Anomalous Pressure Dependence of Dipolar Relaxation Times in Rare-Earth–Doped Lead Fluoride

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Electrical relaxation measurements at high pressures have been carried out on lead fluoride doped with lanthanum and cerium. A single, strong relaxation peak is observed and the relaxation time decreases with increasing pressure. This is contrary to the behavior exhibited by all known relaxations and can be explained by attributing the relaxation to a substitutional trivalent rare-earth ion compensated either by an interstitial fluorine ion with a soft attempt mode or by an electron.

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Lead fluoride has a number of fascinating properties. It exists in two crystalline phases at room temperature and pressure, specifically an orthorhombic and a cubic (fluorite) structure. In the fluorite structure, its properties are vastly different from the isostructural alkaline-earth fluorides (AEF). It has a very large static dielectric constant (31)[1] which decreases as temperature increases and obeys a Curie-Weiss law thus classifying it as an incipient displacive ferroelectric. In contrast, the AEF have small dielectric constants (6–8) which increase as temperature increases.[2] The superionic transition occurs at a much lower temperature than in the AEF.[3] The heat capacity and thermal expansion coefficient give rise to an anomaly in the low-temperature Grüneisen parameter compared with the AEF.[4] Other properties, however, such as the effect of pressure on (a) the elastic constants,[5] (b) the conductivity,[6,7] or (c) the static dielectric constant,[7] are quite similar to those of the AEF.

Concerning electrical relaxation effects in rare-earth–doped PbF_2, it has been shown[8-10] that the electrical relaxation spectra for rare-earth (RE) dopants larger than gadolinium consist of a single, strong peak. The results are reminiscent of lightly doped AEF except in one important feature: in PbF_2 the peak position depends strongly on ion size, while for the AEF's it does not.[11,12] Ion-size–dependent relaxations have been observed in the AEF[11,12]; however, they have been associated with two RE's.[13] It is unlikely that a dimer would be responsible for the relaxation in PbF_2 as this would imply that dipolar defects containing only one RE do not form in PbF_2. For RE's smaller than gadolinium, the spectra are extremely complex, with up to nine relaxations being observed.[8,9] Further, multiple relaxations per defect site are identified. In the present work, the effects of pressure on PbF_2 doped with two large RE's, lanthanum and cerium, are presented.

Single crystals of cubic lead fluoride nominally doped with 0.1 mol% of lanthanum and cerium were grown by the Stockbarger technique as described elsewhere.[14] Irregular platelets approximately 5 cm on a side and about 1 mm thick were cut from the boules and aluminum electrodes were evaporated onto the faces. Audio-frequency complex-impedance measurements were performed at five frequencies with use of a fully automated, microprocessor-controlled impedance bridge constructed by one of the authors (C.G.A.). The high-pressure measurements were performed with use of the multiple-sample bomb described elsewhere.[15] A 50-50 mix of pentane and isopentane was used as the pressure fluid and the

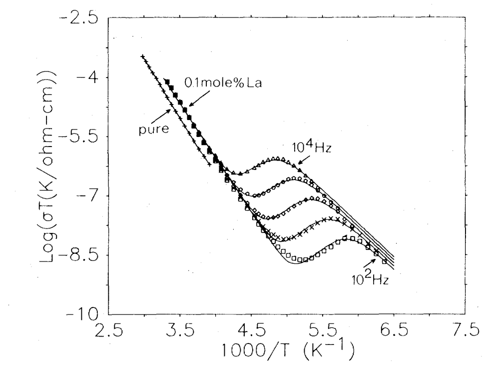

FIG. 1. Log[σT (K/Ω cm)] vs 1000/T (K^{-1}) for "pure" PbF_2 and 0.1-mol% PbF_2:La. The data for the pure sample are at 100 Hz and the frequencies for PbF_2:La are equal logarithmic intervals between those indicated on the drawing. Also shown is the best-fit curve for PbF_2:La.

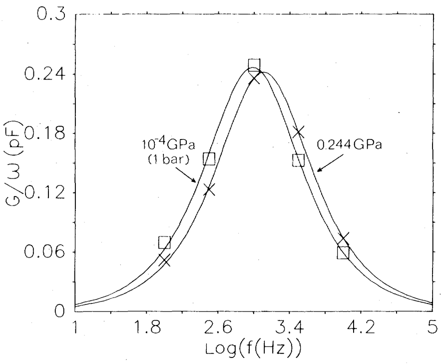

FIG. 2. Log[f (Hz)] vs G/ω (pF) for 0.1-mol% PbF_2:La at 185 K and $P = 0.0001$ GPa (squares) and $P = 0.244$ GPa (crosses). Also shown are the best-fit Cole-Cole curves.

bomb was immersed in a temperature-controlled Freon-11 bath. Zero-pressure measurements were carried out with use of the system which, together with the techniques for converting the raw impedance data to values of the complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$, or the conductivity, $\sigma = \epsilon_0 \epsilon'' \omega$, have been described previously.[11] In the present work, the thermal expansion data of White[4] for pure lead fluoride were used.

For the lanthanum-doped PbF_2 samples, the zero-pressure spectrum consists of a single, strong relaxation superimposed on a dc-conductivity background as shown in Fig. 1. The results of a least-squares analysis in terms of a Cole-Cole peak and Arrhenius conductivity are given elsewhere.[16] The important relaxation parameters are listed in Table I and the best-fit curve is shown in Fig. 1. In the case of PbF_2:Ce, the relaxation peak occurs at a sufficiently low temperature that the contribution from the dc conductivity is extremely small. Therefore the data were fitted by only the Cole-Cole expression, and the parameters are listed in Table I. In both materials it was found that the relaxations did not exhibit perfect Curie-Weiss behavior, the peak height decreasing less rapidly than $1/T$. This will be discussed later.

Clearly, while there are minor differences there is very little in the zero-pressure results which suggests any significant difference between the defect structure of RE-doped PbF_2 and the large number of interstitial-substitutional complexes observed in RE-doped AEF.[12]

The pressure results, on the other hand, indicate a profound difference between the defects in PbF_2 and those in the AEF, or indeed, in any other material. Specifically, in PbF_2, the peak position shifts to a higher frequency as pressure is applied, i.e., the relaxation time decreases with increasing pressure. This can be seen in Fig. 2 where the results for PbF_2:La are shown. For PbF_2:La the conductivity baseline was subtracted with use of results for the pressure dependence of the conductivity which will be discussed in detail elsewhere. For PbF_2:Ce, no conductivity correction was made and the results

TABLE I. Parameters describing the principal relaxation in 0.1-mol% PbF_2:La and PbF_2:Ce.

Dopant	A (K)	τ_0 (10^{-14} s)	E (eV)	α			$d\ln\tau/dP$ (GPa^{-1})	ΔV^* (cm^3/mole)
La	364	0.25	0.40	0.14	Sample 1	181 K	−1.25	−1.88
						185 K	−1.23	−1.89
					Sample 2	181 K	−1.17	−1.76
						185 K	−1.16	−1.78
Ce	261	1.6	0.32	0.04	Sample 1	161 K	−1.34	−1.79

are quite similar to Fig. 2. The Cole-Cole expression was fitted to the data in order to determine the relaxation times at various pressures. The resultant relaxation times versus pressure are shown in Fig. 3 for PbF_2:La and the slopes of the best-fit straight lines for all samples are listed in Table I. The decrease of relaxation time as pressure increases is opposite to that observed for any dipolar relaxation time studied to date including work on ionic crystals[17-20] or polymers.[21]

It may be that the anomalous pressure dependence of the relaxation time is another manifestation of the soft-mode behavior which lead fluoride has been suggested to exhibit.[1,5] Specifically, it might be concluded that the usual reorientation of a charge-compensating fluorine ion [ion compensation (IC)] near a substitutional rare-earth ion is taking place, and that the vibrational mode governing the reorientation is a soft mode. Possibly the best way to illustrate this is via the activation volume:

$$\Delta V_{\mathrm{exp}}{}^* = kT\,\partial \ln\tau/\partial P$$

which yields the negative values listed in Table I. The dynamical-diffusion theoretical expression[20]

$$\Delta V_{\mathrm{th}}{}^* = 2\gamma_a \chi_T g,$$

where χ_T is the compressibility and g is the Gibbs energy, then requires a negative attempt-mode Grüneisen parameter, γ_a, indicating a soft mode, to explain the data.

However, these relaxations exhibit a very strong dependence of peak position or activation energy on dopant ion size as is evident from Table I for PbF_2:La and PbF_2:Ce and Fig. 1 of Ref. 9. It may be that the same spring constants which soften upon application of pressure also enhance the interaction between the RE and the reorienting fluorine interstitial. IC has the additional advantage of easily explaining the relatively high activation energies, 0.4 and 0.32 eV, observed for La and Ce. However, the activation energy for the analogous relaxation in PbF_2:Gd is very low, about 0.11 eV. This suggests an alternative interpretation of the data. The second model proposed is that the RE is charge compensated by an electron (EC) localized around one of the adjacent lattice fluorine ions. The decrease in the relaxation time with increased pressure would then be a result of increased electron wave-function overlap between equivalent wells as pressure reduces the lattice parameter. Further, these same overlap effects will make the electronic relaxation time very sensitive to the extent of the RE's electron wave function and thus explain the variation of activation energy with ion size.

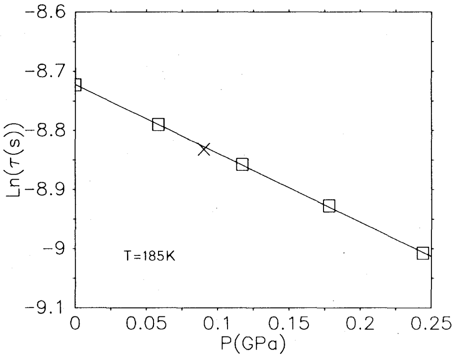

FIG. 3. Ln[τ (s)] vs P (GPa) for 0.1-mol% PbF_2:La. Decreasing pressure, squares; increasing pressure, cross.

These models have the following implications concerning several other unusual features of the electrical response of RE-doped PbF_2. Firstly, the magnitude of the conductivity does not scale with the strength of the principal relaxation over the dopant range 0.1 to 1.0 mol% (nominal) in that the strength of the relaxation increases while the magnitude of the conductivity does not. This result favors the EC model since there should be no correlation of the strength of the relaxation and the magnitude of the conductivity which is primarily ionic.[22,23] (There have been reports of electronic contributions to the conductivity of lead fluoride[24,25] and this increases the plausibility of EC.) Of course, the IC model could explain the results if the association energy is so large that it is not the complex responsible for the extrinsic conductivity. In either case, another defect site must coexist with that responsible for the principal relaxation since the conductivity is well behaved and can be fitted via a classical association model.[22,23] In fact, a relatively weak relaxation is observed in both PbF_2:La and PbF_2:Ce at a slightly higher temperature than the principal relaxation. That is part of the reason for the poor fit of the data shown in Fig. 1. If that site has only a very small dipole moment the concentration could be sufficiently large to give rise to the extrinsic conductivity.

Secondly, the deviation of the relaxations from Curie-Weiss behavior can be understood either in terms of EC or IC. In the case of EC, it could easily be that the dipole moment increases as temperature increases. For either EC or IC a slight potential-well inequivalency could also explain the trend.

Finally, there is the phenomenon of the existence of multiple low-temperature relaxations per defect center observed for PbF_2 doped with RE's smaller than gadolinium.[8,9] This has not been observed in association with ionic relaxations in the AEF. Consequently, those results suggest the existence of at least some electronic compensation.

In summary, it has been shown that for the single, strong relaxation observed in PbF_2 doped with large RE's, the relaxation time decreases as pressure increases. By attributing the relaxation to an electronically compensated or soft-mode related, fluorine-interstitial–compensated substitutional trivalent RE, this anomalous behavior, together with some previously unexplained phenomena, can be understood.

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