, 1.32 mol % YbF_3 ; 7, 2.09 mol % YbF_3 ; 8, 13.0 mol % YbF_3 ; 9, 20.8 mol % YbF_3 .

TABLE I. Analysis of the ionic conductivity results obtained for some solid solutions $\text{SrF}_2\text{-YbF}_3$.

YbF_3 concentration (mol %)	Plot No. (Fig. 8)	E (eV)	E_a (eV)
0.022	2	1.23	0.95
0.041		1.23	0.95
0.11	3	1.02	0.90
0.327	4	1.02	
0.669	5	1.03	
1.32	6	1.11	
2.09	7	1.33	
13.0	8	1.11	
20.8	9	1.10	

system of solid solutions and the anomalous behavior of the space-charge relaxation band we have carried out on some of the materials ionic conductivity experiments. Because the depolarization processes are governed by the same mechanism as the ionic conductivity process we expect some similarities between the results of these different experimental techniques. In Fig. 6 we show the results obtained for some solid solutions of SrF_2 and YbF_3 (the curve for SrF_2 has been taken from Oberschmidt and Lazarus¹⁹). The YbF_3 concentrations are chosen such that they are in the range where the anomalous variations of T_{max} in the ITC experiments have been observed. The analysis of the results have been presented in Table I; here, E corresponds with the activation energy in the low-temperature region where dissociation of the dipoles takes place. E_a is associated with extrinsic conduction: The dissociation of the dipoles is complete. Thus the relation between E_a and E is

$$E_a = E_a^f + \frac{1}{2} E_{\text{diss}}^d, \quad (2)$$

where E_{diss}^d is the dissociation energy of the dipoles.

From the results obtained at relatively low concentrations we find $E_a^f = 0.95$ eV and $E_{\text{diss}}^d = 0.56$ eV (see also Ref. 16). At higher concentrations (≥ 0.1 mol %) we find only one activation energy in the temperature range 500–800 K. The clear correspondence between the ITC results and those obtained from the ionic conductivity measurements is shown in Fig. 7, where it can be seen that a maximum value for T_{max} can be associated with a minimum in the curve of the isothermal conductivity results at 550 K. Qualitatively similar situations are observed if the ITC results are compared with the isothermal conductivity values at 770 and 909 K.

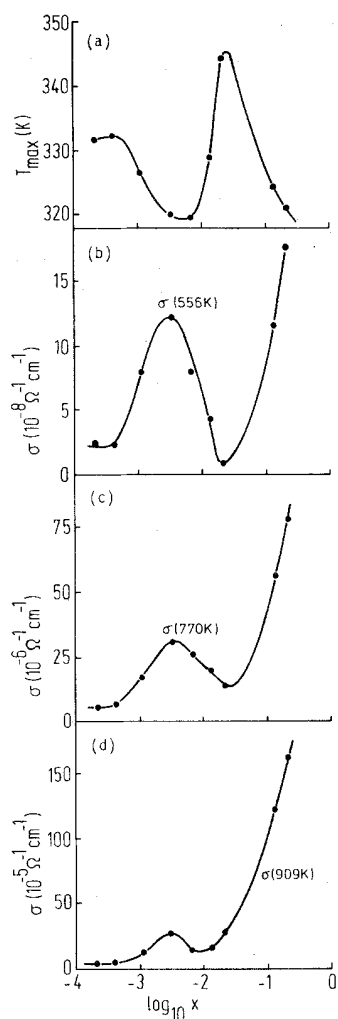


FIG. 7. Demonstration of the correspondence of the ITC and ionic conductivity results. (a) Plot of T_{\max} vs $\log_{10} x$. (b)–(d) Isothermal conductivity results at 556, 770, and 909 K, respectively.

IV. DISCUSSION

In $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$ the space-charge relaxation band has been shown to behave in a very interesting way (see Fig. 3). Another interesting feature of these solid solutions is that the dipole peak, which has been attributed to the presence of NNN charge compensation complexes of the type $\text{Yb}^{3+}\text{-F}_i^-$ and which has a large intensity for Yb^{3+} concentrations of about 0.1 mol %, diminishes for $x \approx 0.015$ (see Fig. 5). This is in contrast with the results obtained for solid solutions of the types $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$, $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$, $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$,

and $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, where dipole peaks can be observed even at R^{3+} concentrations as high as 5 mol %. This observation together with results reported in the literature on solid solutions $A_{1-x}R_x\text{F}_{2+x}$ (Refs. 6–10) indicates that appreciable clustering occurs in $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$. Tallant, Moore, and Wright^{11–13} recently studied very extensively the clustering of Er^{3+} impurities in CaF_2 and they found that many different types of clusters may exist even in crystals with $x < 0.01\%$. In addition we note that Brown *et al.*²⁰ have observed at least four different Er sites in $\text{Sr}_{1-x}\text{Er}_x\text{F}_{2+x}$. The situation in our $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$ samples is probably quite similar to that in $\text{Sr}_{1-x}\text{Er}_x\text{F}_{2+x}$, and we assume that the Er sites observed by Brown *et al.* are at least partly due to clusters.

From the different observations reported in the literature and our ITC and EPR results, i.e., the differences observed for $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$, $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$, and $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$ (see Refs. 18 and 21), we propose that the defect structure of the solid solutions of the type $A_{1-x}R_x\text{F}_{2+x}$ depends upon the radii of the different ions involved. It is not unexpected that the defect structure depends strongly upon the R^{3+} ionic radii in $\text{Sr}_{1-x}R_x\text{F}_{2+x}$; in some of our earlier papers we have reported dipolar defects in these materials for $x \approx 10^{-4}$ and we have observed that depending upon the radius of the R^{3+} ion NN or NNN dipoles are present in these materials.⁶

We expect that clustering influences drastically the behavior of the space-charge relaxation peak in $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$, because we found that this depolarization peak shows a maximum in the plot T_{\max} vs x , which is (for concentrations between 1 and 10 mol %) determined by dipolelike jumps (see also den Hartog and Langevoort¹ and Meuldijk, Mulder, and den Hartog¹⁸). If extensive clustering occurs, the effect of dipolelike jumps on the space-charge relaxation peak position is reduced very strongly, because first the concentration of the defects is reduced, and second the interstitial fluoride ions, associated with the clusters, may be bound more strongly to these defects.

It is possible to explain in a qualitative way the behavior of the value of T_{\max} of the space-charge relaxation peak, as observed in samples $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$, by means of clustering. As mentioned earlier, for low Yb concentrations the number of $\text{Yb}^{3+}\text{-F}_i^-$ dipoles of the NNN-type increases with the concentration of the Yb^{3+} impurities. Assuming that in this concentration range ($0 \leq x \leq 0.003$), the relaxation time associated with the space charges can, just as for the systems $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$, be expressed by Eq. (1b) (see also Refs. 1 and 2); we can understand

the decrease of T_{\max} with increasing Yb^{3+} concentrations in this concentration range.

For $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$ we have observed that with increasing values of x the value of T_{\max} decreases. We know that in these materials the number of dipoles increases with x in the concentration range $0 \leq x \leq 0.01$. From the model employed for the ionic conductivity in these solid solutions it can easily be seen that as long as the number of dipoles increases the value of α increases [see Eq. (1b)]. Therefore, we expect (in terms of the model) that for $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$ the value of T_{\max} decreases in the concentration range $0 \leq x \leq 0.003$, because in this concentration range the number of NNN dipoles increases with x (see Fig. 5). For $x > 0.003$ the concentration of dipoles decreases drastically with increasing values of x as a result of clustering. This reduction of the concentration of dipoles leads to a reduction of the value of α ; using the formula for the relaxation time [Eq. (1b)] we find that the value of T_{\max} increases with increasing values of x in this concentration range. An interesting feature of the results presented in Fig. 3 is that for an Yb^{3+} concentration of 1.57 mol% the value of T_{\max} is larger than the one observed for very low Yb concentrations (0.022 and 0.041 mol%). This indicates that the mobile charges in the crystals are trapped by the clusters, leading to a reduced ionic conductivity and increased values of T_{\max} as compared with crystals with very small amounts of YbF_3 . In this model the ionic conductivity is governed by two processes: (a) the dissociation of the anion interstitials from the cluster traps (E_{diss}^c), and (b) jumps of free interstitial fluoride ions (activation energy E_a^f). From our observations we conclude that the dissociation energy connected with this detrapping process is larger than the corresponding energy for NNN dipoles.

For concentrations higher than 4–5 mol% the space-charge relaxation peak moves towards lower temperatures again with increasing Yb concentration. We expect again that in this concentration range the clustering is very strong; many different types of clusters will be present. This has been found also for the solid solutions $\text{Sr}_{1-x}\text{Er}_x\text{F}_{2+x}$ by means of EPR (Ref. 20) and high resolution spectroscopy (selective laser excitation) by Kurz and Wright.²² We note that probably the Er-doped materials will behave in approximately the same way as the Yb-doped samples, because of the fact that the ionic radii of these impurities are about the same.

It is possible that for very high Yb concentrations ($x > 0.04$) the defect structure changes and that more complicated clusters are formed. This dissociation energy of these clusters, i.e., the energy necessary to remove an interstitial fluoride ion, may be different (lower) from the corresponding value in the

sample containing 2.09 mol% YbF_3 . If this is true, the space-charge relaxation peak is expected to shift to lower temperatures. Another possible explanation for the observed shift of the space-charge relaxation peak may be percolation as described below.

Interstitial fluoride ions within a cluster containing two or more Yb impurities have the possibility to jump from one position in the cluster to alternative positions. With these jumps we can associate an activation energy E_a^c and a characteristic relaxation time τ_c^0 (in the Introduction we have discussed the different possible jumps including these jumps within a cluster). If we assume that there is only one type of cluster present in the concentration range under consideration ($0.01 \leq x \leq 0.20$), we expect that the position of the space-charge relaxation band for low concentrations is determined by two energies, E_a^f and E_{diss}^c . For high concentrations the clusters are close together and interstitial fluoride ions associated with one cluster can often jump directly to a position which is connected with a neighboring cluster; i.e., dissociation is no longer necessary and the value of T_{\max} is determined mainly by the relaxation time,

$$\tau_c = \tau_c^0 \exp(E_a^c/kT). \quad (3)$$

We note that the above described conduction process is very similar to the conduction mechanism proposed by den Hartog and Langevoort¹ for $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, which does not show appreciable clustering. In the present case the relaxation time can be written as

$$\frac{1}{\tau} = \frac{\alpha}{\tau_c^0} \exp(-E_a^c/kT) + \frac{1-\alpha}{\tau_{c,f}^0} \exp(E_{c,f}/kT), \quad (4)$$

where $\tau_{c,f}^0$ and $E_{c,f}$ are the characteristic relaxation time and the activation energy associated with the conduction process which is governed by the jumps of free dissociated fluoride ions. Analogous to Eq. (2) we can write

$$E_{c,f} = E_a^f + \frac{1}{2} E_{\text{diss}}^c, \quad (5)$$

where E_a^f is the jump energy of free anion interstitials and E_{diss}^c is the energy necessary to dissociate an interstitial fluoride ion from a cluster. The analysis given above is only valid if there is one type of cluster present in the heavily doped samples. If there are different types of clusters we have to deal with different values of E_{diss}^c for each of the clusters present. From the linear behavior of the conductivity results presented in Fig. 6 we get the impression that the dissociation energies connected with the clusters, which are involved in the conduction process, do not differ very strongly. From the conduc-

tivity results obtained for the sample containing 2.09 mol % YbF_3 we conclude, using Eq. (5), that $E_{\text{diss}}^c \geq 0.76$ eV, which should be compared with the dissociation energy of NNN dipoles ($E_{\text{diss}}^d = 0.56$ eV). The reason why we are able to give only the lower limit of E_{diss}^c is that it is possible that the conductivity contains contributions from the mechanism associated with the first term in Eq. (4).

In order to describe the conduction processes in the extreme situation of very heavily doped SrF_2 , we assume that here the conductivity is determined almost completely by percolation in which clusters are involved. For very large Yb concentrations the value of T_{max} is approximately constant (~ 316 K), but also the activation energy as determined from the ionic conductivity results is approximately constant (1.10 eV). From these results we tentatively conclude that the activation energy associated with jumps of interstitial fluoride ions within clusters is approximately 1.10 eV.

From the discussion presented above we see that we are able to explain with one model qualitatively the behavior of the ITC peak position (T_{max}) and the ionic conductivity results as a function of the YbF_3 concentration. On the other hand, the close correspondence between the ITC and ionic conductivity results as shown in Fig. 7 demonstrates quite clearly that the model proposed in our earlier papers for the space-charge relaxation band in various crystals of the type $A_{1-x}R_xF_{2+x}$ (Refs. 1 and 2) is correct. Another parameter, which provides us with information about the conduction processes in heavily doped solid solutions, is the width of the ITC peak associated with space-charge relaxation at half height. If we assume that there is no additional broadening of the peaks due to interactions between the defects we can explain the observed behavior of the half width as follows. In the low-concentration range the width of the space-charge relaxation band is determined by the activation energy E (1.23 eV; see Table I). If we use the same value for $\tau_{c,f}^0$ [see Eq. (4)] as we did for τ_f^0 in order to fit both T_{max} and the width of the space-charge relaxation peak in the low-concentration range, we find for the 2.09 mol % sample a width of the space-charge relaxation peak at half-height a value, which is approximately 10% larger than the one at very low YbF_3 concentrations. For intermediate concentrations the width increases as a result of the competition of the two relaxation mechanisms indicated in Eq. (4). A calculation of the shape of the ITC peak as a function of the value of α shows that there is a maximum of the width of the ITC peak at the interval $0 < \alpha < 1$. For values of α close to 1 the width of the theoretically calculated space-charge relaxation band reaches a constant value, just as it has been found

experimentally (see Fig. 4). From Fig. 4 we see that for very large concentrations (i.e., values of α close to 1) the width of the space-charge relaxation band is 27 K. It is now useful to compare this value with the ones found for the systems $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ (Ref. 21) and $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$, which are approximately 15 K. We conclude that also from the behavior of the width of the space-charge relaxation band we can see that for very heavily doped samples of the type $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$ the jump processes are different from those found for the La- and Nd-doped materials. Employing Eq. (4) we calculate that the activation energy connected with jumps within clusters (E_a^c) is significantly larger than the values for the dipolar jumps in $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Nd}_x\text{F}_2$ (the latter one is estimated to be about 0.5–0.6 eV). If we employ the activation energy found from the ionic conductivity experiments we find a value for the width of the space-charge relaxation peak which is approximately correct, indicating that the interpretation given above is consistent.

From the above discussion it is clear that it is not necessary to assume that there is a multitude of different clusters with many different jump types. What this means is that there is one predominant type of jumps in these materials. Another explanation may be that for the different associates there are different jumps of interstitial fluoride ions within the cluster with approximately the same activation energy (i.e., the width of the distribution of activation energies is small). From the results of selective laser excitation several authors have concluded that many different types of clusters are formed in some of the solid solutions.^{11–13,20,22} We are therefore inclined to assume that there are jumps in different clusters with approximately the same activation energy.

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