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Characterization of four phase transitions in $Pb_5Al_3F_{19}$, including a new transition at 670 K, by impedance and NMR spectroscopy

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The ac (alternating current) conductivity of $Pb_5Al_3F_{19}$ between 293 and 743 K has been analyzed within a combined complex impedance, modulus, and permittivity formalism. The antiferroelectric phase IV to ferroelastic phase III, and the phase III to paraelastic phase II, transitions have been characterized; the latter is shown to be accompanied by higher F⁻ ion mobility above T=368 ± 5 K. A new dielectric anomaly observed isochronously in $\epsilon'(f,T)$ at 670 K corresponds to an expected, but hitherto unobserved, transition from phase II to the paraelectric prototype phase I of Pb₅Al₃F₁₉. A ¹⁹F NMR investigation between 125 and 430 K of F⁻ ion diffusion properties in Pb₅Al₃F₁₉ shows that half the anions have become mobile at the ferroelectric phase V to phase IV transition temperature and that almost all the anions are mobile at the phase IV to phase III transition temperature. These motions are shown to be short range, and no correlation is found between phase formation and F⁻ ion diffusion properties in Pb₅Al₃F₁₉ in the temperature range below 320 K. © 1998 American Institute of Physics. [S0021-9606(98)50307-8]

I. INTRODUCTION

Lead aluminum fluoride $Pb_5Al_3F_{19}$ belongs to the ferroelectric $Pb_5M_3F_{19}$ family (M=Al,Ti,V,Cr,Fe,Ga) of MF₆ octahedral fluorides.¹ Two phases only form for M=Ti,V,Cr,Fe,Ga, a lower-temperature ferroelectric and a higher-temperature paraelectric phase; the transition between them at T_c is first order.² Pb₅Al₃F₁₉, by contrast, is characterized by multiple phase formation resulting from the simultaneous presence of the Pb^{2+} lone electron pair and a small trivalent cation. X-ray diffraction, thermal, optical, and dielectric studies of $Pb_5Al_3F_{19}$, using powder, ceramic, and single crystal samples, have revealed three phase transitions between 100 and 400 K,³ with phase transition sequence

V	$270 \text{ K} \rightarrow$	IV	$320 \text{ K} \rightarrow$	III	$360 \text{ K} \rightarrow$	II
ferroelectric		antiferroelectric		ferroelastic		paraelastic
tetragonal	←140 K	tetragonal	←305 K	monoclinic	←360 K	tetragonal
I4cm		P4/n		I2/c		I4/m

Each transition has been shown to be first order. Thermal hysteresis for the transition between phase V and phase IV is unusually large. The structure of phase II, phase IV, and phase V has been determined by single crystal analysis.^{4–8}

It is noteworthy that not one of the space groups formed by centrosymmetric phases IV, III, or II is a supergroup of I4cm, the space group of the ferroelectric phase. The possibility hence exists that a paraelectric prototype phase with likely space group I4/mcm, the supergroup for each of the lower temperature phases, may be found at higher temperature. In view of the new phase transition found at 670 K, see Sec. III A, the previous phase sequence notation has been changed to name the prototype phase I.

The $Pb_{1-x}Al_xF_{2+x}$ ($0 \le x \le 0.12$) solid solution has long been known to exhibit interesting electrical properties caused by the change in F⁻ ion mobility with temperature.^{9,10} Since $Pb_5Al_3F_{19}$ is not far from comparable compositions within the PbF_2-AlF_3 system, an investigation of its ionic conductivity and diffusion properties has been undertaken by impedance and ¹⁹F NMR (nuclear magnetic resonance) spectroscopy. The results reported hereunder include electrical characterization of its four phase transitions.

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TABLE I. Experimental conditions for the $^{19}\mathrm{F}$ and $^{27}\mathrm{Al}$ NMR investigations of $Pb_5Al_3F_{19}.$

	¹⁹ F	²⁷ Al
Spectrometer frequency (MHz)	188.283	52.115
Pulse width (μs)	0.7	1
Dead time delay (μs)	6	6
Recycle delay time (s)	10	20
Spectral width (MHz)	1	1
Filter width (MHz)	2	2

II. EXPERIMENT

A. Preparation

PbF₂ from Cerac (99.99%) was dried 10 h under vacuum at 473 K. AlF₃ was prepared by the reaction of Al₂O₃ with NH_4HF_2 , in the ratio of 1:6 under dry N_2 . The reaction was allowed to take place in several steps, first at 473 K for 2 h, then at 773 K for 2 h, finally at 1073 K for 5 h. After drying the resulting AlF₃ at 473 K for 10 h under vacuum, $Pb_5Al_3F_{19}$ was prepared from the stoichiometric mix of PbF_2 and AlF₃ by grinding in a dry box and placing in a gold tube. The risk of hydrolysis at higher temperature was eliminated by degassing under vacuum at 473 K for 2 h, filling the gold tube with dry argon, and sealing. The tube is then heated at 823 K for 15 h and finally brought to ambient temperature by natural cooling. X-ray diffraction analysis of the powder confirms that the reaction is complete and that the fluoride synthesized is the stable phase IV of Pb₅Al₃F₁₉ at room temperature, characterized by lattice parameters a=b=20.174 ± 0.005 Å and $c = 7.225 \pm 0.005$ Å.^{4,7}

B. Conductivity measurements

Conductivity measurements were made on powder samples pressed to form pellets, compactness about 90%, and sintered in sealed gold tubes under the same operating conditions as for synthesis. Vacuum-evaporated gold was used as electrode material. The electroded pellets were placed in a quartz measurement cell, degassed at 473 K for 2 h, and filled with argon to avoid possible hydrolysis. Electrical properties were measured by the method of Ref. 11, with resistances determined from the complex impedance using a frequency response analyzer (Solartron Model 1260). The frequency range was $10^{-2}-10^{6}$ Hz over a thermal interval 293–743 K in several temperature cycles.

C. ¹⁹F NMR spectroscopy

¹⁹F NMR experiments were performed on a Bruker MSL-200 spectrometer (B_0 =4.7 T) equipped with a standard variable-temperature unit for the range 125–430 K. The polycrystalline sample is maintained at each measurement temperature for 1 h for thermal stability. Storage of the large number of measurements acquired over a 5 h period results in high resolution. The operating conditions in Table I, with the ONEPULSE acquisition program,¹² were selected in view of the range in F⁻ ion diffusion coefficients in Pb₅Al₃F₁₉. The data so obtained were processed by Fourier transformation, using the WINNMR 1D program.¹³



FIG. 1. Complex impedance Cole–Cole plots of Z'' vs Z' for Pb₅Al₃F₁₉ at 418, 463, 478, 493, and 508 K. Frequency is inversely proportional to Z'.

The ¹⁹F NMR spectrum was simulated by use of the WINFIT program,¹⁴ which allows variation of peak position, peak height, linewidth, ratio of Gaussian to Lorentzian function, and relative percentage of their areas. In case a single Gaussian does not exactly fit the spectrum as registered, an appropriate mix of Gaussian and Lorentzian functions is used. This was particularly necessary for spectra measured in the temperature range for which ionic motion causes narrowed linewidth.

D. ²⁷AI NMR spectroscopy

Investigation by ²⁷Al NMR spectroscopy at room temperature has also been undertaken to obtain complementary information on the structure of Pb₅Al₃F₁₉ phase IV. Highresolution signals required 12 h storage times. The experimental conditions of the ²⁷Al NMR study are given in Table I with data processed, as in Sec. II C, by use of the WINNMR 1D program.¹³

III. RESULTS

A. Electrical properties of Pb₅Al₃F₁₉

Complex impedance diagrams of $Z''(\Omega)$ as a function of $Z'(\Omega)$, i.e., Cole–Cole plots,¹⁵ are presented in Fig. 1 for Pb₅Al₃F₁₉ at various temperatures: The bulk ohmic resistance relative to each experimental temperature, i.e., the intragranular resistance, is the intercept Z_0 on the real axis of the zero phase angle extrapolation of the highest frequency curve.¹¹ The conductivity σ is obtained from Z_0 by means of the relation $\sigma = (1/Z_0)(h/S)$, where h/S represents the sample geometry. Cylindrical samples, of diam $S \simeq 8 \text{ mm}$ and height h with $1 \leq h \leq 2$ mm, are generally used. Conductivity is found experimentally to be independent of sample dimensions. The conductivity-temperature dependence between 293 and 743 K, given in Fig. 2 as a plot of log σT against inverse temperature, clearly exhibits Arrhenius-type behavior. A linear fit to $\sigma T = \sigma_0 \exp(-\Delta E \sigma/kT)$ is shown, with correlation coefficient r=0.98, on either side of the transition temperature $T_r = 368 \pm 5$ K. Although the conductivity is not discontinuous, there is a change in slope at T_r . The activation energies on either side of T_r are calculated as $(\Delta E_{\sigma})_{1t} = 0.63 \pm 0.02 \text{ eV}$ in the low-temperature regime,



FIG. 2. Inverse temperature dependence of log σT , also of log f_p , where σ is the conductivity and f_p is the peak frequency of M''_{max} for Pb₅Al₃F₁₉.

and $(\Delta E_{\sigma})_{\rm h.t.} = 0.57 \pm 0.02 \text{ eV}$ in the high-temperature regime. The nearly identical values of $(\Delta E_{\sigma})_{\rm h.t.}$ and ΔE_f , (see below), are indicative of negligible grain boundary effects.

 T_r coincides with the transition temperature $T_{\rm III,II}$ = 360 K between ferroelastic phase III and paraelastic phase II. The present results show the F⁻ ion mobility to be slightly higher in phase II than in phase III. By contrast, the phase IV to phase III transition at T = 320 K does not result in a detectable change in the electrical behavior of Pb₅Al₃F₁₉.

The coexistence of phases IV and III over a small temperature range close to their phase transition was determined by x-ray diffraction as a function of temperature.³ Biphasic mixtures in solid electrolytes may be detected by examination of the electric modulus M'' as a function of frequency (M'') is the imaginary part of M^*). The complex functions Z^* , ϵ^* , and M^* are related by $M^* = 1/\epsilon^* = j\omega C_0 Z^*$, where $j = \sqrt{-1}$, $\omega = 2\pi f$ is the angular frequency, and C_0 is the vacuum capacitance of the empty measuring cell. The electric behavior of an electrolyte containing a mixture of two crystalline phases of different conductivity may be simulated by a series-equivalent circuit containing two parallel R_1C_1 and R_2C_2 elements characterized by relaxation time constants $\tau_1 = R_1 C_1$ and $\tau_2 = R_2 C_2$. For resistance values differing by a factor of 100, for instance, but with capacitance values that are chosen equal, two peaks are observed in the M'' spectroscopy plot since the modulus response emphasises elements with smallest capacitance.^{16,17} The temperature range close to the transition from phase IV to phase III has been examined by analyzing the frequency response of the ac conductivity data of Pb₅Al₃F₁₉ within the complex modulus formalism.



FIG. 3. Plot of normalized modulus M''/M''_{max} against log *f* for Pb₅Al₃F₁₉ at 313, 319, and 328 K, from 1 to 10⁶ Hz.

Values of the normalized modulus M''/M''_{max} versus log *f* for Pb₅Al₃F₁₉, measured at three temperatures close to the phase IV to phase III transition temperature at 320 K, are presented in Fig. 3. The spectra corresponding to T=313 and 328 K form single peaks, whereas that at T=319 K clearly forms two peaks. The phase transition at T=320 K is hence confirmed,³ although the transition is without effective influence on the electrical properties of Pb₅Al₃F₁₉. The temperature range close to the phase transition between phase III and phase II was similarly investigated. The spectra obtained at T=358 and 383 K form a single peak, that at T=363 K forms two peaks, confirming the phase transition observed previously at 360 K,³ see Fig. 4.

The conductivity relaxation parameters for $Pb_5Al_3F_{19}$ were determined at T>368 K in the temperature range where only phase II exists. The plots of M''/M''_{max} versus log *f* as measured between 373 and 478 K are shown in Fig. 5. The curves are slightly asymmetric, in agreement with the nonexponential behavior of the electrical function described by the empirical stretched-exponential Kohlrausch function $\varphi(t) = \exp(-t/\tau_{\sigma})^{\beta}$, where τ_{σ} is the conductivity relaxation time, and β is the Kohlrausch exponent parameter,



FIG. 4. Plot of normalized modulus M''/M''_{max} against log *f* for Pb₅Al₃F₁₉ at 358, 363, and 383 K, from 1 to 10⁶ Hz.

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FIG. 5. Plot of normalized modulus M''/M''_{max} against log *f* for Pb₅Al₃F₁₉ at 373, 393, 418, 448, and 478 K, from 1 to 10^6 Hz.

respectively.^{18–20} The smaller the value of β , the more the relaxation deviates from a Debye-type relaxation. The full width at half-height (FWHH) of the M''/M''_{max} spectrum is greater than the breath of a Debye peak (1.14 decades),²¹ resulting in β =0.65 at 393 K for example. Although the temperature range over which β can be determined is small, the exponent appears independent of temperature within the thermal regime considered; if the parameter is interpreted as representative of a relaxation time distribution,^{20,22} then the latter is relatively narrow.

The peak maxima modulus shifts toward higher frequencies at increasing temperatures, see Fig. 5. The inverse temperature dependence of log f_p , where f_p is the peak frequency, relative to M''_{max} may be compared with the conductivity thermal variation in the same temperature range as presented in Fig. 2, i.e., for T>368 K. Both lines given in Fig. 2 are quasiparallel, typical of Arrhenius behavior; the activation energies determined from the impedance $(\Delta E_{\sigma})_{\text{h.t.}}$ and modulus ΔE_f spectra are very close $[(\Delta E_{\sigma})_{\text{h.t.}} = 0.57 \text{ eV}, \Delta E_f = 0.55 \text{ eV}]$ suggesting that the F⁻ ion transport in phase II of Pb₅Al₃F₁₉ is probably due to a hopping mechanism.²³

Although investigation of the electrical properties of $Pb_5Al_3F_{19}$ in the combined Z^* and M^* formalism confirms both the phase IV to phase III and phase III to phase II transitions, the phase V to phase IV transition could not be studied by impedance spectroscopy since the resistance of Pb₅Al₃F₁₉ samples is too large to be determined with precision at temperatures below 293 K. The ac conductivity data of Pb₅Al₃F₁₉, however, have been analyzed within a complex permittivity formalism from which both isochronous and isothermal values of $\epsilon'(f,T)$ and $\epsilon''(f,T)$ may be derived. The temperature dependence of ϵ' at frequencies from 5×10^4 to 5×10^5 Hz over the range 293–743 K is presented in Fig. 6. No dielectric anomaly at these frequencies is thereby found either at the phase IV to phase III or the phase III to phase II transition temperatures; the minor perturbation discernable close to the latter is without significance.

A major maximum in ϵ' , however, is detectable isochronously at $T \approx 670$ K at frequencies $f \ge 10^5$ Hz, although not at lower frequencies; the ϵ' peak becomes masked by the dielectric contribution from charge carriers that increases



FIG. 6. Temperature dependence of $\epsilon'(f,T)$ between 293 and 740 K. represents 5×10^4 ; \Box , 10^5 ; \bullet , 2×10^5 ; and \triangle , 5×10^5 Hz.

sharply as the frequency decreases and/or the temperature increases. The dielectric anomaly observed at $T \approx 670$ K is reversible and is typical of a phase transition. It is taken as the transition from paraelastic phase II to the previously undetected paraelectric prototype phase I, with probable space group I4/mcm. An x-ray diffraction study of Pb₅Al₃F₁₉ over the range 500–743 K is in progress to confirm this result.

B. ¹⁹F NMR investigation of Pb₅Al₃F₁₉

The polycrystalline sample of $Pb_5Al_3F_{19}$ was cooled to and kept at 100 K for 2 h in order to stabilize phase V, in view of the large known thermal hysteresis at the phase IV to phase V transition.⁶ The ¹⁹F NMR spectrum measured at 17 temperatures over the range 125–430 K is presented in Fig. 7. Two peaks, labeled p_1 and p_2 at frequencies of -5 and -35 kHz, respectively, are discernable below T=190 K; both can be simulated by Gaussians. All F⁻ ions are consequently immobile over the NMR time scale within this temperature regime. These spectra clearly result from two different kinds of F⁻ ions, i.e., occupying distinct sites each of which is characterized by its own chemical shift. Each line is broadened by dipolar interactions with many close-neighbor



FIG. 7. 19 F NMR spectrum (kHz) for Pb₅Al₃F₁₉ at 125 (top), 150, 170, 190, 215, 235, 255, 275, 295, 305, 315, 325, 335, 350, 375, 400, and 430 K (bottom).



FIG. 8. Full (heavy line) and deconvoluted (light line) ¹⁹F NMR spectrum at 275 K for Pb₅Al₃F₁₉; component spectra are denoted p_1 , p_2 , or p_m , see text.

 F^- ions. In view of the weak chemical shift anisotropy for the F^- ions, in comparison with the wide frequency gap between peaks, the spectra cannot correspond to a single kind of F^- ion under an anisotropic chemical shift. The percentage of F^- ions corresponding to each p_1 and p_2 peak area is ~65% and ~35%, respectively; these percentages agree with the number of F^- ions at the Wyckoff 16d and 8c sites (48 and 24, respectively, with an additional 4 F^- ions in the 4a site) in Pb₅Al₃F₁₉ at low temperature (i.e., 63% of the F occupies the 16d, 31.5% the 8c site).⁶ A third peak, p_m , located at -15 kHz between p_1 and p_2 becomes detectable at higher temperatures. This new peak, which increases in area with rising temperature, see Fig. 7, may be simulated by a Lorentzian function representing fluoride ions that become mobile above 190 K on the NMR time scale.

The relative contributions of the three peaks observed at each temperature may be determined by whole spectrum deconvolution. Figure 8 presents, for example, the deconvolution of the ¹⁹F NMR spectrum at 275 K. The temperature dependence of p_m %, the percentage of F⁻ ions mobile over the NMR time scale, is presented in Fig. 9. The experimental points are located on a curve which can be simulated by the Boltzman function $p_m(T)$ % = p_{max} % -{(p_{max} % - p_{min} %)/(1



FIG. 9. Temperature dependence of $p_m(T)$ % (\bigcirc on heating, \bullet on cooling, solid line theoretical, see text).

TABLE II. Theoretical and experimental values of parameters for the simulation function of $p_m(T)\%$.

	Theoretical	Experimental
T_{\min} (K)		170
$T_{\rm max}$ (K)		430
ΔT (K)	17.40	17.4
$p_{\min}\%$	1.9	2.5 ± 1
p_{max} %	91.3	91 ± 2
T_0 (K)	272	

 $+\exp[(T-T_0)/\Delta T]$, where $p_m(T)$ % is the percentage of F⁻ ions mobile at temperature T, p_{max} % is the corresponding percentage at T_{max} =430 K, p_{min} % is the percentage at T_{min} =170 K, T_0 is the center of the Boltzman function, and $\Delta T = \Sigma (T_i - T_i)/n$ is the average temperature difference between two successive experimental temperatures T_i and T_j , with n+1 the number of measurement temperatures. The three calculated and experimental parameters for the simulation function in Table II are in good agreement. T_0 , corresponding to the inflection point on the theoretical curve in Fig. 9 at 272 K, is close to the observed transition from phase V to phase IV at 270 K. Since p_{max} % is almost reached at the 320 K transition temperature from phase IV to phase III, all F⁻ ions at that temperature may be considered mobile on the NMR time scale, whereas only 50% are mobile at 270 Κ.

The transition temperature $T_{V,IV}$ from phase V to phase IV is characterized by very large thermal hysteresis, with T = 270 K on heating and 140 K on cooling; hence cooling phase IV to 200 K for instance, necessarily results in the coexistence of both phases.³ A ¹⁹F NMR investigation of Pb₅Al₃F₁₉ was undertaken at lower temperatures to determine the influence of thermal treatment on the temperature dependence of p_m %. Reducing the temperature from 360 to 160 K gives experimental points that fit the simulation curve in Fig. 9 as well as those determined from measurements at increasing temperature. There is consequently no correlation between the phases formed by Pb₅Al₃F₁₉ over this temperature range and the percentage of F⁻ ions present that are mobile on the NMR time scale.

The variation of the ¹⁹F NMR spectral width at halfheight ($\Delta \nu_{1/2}$) over the same thermal range is presented in Fig. 10: The plateau formed at low temperatures corresponds to the linewidth of a rigid lattice. Above $T \approx 200$ K, $\Delta \nu_{1/2}$ progressively decreases with increasing temperature. The narrowed linewidth is due to mobile F⁻ ion motions that average out the F–F dipolar interactions. Above $T \approx 320$ K, $\Delta \nu_{1/2}$ reaches the limit determined by experimental magnetic-field inhomogeneities. The activation energy of the mobile F⁻ ion relaxation in (ΔE_{σ})_{I,L} may be calculated from the thermal variation of the jump frequency ν_s . Line narrowing occurs when the frequency of ν_s is of the same order as the rigid lattice linewidth. The thermal variation of ν_s may be deduced from that of $\Delta \nu_{1/2}$ by the expression²⁴

$$\nu_{s} = (\alpha |\Delta \nu_{1/2} - \Delta \nu_{r}|) / \{ \tan | (\pi/2) [(\Delta \nu_{1/2} - \Delta \nu_{r}) / (\Delta \nu_{R} - \Delta \nu_{r})]^{2} | \},$$

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FIG. 10. Temperature dependence of $\nu_{1/2}$ (kHz) linewidth for Pb₅Al₃F₁₉.

where $\Delta \nu_{1/2}$ is the halfwidth measured at temperature *T*, $\Delta \nu_R$ is the halfwidth of the rigid lattice determined at low temperature, $\Delta \nu_r$ is a residual halfwidth due to field inhomogeneity, and α is a constant function of line shape. The Gaussian line shape at low temperature led to a choice of unity for the value of α .

The inverse temperature dependence of ν_s over the range $215 \le T \le 375$ K, in Fig. 11, shows that ν_s follows an Arrhenius type relation with $\nu_s = \nu_0 \exp(-\Delta E_{\text{NMR}}/kT)$. The activation energy $\Delta E_{\text{NMR}} \approx 0.26$ eV deduced for this material is clearly lower than the values $(\Delta E_{\sigma})_{\text{l.t.}} = 0.63$ eV and $(\Delta E_{\sigma})_{\text{h.t.}} = 0.57$ eV determined by impedance spectroscopy. This result shows that F⁻ ion motions on the NMR time scale are short range. It should be noted that there is no change in slope at the 270 K transition temperature from phase V to phase IV in the variation of log ν_s versus 1000/T K⁻¹ in Fig. 11. In consequence, no correlation exists be-



FIG. 11. Inverse temperature dependence of log ν_s (Hz) for Pb₅Al₃F₁₉.



FIG. 12. ²⁷Al NMR spectrum for Pb₅Al₃F₁₉ at T = 295 K.

tween the structural phases of $Pb_5Al_3F_{19}$ and the diffusion properties of its F^- ions at temperatures below 320 K.

C. ²⁷AI NMR investigation of Pb₅Al₃F₁₉

The ²⁷Al nucleus is quadrupolar (I=5/2), and strongly influenced by electrical field gradients; for large gradients, as in the present case, it is possible to observe only the -1/2 to 1/2 transition. The quadrupolar shift is second order, averaged over solid angle, since the sample is polycrystalline. The corresponding NMR spectrum of Pb₅Al₃F₁₉ at room temperature contains a single peak, centered at the frequency 32 kHz as shown in Fig. 12. The Al³⁺ ions in Pb₅Al₃F₁₉ phase IV occupy two 2*c*, a 4*f*, and two 8*g* sites,⁴ all located within fluorine octahedra. However, ²⁷Al NMR spectroscopy does not differentiate individual AlF₆ octahedra from those belonging to corner-sharing chains of AlF₆ octahedra along the *c* axis in Pb₅Al₃F₁₉, whereas two ²⁷Al NMR peaks are found in Pb_{1-x}Al_xF_{2+x} and in Pb₉Al₂F₂₄, corresponding to two distinct sites for the Al⁺³ cations in the latter materials.²⁵

IV. SUMMARY AND CONCLUSIONS

X-ray diffraction, thermal, optical, and dielectric studies of $Pb_5Al_3F_{19}$ undertaken previously between 100 and 400 K showed this material undergoes three phase transitions.^{4–8} The four known phases are ferroelectric phase V, with a transition to antiferroelectric phase IV at 270 K on heating, 140 K on cooling. The transition from phase IV to ferroelastic phase III is at 320 K on heating, 305 K on cooling; that from phase III to paraelastic phase II is at 360 K without thermal hysteresis. Impedance and NMR spectroscopy in the complementary temperature ranges 279–743 and 125–430 K, respectively, have characterized the influence of these phases on the ionic conductivity and F^- ion diffusion properties in this material.

The transition temperature from phase V to phase IV is very close (~ 272 K) to that at which the percentage of F⁻ ions mobile over the NMR time scale increases to $\sim 50\%$ although this percentage does not exhibit thermal hysteresis. Since motions detected by ¹⁹F NMR are short range, the F⁻ ion diffusion properties are hence independent of $Pb_5Al_3F_{19}$ structural phase formation in the temperature range $T \leq 320$ K.

Analysis of the ac conductivity data for Pb₅Al₃F₁₉ within the complex impedance, modulus and permittivity formalisms provides electrical characterization of both the phase IV to phase III and the phase III to phase II transitions. Whereas no change in electrical behavior is associated with the former, the mobility of the F⁻ ions at the latter with *T* = 368±5 K becomes strongly enhanced; this temperature coincides with the phase III to phase II transition $T_{\rm III,II}$. The activation energies are $(\Delta E_{\sigma})_{\rm h.t.}=0.63\pm0.02$ eV and $(\Delta E_{\sigma})_{\rm h.t.}=0.57\pm0.02$ eV, respectively, below and above $T_{\rm III,II}$. A hopping mechanism for F⁻ ion transport above 368 K is proposed.

The development of a maximum in $\epsilon'(f,T)$ at ~670 K has been demonstrated isochronously at $f \ge 10^5$ Hz. This dielectric anomaly is stable, reversible, and typical of a new but previously undetected phase transition. It is postulated as the transition, without thermal hysteresis, between the known paraelastic phase II and a new paraelectric prototype phase I.

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