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Fluorine mobility in the aluminum doped CeF_3 crystal: NMR and conductivity studies

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Electrical conductivity and NMR measurements were carried out for the aluminum doped CeF_3 crystal to study influence of substitutional impurities on the superionic fluorine mobility. Activation enthalpy was found to remain constant from low temperatures to about 325 K while it increased compared to that of the pure CeF_3 crystal. Above about 325 K a trand towards gradual conductivity saturation was observed, this change was ascribed to a superionic phase transition, which was not accompanied with structural transformations. NMR also revealed some alterations in local fluorine dynamics compared to that reported for the pure CeF_3 crystal. According to NMR measurements, the superionic phase transition near 325 K results in acceleration of the exchange between rigid or slow fluorine in the F_1, F_2 and F_3 sublattices while highly mobile F_1 fluorine ions move independently at least until 400 K.

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1. Introduction

The cerium fluoride, CeF_3, belongs to a group of trifluoride crystals with tysonite-type structure, which evince high ionic mobility already at room temperature ([1–4] and references therein). The space group is $P\bar{3}c1$ [5]. The pure CeF_3 crustal has three non-equivalent fluorine sublattices with different dynamics ([2–4,6] and references therein). It was found from electrical conductivity measurements [7] that CeF_3, like other fluorides LnF_3 (Ln = La and Nd) [2,7], exhibits at about 435 K strong alterations in the character of fluorine mobility which manifest themselves as an abrupt change in the activation enthalpy but are not accompanied with a structural phase transition. Much weaker change in the activation enthalpy was also observed near 290 K [2,8]. For the neodymium fluoride the temperatures of similar changes in the activation enthalpy were associated with bends on the temperature dependences of the tysonite lattice parameters a and c [2]. Doping the fluoride crystals influences deeply not only the activation enthalpy but also local dynamics of fluorine ions [2–4]. This provides additional information about mechanisms of superionic mobility in trifluoride crystals. In this paper we present results of studies of fluorine mobility in the mixed $Ce_{0.95}Al_{0.05}F_3$ crystal on the basis of electrical conductivity and ^{19}F NMR.

2. Samples and experiment

The mixed cerium aluminum fluoride single crystal with composition of $Ce_{0.95}Al_{0.05}F_3$ was grown by the Bridgman–Stockbarger method. According to x-ray powder diffraction, the crystal structure is tysonite-like and the crystal is single-phase. The lattice parameters are $a = 7.177$ Å and $c = 7.277$ Å. The composition of the crystal was checked by Inductively Coupled Plasma (ICP) optical emission spectrometry and chemical analysis.

The sample for conductivity measurements had a form of a parallelepiped with dimensions of $10.5\times8\times5$ mm cut along the crystallographic axes. The temperature dependence of the conductivity was recorded using an immitance meter E7-14 operating at four fixed frequencies 0.1, 1, and 10 kHz and 1 MHz. The gold film electrodes were made on the sample faces, which were perpendicular and parallel to the c axis. During the measurements the temperature gradually varied within the range of 110 to 510 K with the rate of 1 K/min.

NMR measurements were carried out using a Bruker Avance400 NMR spectrometer within the temperature range of 290 to 400 K. The ^{19}F NMR line for the $Ce_{0.95}Al_{0.05}F_3$ powder sample was observed as the Fourier transform of the free-induction signal after a 90° pulse. The rate of changing temperature was no more than 1 K/min. Prior to each measurement the sample was kept at a fixed temperature for about 10 minutes. The accuracy of temperature control was better than 1 K.

3. Results and discussion

Fig. 1 shows the results of the conductivity measurements along the c axis at four different frequencies. Above about 230 K the sample displays high ionic conductivity which does not depend of frequency at higher temperatures in agreement with the delocalized nature of fluorine mobility. The logarithmic curves are straight lines for lower frequencies between about 230 and 325 K. The activation enthalpy calculated from these curves is equal to 0.54 eV. This enthalpy is somewhat higher than that found

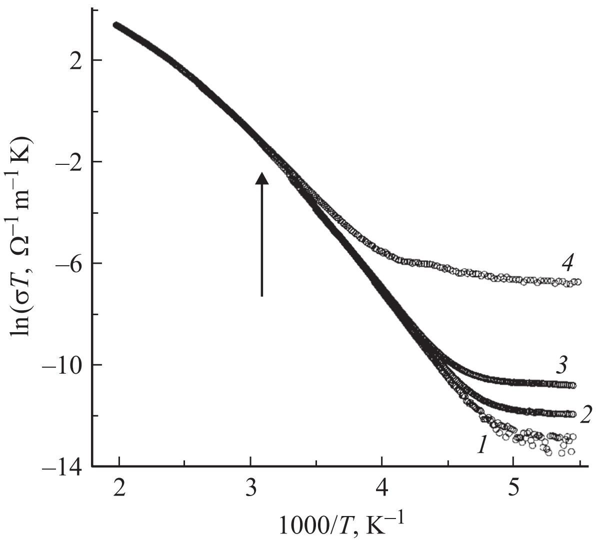

Figure 1. Logarithm of electrical conductivity parallel to the c axis measured at 0.1 (*1*), 1 (*2*), 10 (*3*), and 1 MHz (*4*) multiplied by temperature versus inverse temperature. The arrow marks a temperature of the onset of curve deviation from the linear dependence.

within the corresponding temperature range for the pressed polycrystalline pure CeF$_3$ sample (0.45 eV) [2]. At about 325 K the curves exhibit noticeable changes in the slope. Contrary to pure CeF$_3$ [2], the logarithmic curves for the sample under study cannot be approximated by straight lines above 325 K but rather evidences a gradual saturation of the conductivity with increasing temperature up to 510 K. Note, that the conductivity in the mixed fluoride under study is slightly less than in the pure cerium fluoride [2]. The behavior of the conductivity in the direction perpendicular to the c axis for the sample under study was very similar to that along the c axis in agreement with weak anisotropy of ionic mobility in fluorides with tysonit-like structure [9,10]. Nevertheless, the activation enthalpy evaluated below 325 K was a little higher for conductivity perpendicular to the c axis than for that parallel to the c axis and equal to 0.56 eV.

^{19}F NMR studies showed strong changes in the lineshape with increasing temperature from 190 K reflecting alterations in fluorine mobility. Some NMR spectra are depicted in Fig. 2. Near room temperature the lineshape is very similar to that observed in the pure cerium fluoride crystal near and below room temperature [11]. According to [2–4,6,11], in crystals with tysonite-like structure there are three different fluorine sublattices, usually referred to as F$_1$, F$_2$, and F$_3$. Fluorine ions in the F$_1$ sublattice were found to be mobile even at low temperatures, while the F$_2$ and F$_3$ sublattices (often referred to as the F$_{23}$ sublattice) remained still rigid. Fluorine ions in the second and third rigid sublattices have about the same surroundings and chemical shift, so their NMR lines overlap. The amount of fluorine in the F$_1$ sublattice is about twice as much as in the F$_{23}$ sublattice. Thus, below room temperature in pure tysonite-like crystals one can normally see two distinct peaks ascribed to fluorine in the F$_1$ and F$_{23}$ sublattices with positive and negative chemical shifts, respectively [2,4]. With increasing temperature up to room temperature, an additional peak may appear [2] because of increasing partial exchange of fluorine between the F$_1$ and F$_{23}$ sublattices. Which of the two sublattices, F$_2$ or F$_3$, first starts exchanging with the F$_1$ sublattice and becomes mobile remains still under debate [2,12]. In [12] the additional peak was not observed. Instead of this, the F$_1$ peak slightly shifted and intensified when the F$_1$–F$_{23}$ exchange became faster that was explained by fact interchange within the F$_1$ sublattice.

Thus, two distinct peaks with chemical shifts of about 450 and −400 ppm which were seen in the sample under study near room temperature (where ionic conductivity is still moderate) can be mainly attributed to fluorine in the F$_1$ and in the F$_{23}$ sublattices, respectively. The integral intensity of the F$_{23}$ peak is noticeably less than half of that of the F$_1$ peak. This means that only part of fluorine in the F$_{23}$ sublattice remains rigid. Another part participates in the exchange between the F$_1$ and the F$_{23}$ sublattices. Mobile

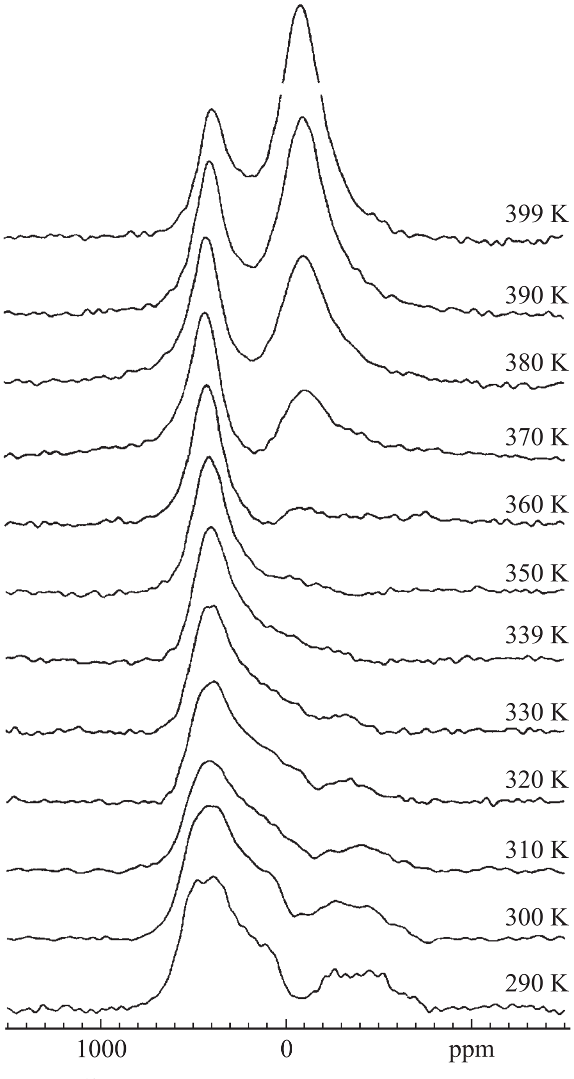

Figure 2. ^{19}F NMR spectra at several temperatures from 290 to 399 K.

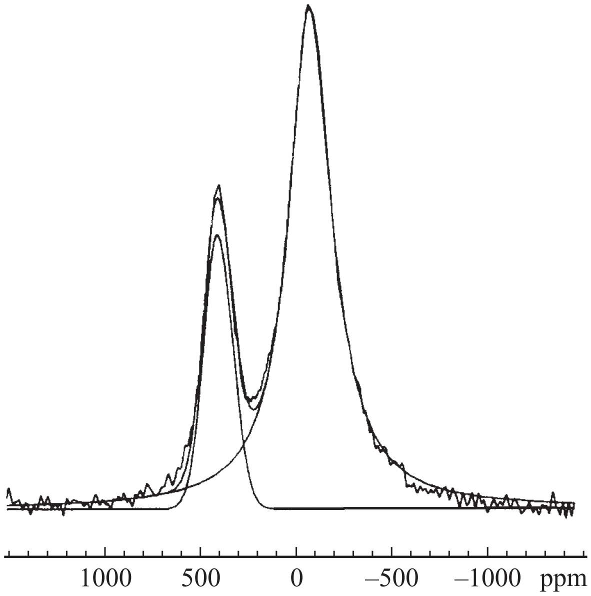

Figure 3. Deconvolution of the ^{19}F NMR spectrum at 393 K.

ions originated from the F_{23} sublattice might from the right shoulder of the high-frequency peak.

Above room temperature the position and the intensity of the main peak with positive chemical shift remains practically unchanged while drastic alterations occur in NMR line at lower frequency region. First, with increasing temperature, the F_{23} peak vanishes completely by 340 K and the low frequency shoulder of the main peak smoothes away. At 350 K one can actually see only rather symmetric single NMR line with the chemical shift of about 400 ppm. Above about 360 K, a new peak appears with the chemical shift of about –100 ppm, its intensity gradually increases with increasing temperature. The shape of this peak can be well fitted by the Lorentzian function contrary to the shape of the higher frequency peak which is well simulated by a Gaussian function as can be seen in Fig. 3 for 393 K. At about 400 K, the new peak dominates the ^{19}F NMR spectrum.

On the whole, the obtained results differ drastically from temperature dependences of NMR spectra in pure CeF_3 which were reported in [2]. The appearance of the new peak above 360 K can be hardly explained by fast exchange between mobile fluorine in the F_1 sublattice and fluorine in the F_{23} sublattice, as it was done for the pure CeF_3 and some other trifluoride crystals in [2,4,12]. In fact, when this peak starts rising, the intensity and position of the F_1 peak do not change noticeably. Another supposition seems to be more credible. One can assume that the single peak at 350 K, which remains stable from room temperature up to at least 399 K, originates from mobile fluorine in the F_1 sublattice. Jumps of those fluorine atoms are mainly responsible for conductivity near and below room temperature with the constant activation enthalpy. Above room temperature acceleration in ion exchange between slow or rigid fluorine in the F_2, F_3, and F_1 sublattices leads first to smearing the relevant resonance lines and then to rising the new peak. Since integral intensity of the new peak at, for instance, 390 K, is higher than that of the high-frequency peak, one can suggest that the number of fluorine ions in the F_1 sublattice, which remain slow or rigid near room temperature, is at least comparable with the number of mobile F_1 fluorine ions. Note that the Lorentzian shape of the new peak corresponds to high mobility of collective fluorine ions.

The change in character of fluorine mobility could be treated as a superionic phase transition in type II ionic conductors [1]. Such superionic phase transitions are accompanied with saturation of conductivity [1] in agreement with the results shown in Fig. 1. According to Fig. 1, the onset of saturation of conductivity starts at about 325 K and this agrees with changes in NMR spectra shown in Fig. 2. A slight step in the lattice parameters and changes in activation enthalpy, which were seen near room temperature for some rare-earth trifluorides [2], support the existence of such a phase transition.

In conclusion, the conductivity and ^{19}F NMR spectra measurements in the $Ce_{0.95}Al_{0.05}F_3$ superionic crystal revealed noticeable distinctions from results for the pure CeF_3. The activation enthalpy near room temperature evaluated from conductivity was higher than in the pure crystal. The gradual conductivity saturation was seen at elevated temperatures contraty to a sharp bend reported for the pure CeF_3. The detailed observations of the NMR spectra evolution upon changing temperature showed that the simple picture of fast exchange between the whole F_1 and F_{23} sublattices used to treat the high-temperature spectra in the pure CeF_3 crystal is no longer valid for the doped crystal under study. The measurements also revealed a superionic phase transition near 325 K which is not accompanied with structural transformations.

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