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Nuclear magnetic resonance study of superionic conductors with tysonite structure

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Abstract. The fluorine mobility in single crystals of the anion-deficient solid solution $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ ($x = 0, 0.001, 0.003, 0.01, 0.03, 0.05$ or 0.16) with the tysonite structure has been studied in the temperature range of 130–520 K by ^{19}F NMR. Different modes of ionic motion were identified and the leading mechanism of ionic diffusion has been suggested. The influences of temperature and fluorine vacancy concentration on the ionic mobility in tysonite have been investigated. In all crystals, fluorine diffusion begins in the F_1 sublattice. On increase in the temperature, ionic exchange between the F_1 and $F_{2,3}$ sublattices becomes observable. Addition of small amounts of Sr ($x < 0.003$) significantly increases the ionic mobility between the sublattices. For $0.003 < x < 0.03$ a further increase in x has no significant influence on the ionic exchange. Around $x \approx 0.01$ the beginning of cluster formation is noticeable. At higher concentrations ($0.03 < x < 0.16$) it is seen that ionic mobility decreases again and the guest-induced vacancies are preferentially located in the F_1 sublattice. At these doping concentrations the influence of large clusters seems to play a significant role.

1. Introduction

The superionic conductor lanthanum trifluoride LaF_3 is known as a good solid electrolyte with potential applications in many different electrochemical devices [1]. It possesses the so-called tysonite structure ($P\bar{3}c1$) and exhibits relatively high ionic conductivity above room temperature [2–6]. In the tysonite structure of LaF_3 , all cations (La) are located in planes which are perpendicular to the main symmetry axis c and indicated in figure 1 by bold lines. The cations remain immobile over the whole temperature range studied. The fluorine anions are located in three distinct positions F_1 , F_2 and F_3 in the ratio of 12:4:2 per unit cell [2, 3]. The fluorine atoms are not only structurally but also dynamically non-equivalent. It is an established fact that ionic diffusion begins in only one fluorine sublattice first, but it is still controversial in which one. In some earlier publications it was concluded that the mobile ions are more probable in the F_2 and F_3 sublattices [7–9], or in the F_3 sublattice only [10]. In contradiction to these studies, others pointed to the fact that F_1 ions have the highest mobility [11–15]. In particular, NMR data obtained in a high magnetic field using line-narrowing multiple-pulse techniques gave strong evidence that ionic diffusion starts in the F_1 sublattice of LaF_3 at around 290 K [16, 17]. The behaviour of fluorine atoms from the F_2 and F_3 sublattices were found to be very similar and for our purposes these sublattices can be considered structurally and dynamically equivalent.

The fluorine mobility in tysonite is due to a vacancy mechanism; the intrinsic point defects in LaF_3 are assumed to be of the Schottky type [9]. The usual way to control

the concentration of vacancies is the heterovalent isomorphous replacement of some La^{3+} cations by Ca^{2+} , Sr^{2+} or Ba^{2+} . With increase in the vacancy concentration the ionic mobility and conductivity also increase [9, 14]. For practical purposes it is very important that LaF_2 can form stable solid solutions with the fluorides MF_2 of alkaline-earth metals over a wide range of guest concentrations x . Such composite materials with a tysonite structure already possess a high ionic conductivity below room temperature, which is an important advantage in practical applications [6].

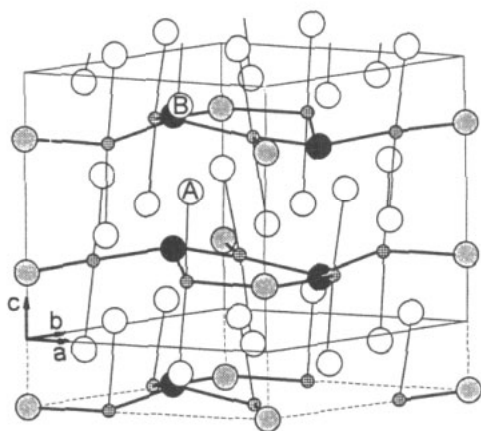


Figure 1. The unit cell of LaF_3 with the tysonite structure. The anions from different sublattices are as follows: open circles, F_1 ; closed circles, F_2 ; shaded circles, F_3 . The cations are as follows: small hatched circles, La. The lattice parameters are $a = b = 7.185 \text{ \AA}$ and $c = 7.351 \text{ \AA}$. For details see text.

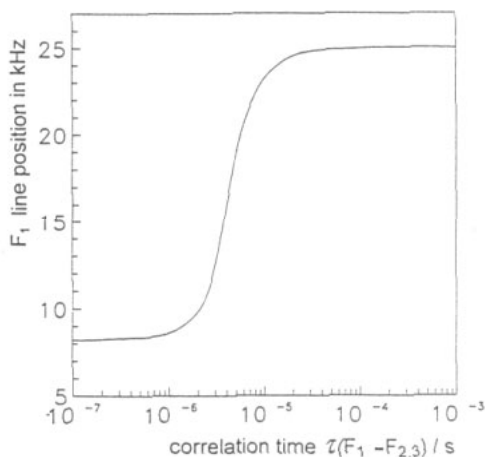


Figure 2. Calculated centre position of the F_1 line as a function of the correlation time $\tau(F_1-F_{2,3})$ of the ionic mobility between the F_1 and the $F_{2,3}$ sublattices. In the rigid limit the F_1 line is at +25 kHz and the $F_{2,3}$ line is at -25 kHz.

In spite of numerous investigations and broad practical use of materials with a tysonite-like structure, several questions about the microscopic mechanism of ionic motion in these crystals are still under debate today. A main problem is how the increase in the vacancy concentration by doping with fluorides MF_2 of bivalent metals affects the mechanism of fluorine mobility in the different structurally non-equivalent fluorine sublattices. As NMR is known to be a method well suited to the investigation of atomic motion in solids, we have applied ^{19}F NMR to the analysis of atomic mobility in tysonite crystals. In this paper we report a study of the influence of the fluorine vacancy concentration (created by heterovalent isomorphous replacement of La^{3+} cations by Sr^{3+}) on the ionic mobility in solid solutions of $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ ($x = 0, 0.001, 0.003, 0.01, 0.03, 0.05$ or 0.16) at temperatures ranging from 130 to 520 K. The high spectral resolution resulting from the pronounced chemical shifts in a strong magnetic field ($B_0 = 7 \text{ T}$) allows us to separate the spectral components of the different fluorine sublattices, and to investigate their temperature behaviours independently. The lineshape resulting from dipolar spin coupling as well as from the chemical shifts is very sensitive to the atomic mobility. From the comparison with calculated dipolar spectra it is possible to identify the fluorine sublattices clearly. From the variation in the F_1 dipolar lineshape with temperature the correlation times of fluorine jumps can be calculated. For the thermal diffusion within the separated F_1 sublattice, activation energies can be determined. From the changes in the line position with rising temperature, information

about the correlation time of ionic exchange between the F_1 and $F_{2,3}$ sublattices can be evaluated, and its activation energy calculated.

2. Experimental details

The experimental ^{19}F NMR spectra are Fourier transforms of the free induction decays recorded with a Bruker CXP-300 spectrometer at 7.05 T corresponding to a resonance frequency of 282 MHz. The length of the 90° RF excitation pulse is 1 μs , which is sufficiently short to excite the necessary spectral range.

The single crystals of $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ ($x = 0, 0.001, 0.003, 0.01, 0.03, 0.05, 0.10$ or 0.16) were grown by means of a modified Stockbarger method as described in [9]. The samples were tested optically with respect to their single-crystal nature and the alignment of their c axis which is the main symmetry axis perpendicular to the $\text{La}-\text{F}_{2,3}-\text{La}$ plane. The dimensions of the NMR sample crystals are about $3 \times 3 \times 6$ mm. All crystals were kept under vacuum and were oriented in the magnetic field with $B_0 \parallel c$ with an accuracy of $\pm 2^\circ$.

3. Calculations

In ^{19}F NMR it is safe to assume that the spectral shape is dominated by the magnetic dipole interaction and the chemical shift. Since an exact calculation of dipolar NMR spectra in solids is impossible owing to the enormous number of interacting spins, we used an approximation method as described in an earlier article [16]. For the determination of the correlation times for the ionic jumps between the F_1 and $F_{2,3}$ sublattices the NMR spectrum was calculated on the basis of a two-site exchange between non-equivalent spectral positions [18]. The shift in the F_1 line position as a function of the F_1 - $F_{2,3}$ exchange rate is very sensitive to the correlation time of this process in the range of 10^{-4} - 10^{-6} s as seen in figure 2. The shift values for the individual rigid fluorine sublattices were determined from the experiments at a low temperature (160 K). The activation energies E_a were taken from an Arrhenius fit of the corresponding correlation times $\tau \propto \exp(E_a/kT)$.

4. Results

In figure 3 the dipolar broadened spectra of single crystals with B_0 oriented along the c axis are shown for different temperatures; in this particular example the composition is $\text{La}_{0.99}\text{Sr}_{0.01}\text{F}_{2.99}$, but the general structure of the spectra is similar for all values of x . At low temperatures the NMR spectrum of all crystals consists of two components with an intensity ratio of around 2:1 and chemical shift values σ_{F_1} of 92 ppm and $\sigma_{F_{2,3}}$ of 172 ppm with reference to liquid C_6F_6 . The large component corresponds to the F_1 sublattice and the small component is a superposition from the F_2 and F_3 sublattices [16]. The doublet structure of the F_1 signal is caused by strong dipole-dipole interaction within pairs of spins which are nearest neighbours in the direction of the c axis. In figure 1 for one representative pair these spins are denoted as A and B, respectively. The doublet splitting of the F_1 line, 20.5 kHz, is in full agreement with the distance between them, 2.48 Å. The dipole-dipole interaction between all other fluorine spins is much smaller and produces only additional broadening of the resonance lines. The F_2 and F_3 ions have an almost identical NMR lineshape with

very similar chemical shifts; hence to a good approximation they can be described as one common $F_{2,3}$ sublattice.

Partial substitution of La^{3+} cations by Sr^{2+} in the tysonite lattice induces additional fluorine vacancies. Using the F_1 to $F_{2,3}$ intensity ratio of the spectral components at low temperatures it can be determined for all crystal compositions in which of the sublattices these vacancies are more probably located. From our data this ratio has a tendency to decrease with increasing guest concentration x . The F_1 to $F_{2,3}$ ratio is 2.00 ± 0.05 for $0 \leq x \leq 0.03$, 1.95 ± 0.05 for $x = 0.05$ and 1.80 ± 0.05 for $x = 0.16$. From this we conclude that at low temperatures the fluorine vacancies are located preferentially in the F_1 sublattice. This agrees with results of extended x-ray absorption fine-structure measurements on $CeF_3:SrF_2$ solid solutions also having a tysonite structure, which suggests that F^- defects are preferentially formed in the F_1 sublattice [17]. The temperature behaviour of the ionic mobility has the same character in all crystals investigated and can be subdivided into three stages.

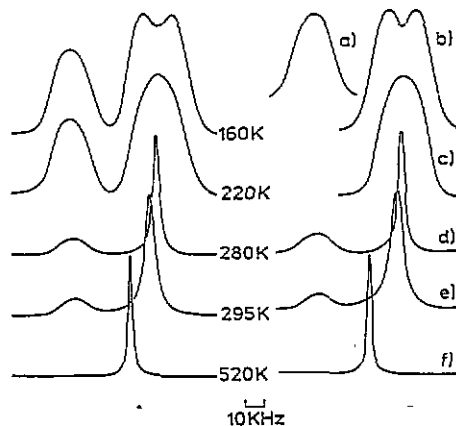


Figure 3. ^{19}F NMR spectra of single-crystal $La_{0.99}Sr_{0.01}F_{2.99}$ for $B_0 \parallel c$, showing the experimental spectra for different temperatures on the left and the calculations for the following on the right: curve (a) rigid $F_{2,3}$ sublattice; curve (b), rigid F_1 sublattice; curve (c), same as curve (b) with F_1-F_1 ionic exchange with $\tau(F_1-F_1) = 2 \times 10^{-5}$ s; curve (d), F_1-F_1 exchange with $\tau(F_1-F_1) = 10^{-6}$ s and $F_1-F_{2,3}$ exchange with $\tau(F_1-F_{2,3}) = 10^{-3}$ s; curve (e), same with $F_1-F_{2,3}$ exchange with $\tau(F_1-F_{2,3}) = 2 \times 10^{-5}$ s, curve (f), exchange between all positions with $\tau = 10^{-7}$ s. The signal amplitudes are scaled to give the same maximum, except for curve (a) where the integrated intensity is scaled to half the value for curve (b) in accordance with the relative spin population of the respective sublattices.

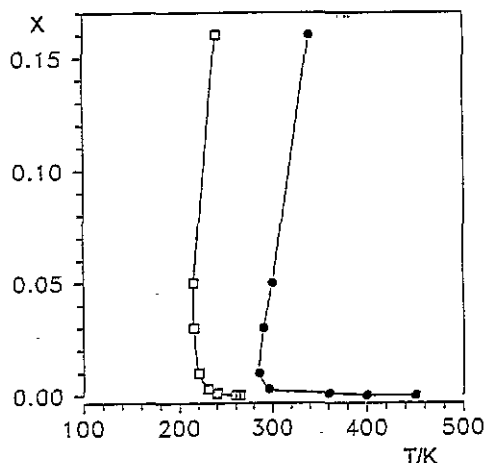


Figure 4. Variation in the characteristic temperature (for which the ionic exchange has the correlation time $\tau \approx 2 \times 10^{-5}$ s) with guest concentration x : \square , mobility within the F_1 sublattice; \bullet , ionic exchange between the F_1 and $F_{2,3}$ sublattices.

At first, intense ionic motion begins in the F_1 sublattice as inferred from motional line narrowing and the eventual disappearance of the doublet structure at a characteristic temperature $T(F_1-F_1)$. For this temperature the correlation time of the ionic jumps is $\tau(F_1-F_1) \simeq 2 \times 10^{-5}$ s as seen in figure 3, curve (c). In figure 4 the variation in $T(F_1-F_1)$

is shown as function of the guest concentration x . Above $T(F_1-F_1)$ the F_1 signal is a single line because of the averaging of dipolar coupling F_1-F_1 by the ionic motion. From further narrowing of the residual F_1 dipolar linewidth with rising temperature the activation energy $E_a(F_1-F_1)$ of diffusion between F_1 positions can be evaluated. Within the margin of experimental accuracy these energies have the same value $E_a(F_1-F_1) = 0.20 \pm 0.02$ eV for all crystals with $x \leq 0.03$ and show the tendency to decrease for higher x concentrations. In the latter case the accuracy is not sufficient for a quantitative evaluation because of increasing difficulties in separating F_1-F_1 ionic diffusion from $F_1-F_{2,3}$ jumps. Our results are in good agreement with earlier measurements obtained with different techniques; in NMR relaxation studies the activation energy of the F^- motion in the fast sublattice of pure LaF_3 was found to be 0.27 eV [15]. Also, thermally stimulated depolarization currents measured in single crystals of LaF_3 doped with 0.5 mol% CaF_2 showed that the activation energy of the reorientation of Ca^{2+} -fluorine vacancy complexes is 0.19 eV in the temperature range above 120 K [19].

The high mobility in the F_1 sublattice has almost no effect on the dipolar broadening of the F_2 component because of the comparatively small size of the $F_1-F_{2,3}$ dipolar interactions. As neither the lineshape of the F_2 component nor the positions of the F_1 and $F_{2,3}$ lines show significant changes, we can conclude that ionic exchange between F_1 and $F_{2,3}$ positions remains slow in this temperature range. This confirms that, under these conditions, ionic mobility occurs only in the F_1 sublattice. Narrowing of the F_1 line with no change in its centre position is observed only for the crystals with low concentration $x (< 0.01)$ and only up to some temperature limit above which the F_1 component becomes broader again with its position shifting towards the $F_{2,3}$ line. This reflects the beginning of ionic exchange between the F_1 and $F_{2,3}$ structural positions which is characteristic of the second stage of ionic motion (cf figure 3, curve (e)).

It is remarkable that first the F_1 to $F_{2,3}$ intensity ratio increases, while the position of the $F_{2,3}$ component and its width are still nearly the same as without $F_1-F_{2,3}$ exchange. This indicates that more and more $F_{2,3}$ ions are jumping into F_1 positions and back. The contribution of these jumping ions to the NMR spectrum is suppressed because of motional broadening and hence a decrease in the amplitude of the NMR line. At the same time the NMR signal from immobile $F_{2,3}$ ions (correlation time $\tau_{F_{2,3}} \gg 10^{-5}$ s) is predominantly determined by $F_{2,3}-F_{2,3}$ and $F_{2,3}$ -La dipole-dipole interactions; thus its shape stays unchanged. On the other hand the shift in the F_1 position (figure 2) can be used to evaluate the correlation times of ionic exchange between F_1 and $F_{2,3}$ positions. In figure 4 the temperatures are shown for which the correlation time $\tau(F_1-F_{2,3})$ has the value of 2×10^{-5} s. It can be seen that the addition of even a small amount of SrF_2 ($x \leq 0.003$) strongly lowers the onset temperature of $F_1-F_{2,3}$ exchange. For example in $\text{La}_{0.997}\text{Sr}_{0.003}\text{F}_{2.997}$ this temperature is 150 K lower than in pure LaF_3 . For comparison the corresponding temperature decrease in the F_1-F_1 exchange is only about 50 K.

Raising the guest concentration x beyond 0.01 has no significant effect on the ionic exchange. For the highest x -values there is even an indication of decreasing ionic mobility, since the ionic exchange reaches the correlation time τ of about 2×10^{-5} s at increasing temperatures when x is raised beyond 0.03.

We interpret this as an indication of a change in the vacancy interaction character at high doping concentrations, which leads to the formation of impurity clusters. A similar cluster formation was observed in CaF_2 ionic crystals doped with M^{3+} [20, 21].

From the temperature dependence of the correlation times $\tau(F_1-F_{2,3})$ the activation energies of the $F_1-F_{2,3}$ exchange process have been determined. For the samples with $x < 0.03$ we obtained $E_a(F_1-F_{2,3}) = 0.08 \pm 0.02$ eV. For high concentrations x this energy

increases. For tysonites with $0.03 \leq x \leq 0.16$ and temperatures higher than 500 K a significant deviation from Arrhenius behaviour is observed. The lowest temperatures for the beginning of significant mobility are found for samples with $x = 0.003$ – 0.03 .

Finally, in a third stage of ionic mobility, the separation of the F_1 and $F_{2,3}$ lines disappears and only one common NMR line is observed at an intermediate position σ which is in good agreement with the rule for fast spectral exchange:

$$\sigma = \frac{\sigma(F_1)N(F_1) + \sigma(F_{2,3})N(F_{2,3})}{N(F_1) + N(F_{2,3})}$$

where $N(F_1)$ and $N(F_{2,3})$ are the spin population numbers of positions $\sigma(F_1)$ and $\sigma(F_{2,3})$. This means that the ionic exchange occurs now among all structural positions F_1 and $F_{2,3}$ in tysonite and has a correlation time $\tau(F_1-F_{2,3}) < 10^{-6}$ s (see figure 3(f)). Because of the limited accessible temperature range in our experiments the latter effect has been observed only for crystals with $x > 0.01$.

5. Conclusions

Solid electrolytes of the composition $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ with the tysonite structure exhibit a complicated process of ionic mobility, which can be satisfactorily described by a structural model with two fluorine sublattices. In the beginning, significant diffusion is restricted to the sublattice F_1 which forms layers of fluorine ions. The fluorine ions in the La plane (the $F_{2,3}$ sublattice) remain in comparatively slow motion. With increase in the temperature the ionic exchange between the F_1 and $F_{2,3}$ sublattices begins, but the internal mobility of $F_{2,3}$ remains small. At even higher temperatures, ionic exchange occurs between all structural positions in the crystal lattice. Increasing the ionic vacancy concentration by means of heterovalent isomorphous replacement of La^{3+} cations with Sr^{2+} can very strongly lower the onset temperatures of ionic diffusion.

We can distinguish three regimes when increasing the Sr^{2+} concentration. First, for $0.0 \leq x \leq 0.003$, a very pronounced decrease in the onset temperatures of ionic mobility occurs while the activation energies stay unchanged. Here, the vacancies are probably located in both sublattices. Then, for $0.003 \leq x \leq 0.03$, a further increase in x has no significant effect on the temperature behaviour of the ionic exchange or on the activation energies. The vacancies tend to occupy the F_1 sublattice preferentially. Our results indicate that in the heterovalent solid solution $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ we have the beginning of cluster formation at $x \geq 0.01$. Finally, for $0.03 \leq x \leq 0.16$, the vacancies are mainly located in the F_1 sublattice. The temperatures of constant ionic diffusion among the sublattices are slightly increasing. The activation energy of F_1 – F_1 diffusion decreases, while the activation energy of F_1 – $F_{2,3}$ diffusion increases. At these doping concentrations the influence of large clusters seems to play a predominant role.

For constant temperature the fastest ionic diffusion in the solid electrolytes $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ with the tysonite structure is observed when $0.003 \leq x \leq 0.03$. In this region the mobility parameters are rather insensitive with respect to changes in x , an important advantage for practical applications; altogether the sample composition of $\text{La}_{0.99}\text{Sr}_{0.01}\text{F}_{2.99}$ has the optimum properties for electrochemical applications.

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