PHYSICAL REVIEW B VOLUME 44, NUMBER 1 1 JULY 1991-I

Clustering and percolation of defects in Pr^{3+}:SrF_2 using site-selective spectroscopy

Curtis D. Cleven, Steven H. Lee,* and John C. Wright
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

(Received 9 January 1991)

Site-selective laser spectroscopy has been used to study Pr^{3+}-doped SrF_2 in order to identify whether the dopant substitution is random or whether preferential clusters of several Pr^{3+} ions form along with their charge-compensating fluoride interstitial ions. At very low dopant concentrations, a single locally compensated Pr^{3+} site dominates the spectrum. It corresponds to the simple dipoles that are observed by ionic thermal current and dielectric relaxation experiments. At concentrations of 1 mol %, three centers are observed that are associated with preferential clusters. There are many additional centers that are also observable at this concentration. These observations provide clear evidence that the dopant substitution in SrF_2 is not random and that models for the percolation of fluoride interstitial ions must be modified to accommodate preferential clusters.

INTRODUCTION

The alkaline-earth fluorides (MF_2) are important models for understanding the solid-state chemistry of point defects in insulating crystals. The extensive experimental[1–27] and theoretical work[28–37] in these systems has resulted in a detailed microscopic picture of the solid-state chemistry when these materials are doped with trivalent rare-earth ions. Fluoride interstitial ions (F_i') charge compensate the rare earth distantly so the rare earth has cubic symmetry or locally in either nearest-neighbor (NN) or next-nearest-neighbor (NNN) positions so the rare earth has tetragonal or trigonal site symmetry, respectively. The NN compensation is favored when the ratio of dopant to host-cation radius is small; NNN compensation, when it is large.[30] The NN or NNN single pairs of rare-earth–F_i' ions have dipole moments that are measured in dielectric and ionic thermal current (ITC) experiments.[19–27] At dopant concentrations between 0.05 and 1 mol % clusters begin to form.[5,8] Smaller dopant ions form extensive clusters, the largest being $(6|0|8+4n|6+n)$ hexamers that can getter n extra F_i' ions (where $n=0$–6).[29,31,27,33–35,38,39] Larger dopant ions form dimers $(2|0|2|2+n)$ and trimers $(3|0|2|3+n)$ that also getter extra F_i' ions.[40]

The relative importance of these sites changes dramatically with changes in dopant concentration and annealing temperature. As the dopant concentration is raised, there is more extensive clustering that getters F_i' ions.[9–18,39–40] The lower F_i' concentration causes an anomalous increase in the number of cubic sites relative to single-pair dipoles as the dopant concentration is raised. In addition, it has been shown that strain interactions between defect centers augments the Coulombic interactions responsible for the nonideality corrections in defect equilibria so there is also an increased dissociation of the dipoles from these activity effects.[16–18] These effects are caused because the free energy of a site is affected by its strain and Coulombic interactions with surrounding defect centers. The combination of the nonideality corrections and the gettering by clusters cause the absolute concentration of the single pairs to reach a maximum and then decrease as the dopant concentration is raised. The nonideality corrections also cause the NNN to NN single-pair ratio to increase with dopant concentration because the free energy of the sites changes differently. When the crystals are annealed at a high temperature, the clusters dissociate to form cubic sites, single pairs, and F_i' ions. Since there are more F_i' ions, there is a higher ratio of single pairs to cubic sites in contrast to the lower ratio that one would expect if gettering was not an important factor.

In contrast to this picture, there has been some very interesting work by den Hartog and co-workers in SrF_2 doped with the larger rare earths (La, Ce, Pr, and Nd) that assumes the rare-earth dopants are randomly distributed and the only important sites are cubic and single-pair dipoles.[41–48] Consequently, they feel it is an ideal system to study percolation dynamics.[48] In den Hartog's model, clustering is important for small rare earths in CaF_2 and SrF_2 but is unimportant for large rare earths in SrF_2. The model focuses on ionic thermal current (ITC) and dielectric measurements and it assumes that the only important defect centers in this picture are the single-pair dipoles. The cubic sites do not play an important role because the pairing between the large rare earths (La, Ce, Pr, and Nd) in SrF_2 and the F_i' is strong and there is little dissociation. The model assumes a completely random distribution of rare-earth dopant ions. As the dopant concentration is raised, there is an increased probability that another dopant ion or dipole will be within a critical distance of any given dipole. Dipoles that have another dopant within the critical distance are not sensed in dielectric relaxation and ITC measurements because the nearby rare earth causes an anisotropy around the dipole that hinders the free movement of the F_i' necessary for dipole reorientation. These dipoles are called statistical clusters to distinguish them from preferential clusters where two dipoles have coalesced to form a new center. The long-range transport of F_i' ions is believed to occur more easily between statistical clusters than when it occurs in the unperturbed fluorite lattice. A percolation threshold was found when the dopant concentration in SrF_2 reached the critical value required for the statistical clusters to become connected. Long-range F_i' transport then occurs with a low activation energy. The simplicity of the model suggested that SrF_2 could serve as a model system for studies of percolation and fractal networks.[48]

In this paper, we present the results of site-selective laser spectroscopy of Pr^{3+}:SrF_2, a system where den Hartog finds a random rare-earth distribution.[41,43] We find that the rare-earth ions are not distributed randomly and there are important contributions from preferential clusters. Crystals with 0.01 and 0.1 mol % concentrations have spectra that are dominated by single pairs with no evidence of appreciable clustering. A 1 mol % concentration crystal has a very different spectrum. There are three dominant sites that are attributed to clusters and many other more minor sites and nonfluorescent centers that are probably associated with clusters.

Although these measurements clearly show that clusters are important for large rare-earth dopants, we suggest that the model of den Hartog is still a useful phenomenological model that describes the important aspects of these systems. ITC and dielectric measurements do not have the resolution to differentiate between defect structures that may be simultaneously present nor are they sensitive to centers that have no dipole relaxation. The changes in the high-temperature ITC peak shifts that were used to identify when clustering was important may instead reflect the changes to a different form of cluster when different size dopant ions are used. This interpretation might be particularly attractive because the extra F_i' ions that are gettered by the clusters would be expected to contribute to the high-temperature ITC peak. In a modified model, the critical radius about a dopant ion may represent the distance within which F_i' hopping is facilitated. The same percolation model would be appropriate but the underlying picture would change. Now, F_i' transport would involve motion between clusters instead of locally compensated pairs.

EXPERIMENTAL

Fluorescence spectra were obtained using a N_2-laser-pumped dye laser (0.02 nm linewidth) to excite the crystals and a 1-m monochromator to measure the spectrum. Excitation spectra of the total fluorescence were obtained by scanning the dye laser while monitoring the fluorescence with a photomultiplier. Since-site excitation spectra were obtained by scanning the dye laser while the monochromator observed a specific fluorescence line. A mechanical chopper was used to block the laser output from the detector during the measurement of fluorescence that was close to or at the frequency of the excitation laser. Absorption spectra were obtained by passing a tungsten lamp output through the crystals and measuring the transmittance with the 1-m monochromator. The crystals were mounted on a closed cycle refrigerator and cooled to ~10 K. The SrF_2 single crystals were purchased from Optovac Inc. and had 0.01, 0.1, or 1.0 mol % Pr^{3+} concentrations.

RESULTS

Figure 1 shows excitation spectra of the total fluorescence from three different concentration crystals in the region of the ${}^3H_4 \rightarrow {}^3P_0$ and ${}^3H_4 \rightarrow {}^3P_2$ transitions along with the assignments of the lines to specific sites by site-selective spectroscopy. The 0.01 and 0.1 mol % Pr^{3+}:SrF_2 crystals have almost identical spectra that can be assigned to a single site labeled *C*. There are additional lines from minor sites that can be seen in the expanded spectra. The 1 mol % crystal spectrum is different from the others. The *C* site lines are still dominant but they are broader. In addition, new lines appear with a comparable intensity to the lines in the low-concentration crystals.

The *C* site is assigned to the single-ion pair with NN compensation $(Pr_{Sr} \cdot F_i)^{\times}$ that has been observed previously by dielectric relaxation and ITC experiments.[43] The single-ion pair always dominates the spectrum at low concentrations. The cubic site does not appear in the spectrum because its transitions are electric dipole forbidden. The new sites are assigned to clusters on the basis of their strong concentration dependence. It is interesting to note that the *C* site lines are shifted to higher energy from the cluster lines. Their positions are nearly the same as those found in Pr^{3+}:CaF_2.[49]

There are a number of other sites that do not appear in the fluorescence or excitation spectra. Figure 2 shows the same excitation spectra for the 1 mol % crystal along with the absorption spectra of the same region. Each of the lines in the excitation spectra match lines in the absorption spectra. There are a number of lines in the absorption spectra that do not have a counterpart in the excitation spectra because they do not excite fluorescence. These lines probably also correspond to clusters. The clusters may not fluoresce because of fluorescence quenching by energy transfer within the clusters. The absorption spectra of the lower-concentration crystals show

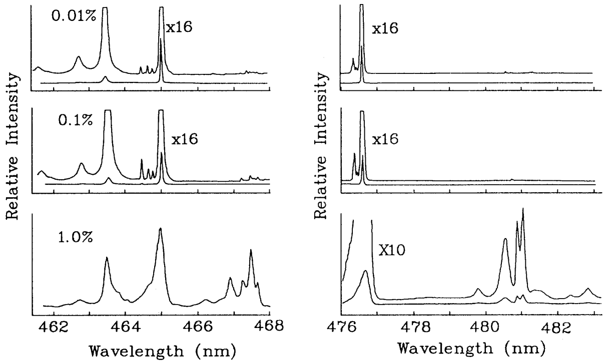

FIG. 1. Excitation spectra of the ${}^3H_4 \rightarrow {}^3P_{0,2}$ transitions in Pr^{3+}:SrF_2. The concentrations of the samples are indicated on the left side of the figure.

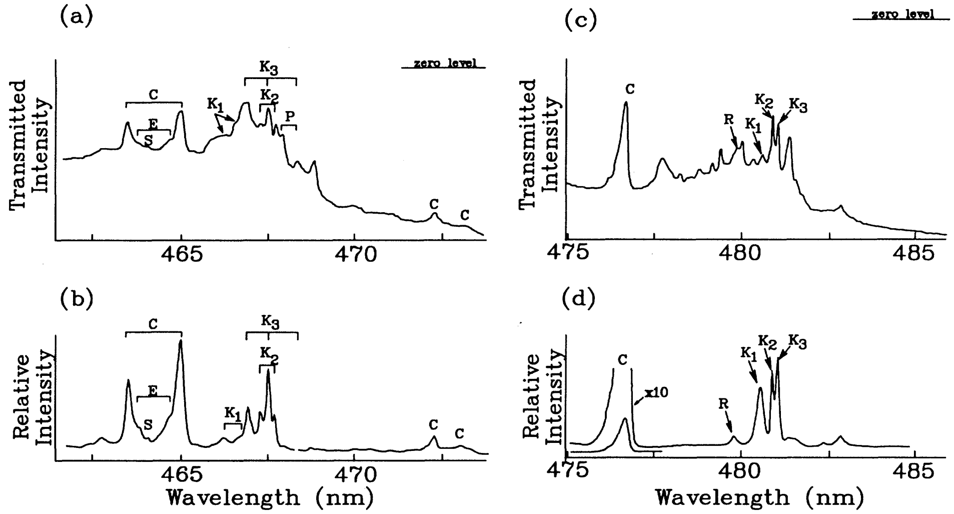

FIG. 2. Uncorrected absorption (a) and (c) and excitation (b) and (d) spectra of 1 mol % Pr^{3+}:SrF_2. The y axis in the absorption spectra is the transmitted light signal. The zero light level is also indicated on the spectra. The lines that are assigned to the different Pr^{3+} sites are shown in the figure. A number of lines in the absorption spectra do not appear in the excitation spectra because the fluorescence was too weak.

only the *C* site lines and do not have additional features from nonfluorescent sites. The *C* site's peak absorbance decreases by 2.0 from the 1.0 mol % to the 0.1 mol % samples.

Fluorescence spectra were obtained by systematically setting the dye laser for each of the lines in the absorption spectra. The fluorescence spectra of the dominant features could be attributed to four sites whose spectra are shown in Figs. 3(a)–3(d). These sites are labeled *C*, K_1, K_2, and K_3. The fluorescence at 482.5 nm contains contributions from all of the K_i sites but there may be a fourth cluster that also contributes at this wavelength. Definitive single-site spectra could not be obtained because of the overlap from other sites.

Four minor sites could also be identified and their fluorescence spectra are shown in Figs. 3(e)–3(h). These sites are labeled *R*, *E*, *S*, and *P*. There are lines from the four major sites in these spectra because of spectral overlap. The overlapping lines have been noted in the spectra. The *E* site and the *S* site have spectra that are almost

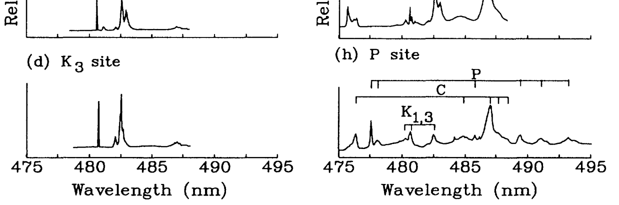

FIG. 3. Fluorescence spectra from the $^3P_0$ level of the 1 mol % Pr^{3+} crystal for each of the sites labeled in the figure. Lines from other sites that appear because of overlap with the indicated site are labeled on the figure. The excitation wavelengths used to obtain each spectrum are (a) 476.6, (b) 480.2, (c) 480.8, (d) 480.95, (e) 479.59 (f) 464.65, (g) 463.95, and (h) 470.81 nm.

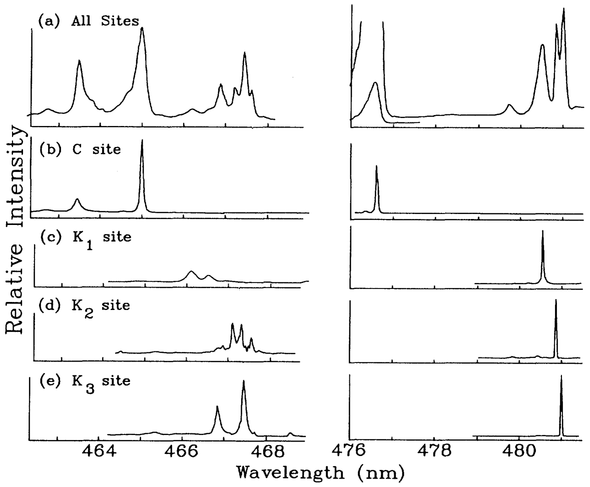

FIG. 4. Excitation spectra for the $^3H_4 \rightarrow {}^3P_{0,2}$ transitions of the 1 mol % Pr^{3+} crystal for each of the major sites in the spectra. The wavelengths used to monitor the fluorescence are (a) broadband monitoring, (b) 467.6, (c) 480.2, (d) 480.8, and (e) 480.95 nm.

identical to the *C* site but their lines are shifted. They are clearly different sites because the line positions are independent of the excitation wavelength. There is no shifting in position that would be found if the lines were associated with fluorescence line narrowing of the inhomogeneously broadened *C* site. The sites may represent a NN single-pair site that is perturbed by a nearby defect center.

If one now tunes the 1-m monochromator to the major fluorescence lines for each of the sites in Fig. 3, one can obtain single-site excitation spectra. Figure 4 shows the single-site excitation spectra of the four dominant sites along with the excitation spectra of the total fluorescence. It can be seen that the dominant lines are all explained by the four sites whose spectra are shown. The *C* site excitation spectra are sharper than the lines in the excitation spectra of total fluorescence because of fluorescence line narrowing.

DISCUSSION

The strong clustering that occurs in Pr^{3+}:SrF_2 is most evident from the absorption spectra of the 0.1 and 1 mol % crystals. The low-concentration crystal has only sharp line transitions from the *C* site that are identical to that seen in the excitation spectrum in Fig. 1. The absorption spectrum of the higher-concentration crystal has extensive contributions from the cluster sites that are now important. The concentration levels where clustering becomes important is different from previous work. In Pr^{3+}:CaF_2, clusters were dominant in spectra of 0.1 mol % crystals. Similar behavior is seen for all of the other dopants studied previously.[18] In Pr^{3+}:SrF_2, there is little clustering at this concentration. Clearly there is less tendency to cluster as was pointed out by Meuldijk, van der Meulen, and den Hartog.[43]

It is well established that the amount of clustering is sharply dependent on the crystal's annealing conditions. Fluorite crystals can be quenched quickly enough from high temperature to freeze in a high-temperature site distribution where the clusters have dissociated to form simple single-pair sites and cubic sites. The crystals used in this study were obtained commercially from Optovac. They were grown by the Bridgman method and cooled slowly to room temperature. Under these conditions, clusters are almost as prominent as found in samples that are annealed at low temperatures for extensive periods of time.[16]

This work is in disagreement with the den Hartog and co-workers' dielectric and ITC measurements that show the larger rare-earth dopants enter the SrF_2 randomly up to dopant concentrations of 35 mol %.[41-48] If the substitution were random, one would expect to see only the *C* site lines at all concentrations. They would be sharp at low concentrations but would broaden as the concentration increases and the statistical clusters become important. Instead, we see new cluster lines appearing that show there are preferential arrangements of the Pr^{3+} and F_i' ions in clusters. Furthermore, the total area under the peaks of the clusters in the absorption spectrum of the 1 mol % concentration crystal exceeds the total area of the *C* site lines indicating that the clusters are very important. The spectroscopy of the SrF_2 system shows strong similarities to the other fluorites, suggesting that the same factors are important in all fluorites.[18] We do not believe the disagreement arises from differences in the crystal preparation since the method used by Meuldijk, Mulder, and den Hartog is quite similar to that used for our samples.[50]

It is appropriate to carefully examine the foundation underlying the work of den Hartog and co-workers and to develop alternative interpretations. These workers have made a number of observations that form the background for their model of SrF_2 doped with large rare earths. They are summarized below.

(1) EPR measurements with Gd probe ions show only cubic and single-pair sites in SrF_2 samples codoped with high concentrations of La or Nd ions. There is no evidence for clusters.[41]

(2) The EPR linewidth increases with codopant concentration. The dependence can be modeled by assuming a random dopant distribution which perturbs the NN or NNN site in proportion to the distance between the dipole and the perturbing ion.[41]

(3) ITC and dielectric relaxation measurements show dipolar relaxation peaks that are attributed to NN and NNN dipoles. There are no peaks associated with clusters.[43]

(4) The relative importance of the NN and NNN peaks changes as a function of concentration because of defect-defect interactions.[43]

(5) The dipolar relaxation peak reaches a maximum as a function of concentration. The maximum occurs at ~0.4 mol % for small rare-earth dopants and 1 mol % for large ones.[42-45]

(6) The high-temperature (HT) peak associated with the interfacial space charge shifts with dopant concentration.[42-45] The position (T_m) depends on the mobility of the F_i'. For large ions, T_m decreases with increasing dopant concentration, first slowly as the F_i' concentration grows and then more rapidly as the F_i' begins to move between statistical clusters. For small ions, it decreases initially as the F_i' concentration grows, then increases as the preferential clusters trap F_i' ions, and finally decreases again as the F_i' begin to move between clusters. The linewidth of the HT band (ΔT_m) is also correlated with the clustering.

(7) If the crystals are quenched from a high temperature, there is a large change in T_m and a large increase in the dipolar relaxation peak.[45] These changes are assigned to the randomization of residual order in the dopant ions.

(8) If the ITC measurements are performed with a partially polarized sample, the HT peak can be reduced and a cluster peak can be observed beneath it.[47] This peak is assigned to statistical clusters.

(9) The changes in the electron paramagnetic resonance (EPR) linewidth, the change in the NN to NNN dipole ratio, the maximum that is reached in the dipole relaxation, and the shifts in T_m and ΔT_m occur over the same range of dopant concentration.[41-48]

All of these observations are explained by a simple model that makes the following assumptions:[41–48]

(1) Large dopant ions are distributed randomly and small dopant ions form preferential clusters that are in turn distributed randomly.

(2) If a dopant ion is located within a critical distance of a dipole, its perturbation on the dipole favors a specific orientation of the F_i' within the dipole so it cannot reorient and contribute to the ITC or dielectric relaxation peak. The ions within the critical radius are considered to be statistical clusters.

(3) A F_i' ion migrates with an activation energy of $E_{a,0}^{d}$ or $E_{a,0}^{f}$ depending upon whether the migration is between dipoles that are involved with statistical clusters or between normal lattice sites, respectively. The fraction of F_i' jumps that are dipolelike is given by α.

In this model, the dipole relaxation peak reaches a maximum and then decreases, not because the absolute concentration of dipoles reaches a maximum but because increasing numbers of dipoles no longer contribute to the relaxation peaks as the number of statistical clusters increase. The model assumes that $E_{a,0}^{d} < E_{a,0}^{f}$. With this assumption, T_m decreases rapidly when the statistical clusters overlap so percolation occurs and $\alpha \approx 1$. A F_i' ion can move easily by dipole like jumps completely within the framework fixed by the statistical clusters. The model has been made quantitative and quite good fits have been achieved between theory and experiment.[41–48]

The observations are not definitive indications of the presence or absence of clustering. The same behaviors are seen in fluorites where clustering is of demonstrated importance. The failure to observe cluster-associated peaks in EPR, ITC, or dielectric relaxation experiments is commonly found in fluorites where clustering is present.[2,9–27] Similarly, it has been found that the NN and NNN dipoles reach maximum absolute concentrations in all of the materials that have been studied and there is no need to invoke statistical clusters that freeze the F_i' ions within the dipoles.[14–18] Furthermore, the dopant concentration required to reach the maximum dipole concentration increases as the dopant ionic radius increases, as observed by den Hartog and co-workers.

An observation that is unique to den Hartog's work is the behavior of T_m for the HT peak.[42,45] Systems without clusters are believed to have a monotonic decrease in T_m as the dopant concentration increases while systems with clustering have complex dependences. There is no evidence that a monotonic decrease in T_m proves the absence of clustering. In fact, the complex behavior seen in samples with clustering will only be observed if there is an appreciable difference between the dissociation energies of clusters and dipoles and if the F_i' ions are more tightly bound to the clusters than the dipoles. It is accepted that the type of cluster in CaF_2 changes for dopants with different ionic radii.[37,38,40] Small dopants form hexamers while larger dopants form dimers and trimers. Furthermore, there is evidence that gettering is more extensive with the smaller dopant ions.[40] It would be expected that the dissociation energy of F_i' would change for different types of clusters and therefore T_m could shift differently for different dopants. It has been suggested that the decrease in the superionic transition temperature for rare-earth doped fluorites is the result of the low dissociation energy for the gettered F_i' ions in the clusters.[51–54] Therefore, we suggest that the behavior of T_m reflects the differences in the types of clusters forming in SrF_2 as one changes dopants. Complex behavior is observed for larger clusters with more extensive gettering and smaller dissociation energies for F_i' ions. Monotonic behavior is observed for smaller clusters with more tightly bound F_i' ions.

A number of the observations described above lend support to this viewpoint. The observations by den Hartog and co-workers that showed quenching decreases T_m and increases the dipole concentrations[45] are suggestive of results found in CaF_2. Here, it was shown that quenching from high temperatures causes breakup of preferential clusters and an increase in the dipole concentration. The same behavior is probably occurring in $Pr^{3+}:SrF_2$. The increased F_i' concentration would decrease T_m as observed by den Hartog and co-workers. The effects are quite large in crystals with 3.3 mol % concentration. Quenching produces a T_m change that is equivalent to a doubling of the dopant concentration and a dipole concentration change that is equivalent to halving the dopant concentration. Such large effects suggest more dramatic changes than small deviations from random distributions.

The partial polarization experiments are actually successful in directly observing a relaxation peak that is associated with a cluster.[47] In these experiments, the sample was polarized at a temperature where only the F_i' ions with lower activation energies could move. The HT peak associated with the interfacial space charge was sharply reduced and a new peak occurred that was associated with clustering. Although it was assigned to a statistical cluster, it would be quite reasonable to assign it to one or more of the preferential clusters observed in this work.

The most important results obtained by den Hartog and co-workers are the ITC, time-domain reflectometry, ac-impedence, and dc ionic conductivity measurements that showed sharp changes in the transport efficiency at ≈ 5 mol % Pr^{3+}.[47,48] The change was interpreted as a percolation threshold and it was suggested that $Pr^{3+}:SrF_2$ might be an ideal material to study percolating networks.[48] Although it is now clear that SrF_2 doped with large rare earths is not as simple as was assumed, we still believe that the percolation picture presented by den Hartog has merit and that many of the observations provide important insights to the mechanisms controlling the defect chemistry. The percolation model of den Hartog does not require that percolation occur between dipoles. It could also occur between clusters or dipoles and clusters. The many sites that a F_i' could occupy in a gettering cluster may make a particularly easy pathway for transport. In this picture, the percolation threshold depends on a critical radius about a cluster within which another cluster or dipole must fall for a F_i' to migrate with a lower activation energy, $E_{a,0}^{d}$. It should be noted that the dopant level where clusters appeared in the spectroscopy is in the same range as where the dipole concentration reaches a maximum, the NN to NNN dipole ratio changes, the value of T_m shifts, the HT peak broadens, the dipole linewidth increases, and the transport becomes much more efficient. Certainly, these effects are all associated with the same interactions between defects.

Finally, it should be mentioned that the observations of den Hartog and co-workers give strong evidence for the strain interactions between defect structures that have been postulated to cause the nonideality effects responsible for the anomalous site distributions of cubic and single-pair sites. The broadening of EPR,[41] ITC, and dielectric relaxation[42,45] features, the changes in the NN to NNN dipole ratio,[43] and the percolation between defect centers[47,48] would not be important without interactions between defect centers. The models given by den Hartog and co-workers and their excellent fits with experimental data can perhaps be used as the foundation for obtaining a better understanding of these important interactions.

CONCLUSIONS

Site-selective laser spectroscopy has been used to identify the number and type of defect centers found in Pr^{3+}:SrF_2. A single-ion site is identified in low-concentration crystals that corresponds to the NN dipole observed by other workers. At a Pr^{3+} concentration of 1 mol %, three other fluorescent sites are found. In addition, there are a number of nonfluorescent sites and several minor sites. These sites are assigned to clusters containing multiple Pr^{3+} ions. These observations are in disagreement with other work that finds a percolation threshold at a critical dopant concentration, assuming a random distribution of Pr^{3+} ions. It is suggested that the percolation model can be modified to account for the preferential clusters found in this work. Percolation can occur by F_i' hops between clusters or dipoles that are within a critical distance of each other.

It would be interesting to investigate the percolation network in samples that had been quenched to dissociate the clusters. It may be possible to create a more random distribution that would prove to be a more ideal system for percolation studies.

This work suggests that SrF_2 doped with large rare earths does not have important differences from other fluorite systems although all fluorite systems have important differences that depend on the dopant ion size. Small ions form larger clusters like hexamers while large ions form smaller clusters like dimer and trimers. The clusters getter extra F_i' that decreases the importance of single pairs and increases the cubic sites. Defect interactions cause line broadening, changes in the formation energy of NN and NNN pairs, and nonideality corrections that destroy random distributions and increase the shielding effects that are important in determining the activity coefficients in the mass action relationships. Quenching can destroy the clusters and increase the number of cubic and single-pair sites. The activity effects are still important enough to cause anomalous ratios in the cubic to single-pair site ratio.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grant No. DMR-8815398. Acknowledgment is also made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

---

*Present address: Department of Chemistry, Walla Walla College, College Place, WA 99324.

[1] R. W. Ure, J. Chem. Phys. **26**, 1363 (1957).

[2] C. W. Rector, B. C. Pandey, and H. W. Moos, J. Chem. Phys. **45**, 171 (1966).

[3] V. V. Osiko, Fiz. Tverd. Tela (Leningrad) **7**, 1294 (1965) [Sov. Phys. Solid State **7**, 1047 (1965)].

[4] Yu. K. Voron'ko, V. V. Osiko, and I. A. Shcherbakov, Zh. Eksp. Teor. Fiz. **56**, 151 (1969) [Sov. Phys. JETP **29**, 86 (1969)].

[5] J. Makovsky, J. Chem. Phys. **46**, 390 (1967).

[6] L. D. Livanova, I. G. Saitkulov, and A. L. Stolov, Fiz. Tverd. Tela (Leningrad) **11**, 918 (1969) [Sov. Phys. Solid State **11**, 750 (1969)].

[7] V. V. Orsyankin and P. P. Feofilov, Opt. Spectrosc. **31**, 510 (1971).

[8] J. B. Fenn, J. C. Wright, and F. K. Fong, J. Chem. Phys. **59**, 5591 (1973).

[9] A. D. Franklin and S. Marzullo, Proc. Brit. Ceram. Soc. **19**, 135 (1971).

[10] G. K. Miner, T. P. Graham, and G. T. Johnston, J. Chem. Phys. **57**, 1263 (1972).

[11] J. M. O'Hare, T. P. Graham, and G. T. Johnston, J. Chem. Phys. **61**, 1602 (1974).

[12] A. D. Franklin, J. Chem. Phys. **64**, 1509 (1976).

[13] P. P. Yaney, D. M. Schaeffer, and J. L. Wolf, Phys. Rev. B **11**, 2460 (1975).

[14] D. R. Tallant, D. S. Moore, and J. C. Wright, J. Chem. Phys. **67**, 2897 (1977).

[15] R. J. Hamers, J. R. Wietfeldt, and J. C. Wright, J. Chem. Phys. **77**, 683 (1982).

[16] D. S. Moore and J. C. Wright, J. Chem. Phys. **74**, 1626 (1981).

[17] J. R. Wietfeldt and J. C. Wright, J. Chem. Phys. **86**, 400 (1987).

[18] J. C. Wright, Cryst. Latt. Def. Amorph. Mater. **12**, 505 (1985).

[19] A. Edgar and H. K. Welsh, J. Phys. C **8**, L336 (1975).

[20] C. Andeen and J. Fontanella, J. Phys. Chem. Solids **38**, 237 (1977).

[21] J. Fontanella, C. Andeen, and D. Schuele, Phys. Rev. B **17**, 3429 (1978).

[22] C. Andeen, G. E. Matthews, Jr., M. K. Smith, and J. Fontanella, Phys. Rev. B **19**, 5293 (1979).

[23] C. Andeen, J. Fontanella, and M. C. Wintersgill, J. Phys. C **13**, 3449 (1980).

[24] C. Andeen, D. Link, and J. Fontanella, Phys. Rev. B **16**, 3762 (1977).

[25] J. Fontanella, D. Treacy, and C. Andeen, J. Chem. Phys. **72**, 2235 (1980).

[26] M. C. Wintersgill, J. Fontanella, P. Welcher, R. J. Kimble, and C. Andeen, J. Phys. C **13**, L661 (1980).

[27] C. G. Andeen, J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, R. J. Kimble, and G. E. Matthews, J. Phys. C **14**, 3557 (1981).

[28] C. R. A. Catlow, M. J. Norgett, and T. A. Ross, J. Phys. C **10**, 1627 (1977).

[29] C. R. A. Catlow, J. Phys. C **6**, L64 (1973).

[30] C. R. A. Catlow, J. Phys. C **9**, 1845 (1976).

[31] C. R. A. Catlow, J. Phys. C **9**, 1859 (1976).

[32] C. R. A. Catlow, M. J. Norgett, and T. A. Ross, J. Phys. C **10**, 1627 (1977).

[33] J. Corish, C. R. A. Catlow, P. W. M. Jacobs, and S. H. Ong, Phys. Rev. B **25**, 6425 (1982).

[34] C. R. A. Catlow, A. V. Chadwick, and J. Corish, J. Solid State Chem. **48**, 65 (1983).

[35] P. J. Bendall, C. R. A. Catlow, J. Corish, and P. W. M. Jacobs, J. Solid State Chem. **51**, 159 (1984).

[36] P. J. Bendall, C. R. A. Catlow, and B. E. F. Fender, J. Phys. C **17**, 797 (1984).

[37] C. R. A. Catlow, A. V. Chadwick, J. Corish, L. M. Moroney, and A. N. O'Reilly, Phys. Rev. B **39**, 1897 (1989).

[38] C. R. A. Catlow, A. V. Chadwick, G. N. Greaves, and L. M. Moroney, Nature **312**, 601 (1984).

[39] D. S. Moore and J. C. Wright, Chem. Phys. Lett. **66**, 173 (1979).

[40] K. M. Cirillo-Penn and J. C. Wright, Phys. Rev. B **41**, 10 799 (1990).

[41] H. W. den Hartog, Phys. Rev. B **27**, 20 (1983).

[42] J. Meuldijk, G. Kiers, and H. W. den Hartog, Phys. Rev. B **28**, 6022 (1983).

[43] J. Meuldijk, R. van der Meulen, and H. W. den Hartog, Phys. Rev. B **29**, 2153 (1984).

[44] P. Dorenbos and H. W. den Hartog, Phys. Rev. B **31**, 3932 (1985).

[45] P. Dorenbos, S. Vrind, J. Dolfing, and H. W. den Hartog, Phys. Rev. B **35**, 5766 (1987).

[46] P. Dorenbos, H. W. den Hartog, R. Kruizinga, and S. Vrind, Phys. Rev. B **35**, 5774 (1987).

[47] P. Dorenbos, A. v. d. Lee, and H. W. den Hartog, Phys. Rev. B **37**, 10 312 (1988).

[48] P. Dorenbos and H. W. den Hartog, Phys. Rev. B **40**, 5817 (1989).

[49] B. M. Tissue and J. C. Wright, Phys. Rev. B **36**, 9781 (1987).

[50] J. Meuldijk, H. H. Mulder, and H. W. den Hartog, Phys. Rev. B **25**, 5204 (1982).

[51] H. W. den Hartog and J. van der Veen, Phys. Rev. B **37**, 1807 (1988).

[52] P. M. Mjwara, J. D. Comins, P. E. Ngoepe, and A. V. Chadwick, Cryst. Latt. Def. Amorph. Mater. (to be published).

[53] C. R. A. Catlow, R. T. Harley, and W. Hayes, J. Phys. C **10**, L559 (1977).

[54] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, W. Hayes, and I. B. Owen, J. Phys. C **14**, 329 (1981).