Journal of the European Ceramic Society **19** (1999) 777–779

PII: S0955-2219(98)00311-2
0955-2219/99/$ - see front matter

Impedance Spectroscopy Analysis of $Pb_5Al_3F_{19}$

Jean-Maurice Réau, Annie Simon,* Mohamed El Omari and Jean Ravez

Institut de Chimie de la Matierre Condensée de Bordeaux, 87 Avenue du Docteur Albert Schweitzer, 33608 Pessac Cedex, France

Abstract

The ac 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 iso-chronously in ε′ (*f,T*) at 670 K corresponds to an expected, but hitherto unobserved, transition from phase II to the paraelectric prototype phase I of $Pb_5Al_3F_{19}$.*

Keywords: $Pb_5Al_3F_{19}$, spectroscopy, electrical conductivity, ferroelectric properties, impedance.

1 Introduction

Ferroelectric $Pb_5Al_3F_{19}$ is distinguishable from other members of the $Pb_5Al_3F_{19}$ series (M = Ti, V, Cr, Fe, Ga) by the existence of several phase transitions, whereas the other $Pb_5Al_3F_{19}$ phases are characterized by the presence at T_c of only one ferroelectric–paraelectric transition.[1] The multiple phase formation in $Pb_5Al_3F_{19}$ results from the simultaneous presence of the Pb^{2+} lone electron pair and a small trivalent cation (Al^{3+}). X-ray diffraction, thermal, optical and dielectric studies of $Pb_5Al_3F_{19}$ have revealed three phase transitions between 100 and 400 K, with the phase transition sequence:[2,3]

V	270 K → / 140 K ←	IV	320 K → / 305 K ←	III	360 K → / 360 K ←	II
ferroelectric tetragonal I 4cm		antiferroelectric tetragonal P 4/*n*		ferroelastic monoclinic I 2/c		paraelastic tetragonal I 4/*m*

An investigation of $Pb_5Al_3F_{19}$ by impedance spectroscopy has been undertaken over a large thermal interval (293–750 K) in view to show if a prototype phase with likely space group I 4/mcm, the super group for each of the lower temperature phases, may be found at high temperature.[4–6]

2 Experiments

Electrical conductivity measurements were carried out by the complex impedance method using a 1260 Solartron frequency response analyser. The frequency range used was 10^{-2}–10^{+6} Hz. The bulk ohmic resistance relative to each experimental temperature is, in the Z″ = funct. (Z′) diagram, the intercept Z_0 on the real axis of the zero phase angle extrapolation of the highest frequency curve. The conductivity σ is obtained from Z_0 by means of the relations $\sigma = (1/Z_0)$ (e/S), where e/S represents the sample geometric factor. Biphasic mixtures in solid electrolytes may be detected by examination of the dielectric modulus M″ as a function of frequency (M″ is the imaginary part of M*). The complex functions Z*, ε^*, and M* are related by $M^* = 1/\varepsilon^* = j\omega C_0 Z^*$, where $j = \sqrt{-1}$, $\omega = 2\pi f$ is the angular frequency, and C_0 is the vacuum capacitance of the empty measuring cell.

3 Results and Discussion

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 (Fig. 1). T_r coincides with the transition temperature $T_{\mathrm{III,II}} = 360$ K.

Variations of the normalized modulus M''/M''_{max} versus $\log f$ for $Pb_5Al_3F_{19}$ at three temperatures close to the phase IV to phase III transition temperature are presented in Fig. 2. The spectra relative to $T = 313$ and 328 K single peaks whereas that at $T = 319$ K clearly forms two peaks. The phase transition IV–III at $T = 320$ K is hence confirmed, although the transition is without effective influence on the electrical properties of $Pb_5Al_3F_{19}$. The phase transition between phases III and II was similarly confirmed.

The ac conductivity data of $Pb_5Al_3F_{19}$ have been also analyzed within a complex permittivity formalism from which both isochronous and isothermal

*To whom correspondence should be addressed. Fax: +33-05-5684-2761; e-mail: simon@chimsol.icmcb.u-bordeaux.fr

values of $\varepsilon'(f, T)$ and $\varepsilon''(f, T)$ may be derived. The temperature dependence of ε' at several frequencies is presented in Fig. 3. No dielectric anomaly is found either at the phase IV to phase III or the phase III to phase II transition temperatures. On the contrary, a major maximum in ε' is detectable isochronously at $T \simeq 670$ K at frequencies $f \geq 10^5$ Hz, although not at lower frequencies; the ε' peak becomes masked by the dielectric contribution from charge carriers that increases sharply as the frequency decreases and/or the temperature increases. The dielectric anomaly observed at $T \simeq 670$ K is reversible and is typical of

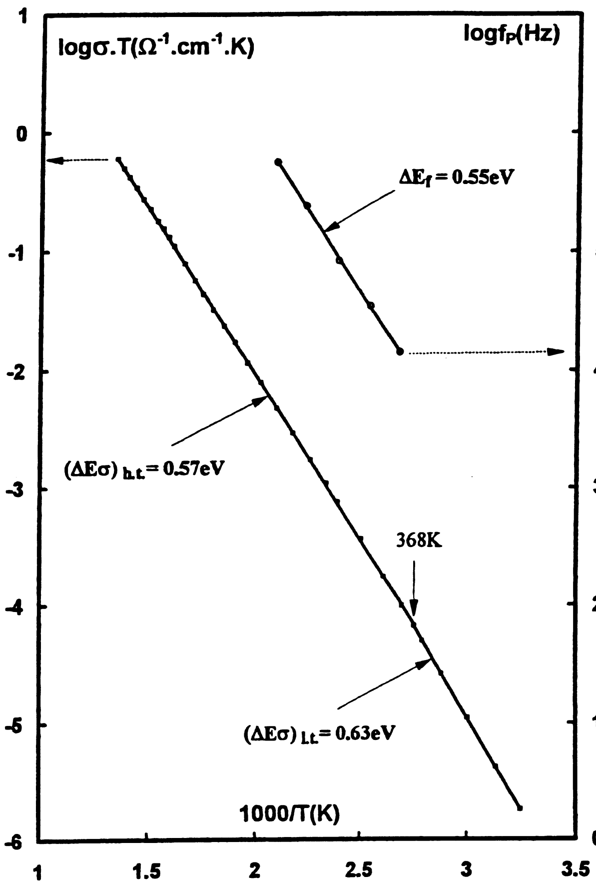

Fig. 1. Temperature dependence of log σT and log (f_p), where f_p is the M''_{max} peak frequency, for $Pb_5Al_3F_{19}$ (σT, before and after $T = 368$ K, and f_p are of Arrhenius-type with a fitting $R \approx 0.98$).

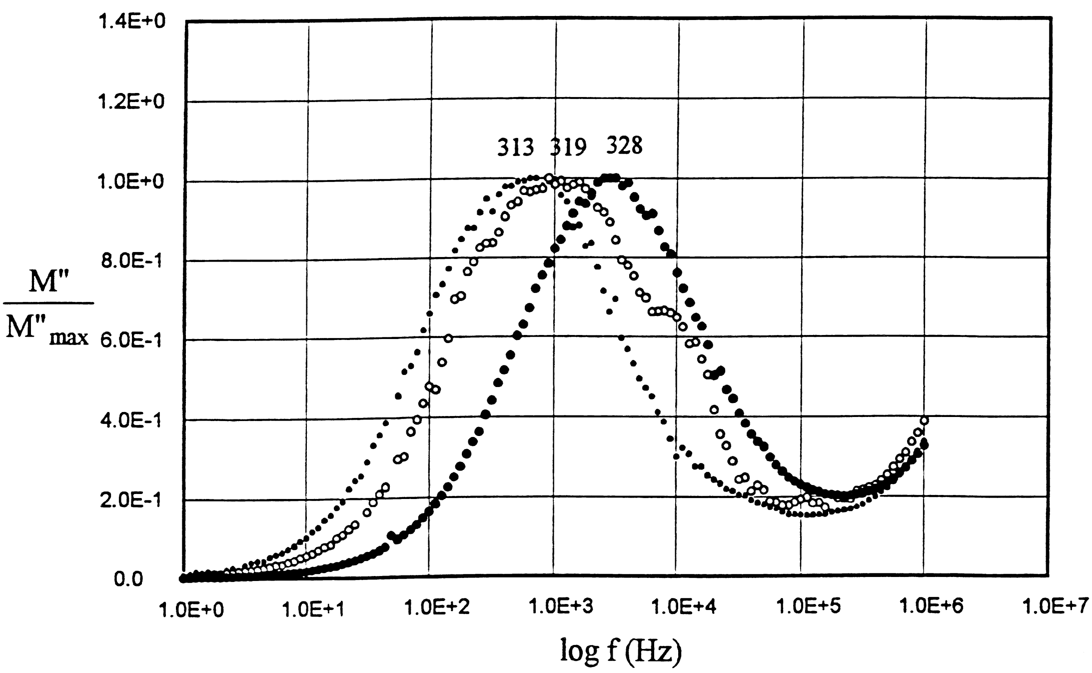

Fig. 2. Plots of normalized modulus $\left(\frac{M''}{M''_{max}}\right)$ versus log (f) for $Pb_5Al_3F_{19}$ at 313, 319 and 328 K.

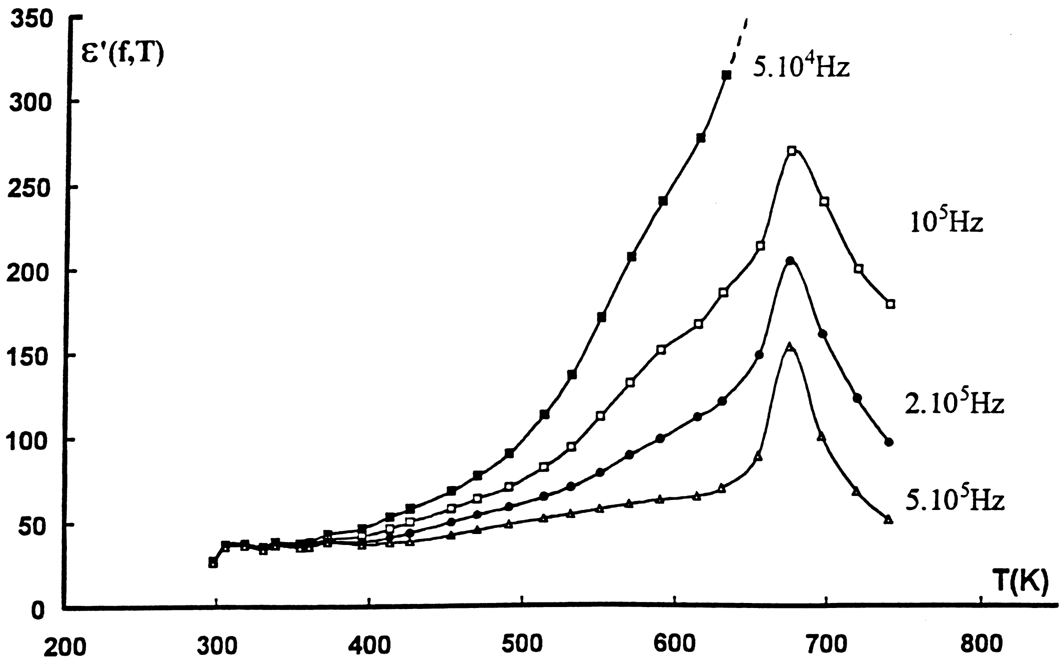

Fig. 3. Temperature dependence of $\varepsilon'(f, T)$ at various constant frequencies.

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 I 4/mcm.

References

1. Abrahams, S. C. and Ravez, J., *Ferroelectrics*, 1992, **135**, 21.
2. Ravez, L., Andriamampianina, V., Simon, A., Rabardel, L., Ihringer, J. and Abrahams, S. C., *J. Appl. Crystallogr.*, 1994, **27**, 362.
3. Sarraute, S. and Ravez, L., *Phase Trans*, 1996, **57**, 225.
4. Andriamampianina, V., Gravereau, P., Ravez, J. and Abrahams, S. C., *Acta Crystallogr., Sect. B* 1994, **50**, 135.
5. Sarraute, S., Ravez, J., Bravic, G., Chasseau, D. and Abrahams, S. C., *Acta Crystallogr., Sect. C* 1995, **51**, 1731.
6. Sarraute, S., Ravez, L., Von Der Mühll, R., Bravic, G., Feigelson, R. S. and Abrahams, S. C., *Acta Crystallogr., Sect. B* 1996, **52**, 72.