Ultrasonic attenuation peaks near the diffuse solid-electrolyte transition temperature in PbF_2 and BaF_2

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The attenuation of 10-MHz longitudinal and transverse ultrasound in PbF_2 and 10-MHz longitudinal ultrasound in BaF_2 was studied as a function of temperature near the diffuse solid-electrolyte transition temperature T_c as defined by the heat-capacity peak. The ultrasonic attenuation peaks are associated only with the ionic-conductivity saturation rather than in combination with crystallographic phase transitions found in many other solid electrolytes. The relaxation rates and Arrhenius activation energies for anion motion above T_c were obtained from the temperature dependence of the ultrasonic attenuation and the theory of local site fluctuations. The present results for Arrhenius activation energies above T_c are comparable to the nuclear-magnetic-resonance and ionic-conductivity measurements. These results support the understanding that anion motion above T_c is more complicated than anion Frenkel motion and is associated with an anion redistribution among energetically inequivalent sites.

INTRODUCTION

A class of materials exist in which ionic conductivity is comparable to that in molten salts. These solids are called solid electrolytes, superionic conductors, or fast-ion conductors. In 1834, Faraday[1] reported that the conductivity of PbF_2 increased dramatically when its temperature was increased above a particular temperature, T_c, which was below the melting temperature. PbF_2 and BaF_2 exhibit a broad specific-heat anomaly[2-4] as well as anomalies in many other properties at T_c, also known as the Faraday temperature. These phenomena are generally assumed to be associated with the development of extensive Frenkel disorder in the anion sublattice with the disorder giving rise to the fast-ion behavior.[4]

PbF_2 and BaF_2 undergo a diffuse transition at the temperatures 711 and 1235 K, respectively, as specified by both a heat-capacity peak[3,4] and ionic-conductivity saturation or negative deviation from Arrhenius behavior.[5-8] Associated with the peak in the specific heat and the saturation of the ionic conductivity in these materials is the anomalous property of a softening of the lattice as measured by both Brillouin[9] and neutron[10] scattering and by ultrasonics.[11,12] While Brillouin[9] and neutron[10] scattering yield information about the acoustic phonons, neither experiment has been able to measure energy loss associated with the anion-phonon interaction in fluorite materials. We report for the first time experimental results of the effect of the anion disorder and anion motion on the ultrasonic attenuation in PbF_2 and BaF_2, which do not have any crystallographic phase transitions to complicate the analyses. Comparison of activation energies obtained from the ultrasonic-attenuation measurements can be made with those obtained from other experiments including NMR.

THEORY

Ultrasonic attenuation and velocity changes near the diffuse transition in superionic conductors are primarily influenced by the interaction of the mobile anions with the ultrasonic wave. The attenuation of ultrasonic waves interacting with thermal phonons must be considered also. Woodruff and Ehrenreich[13] and Bommel and Dransfeld[14] have used a statistical transport model based on the work of Akhieser[15] to derive an expression for the ultrasonic attenuation due to the lattice vibrations in the low-frequency regime, $\omega_K \tau_P \ll 1$, where ω_K is the angular frequency of the propagating acoustic wave and τ_P is the phonon-phonon collision time. They concluded that this attenuation is independent of temperature above the Debye temperature which is 237 and 286 K for PbF_2 (Ref. 16) and BaF_2 (Refs. 17 and 18), respectively. The magnitude of the Akhieser attenuation in alkaline-earth-metal fluorides at 10 MHz is much less than 0.1 dB/cm at room temperature[19,20] and therefore much smaller than the effect observed near the diffuse transition temperature in addition to being temperature independent. The theory of the dynamics of the coupled crystalline-cage-charged-liquid fluctuations derived by Huberman and Martin[21] predicts that the effect of local-site fluctuations on the phonon dynamics dominates over other fluctuations. For the weak-coupling and low-frequency limit of this theory, i.e., $\omega_K \tau \ll 1$, the ultrasonic attenuation due to mobile ions can be written[5] as

$$\alpha = \omega_K^2 T_c (\rho/C)^{1/2}/[R(T)T] , \qquad (1)$$

where ρ is the material's mass density, C is the elastic constant, T_c is the diffuse transition temperature, and T is the temperature. The relaxation rate or frequency $R(T)$ reflects the coupling of the pseudospin, which de-

scribes the local degrees of freedom of site occupation, to the thermal reservoir provided by the crystalline cage and in general has Arrhenius behavior,

$$R(T) = 1/\tau = R_0(T)\exp(-E/kT) ,\qquad (2)$$

where τ is the relaxation time, $R_0(T)$ is the attempt relaxation rate or frequency expected to be of the order of an optical-phonon frequency (taken to be 10^{12} Hz in this work) and E is the Arrhenius activation energy for anion motion. This approach was applied successfully[22] to analyze the ultrasonic-attenuation measurements in the ionic conductor β-Ag_3SI.

EXPERIMENT

The pulse-superposition method[23,24] has been used to measure the round-trip transit time and the change in amplitude of the ultrasonic wave propagating in single-crystal specimens of fluorite-structured PbF_2 and BaF_2. The experimental techniques including the bond and transducers are described elsewhere.[25-27] Using this simple technique, the changes in ultrasonic attenuation can be adequately measured with a precision of ±0.5 dB. The apparent attenuation due to nonparallelism,[28] bond,[28] and diffraction[29] effects were identified and subtracted from the measured ultrasonic attenuation where possible.

The longitudinal ultrasonic-attenuation measurements were made in a single-crystal sample of PbF_2 with the fluorite structure. The axis of this crystal obtained from Optovac, Inc.[30] was determined by back-reflection Laue photography to be oriented 23° from the [100] direction. The apparent attenuation due to nonparallelism, bond, and diffraction effects were estimated and subtracted from the longitudinal-attenuation measurements.

The transverse ultrasonic attenuation measurements were made for an acoustic wave propagating in the [110] direction within 2° and polarized in the [$1\bar{1}0$] direction in a single-crystal cubic PbF_2 previously used for transverse ultrasonic velocity measurements[11] and reported as $(C_{11}-C_{12})/2$. Since the acoustic bond used in this work (DuPont 9770) was not rigid enough to couple the transverse acoustic wave into the crystal below the drying
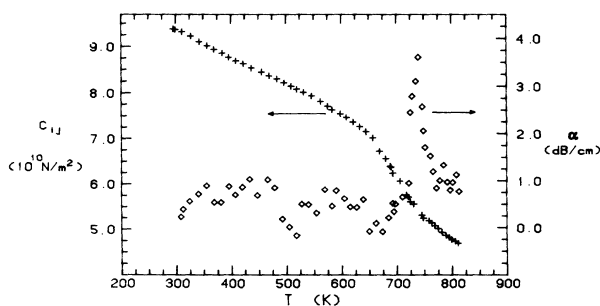
temperature of the bond, the apparent attenuation described above could not be measured at room temperature and was not estimated for the transverse-attenuation measurements in PbF_2.

The longitudinal ultrasonic attenuation in single-crystal BaF_2 corresponding to the elastic constant $\rho v_L^2 = C_{11}$ reported previously[12] was corrected for the apparent attenuation described above. Similar measurements below the transition temperature have been reported previously.[27]

RESULTS

Figures 1–3 show the ultrasonic attenuation of longitudinal and transverse ultrasound at 10 MHz in PbF_2 and BaF_2 along the associated elastic constant $C = \rho v^2$ where v is the sound velocity of the ultrasonic wave generated. Similar ultrasonic measurements in [110]-oriented PbF_2 with the polarization along the [001] direction for a direct measurement of the pure shear mode associated with C_{44} did not yield an identifiable attenuation peak. More extensive measurements in these materials at other frequencies or to higher temperatures relative to T_c were restricted by the availability of large crystals of PbF_2 as well as the propensity of the available crystals of PbF_2 to oxidize above T_c even at pressures of 4×10^{-3} Pa
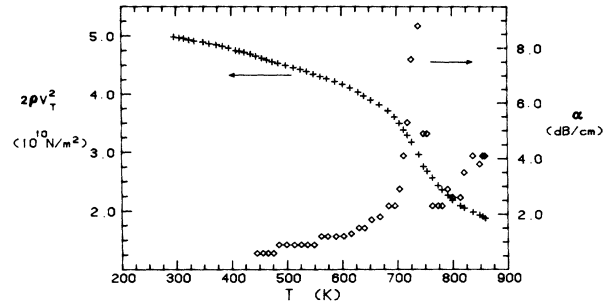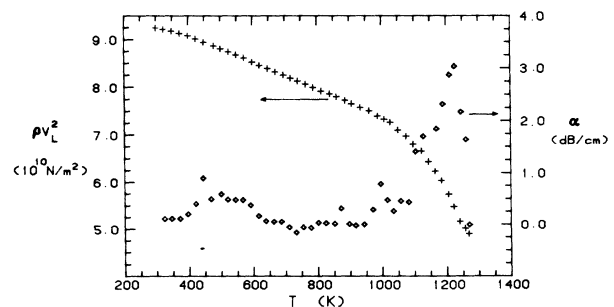
FIG. 2. Temperature dependence of transverse ultrasonic attenuation, α ($\lozenge$), of PbF_2 measured simultaneously with $2\rho v_T^2 = (C_{11}-C_{12})$ ($+$) at 10 MHz. Temperature dependence of the elastic constant $(C_{11}-C_{12})$ is taken from Ref. 11.

FIG. 1. Temperature dependence of longitudinal ultrasonic attenuation, α ($\lozenge$), of PbF_2 measured simultaneously with $\rho v_L^2 = C_{ij}$ ($+$) 23° from [100] at 10 MHz.

FIG. 3. Temperature dependence of longitudinal ultrasonic attenuation, α ($\lozenge$), of BaF_2 measured simultaneously with $\rho v_L^2 = C_{11}$ ($+$) at 10 MHz. Temperature dependence of the elastic constant, C_{11}, is taken from Ref. 12.
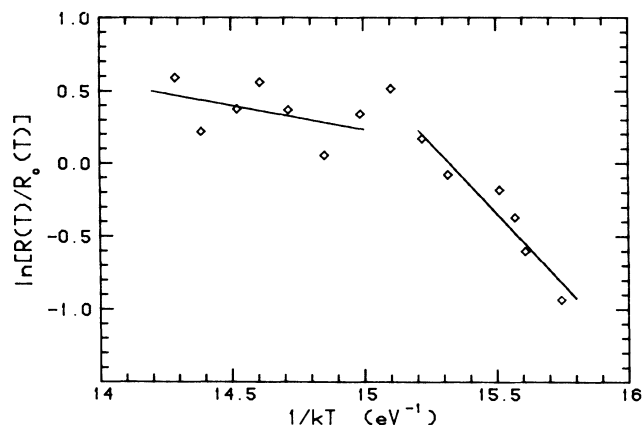
FIG. 4. The calculated values of $R(T)/R_0(T)$ from the ultrasonic-attenuation data of Fig. 1 above the transition temperature are given with the solid line as a first-order least-squares fit of the data whose slope represents the Arrhenius activation energy of the mobile anions in PbF_2.
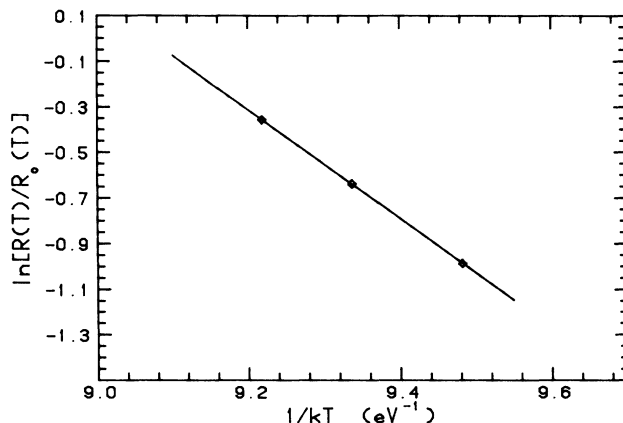
FIG. 5. The calculated values of $R(T)/R_0(T)$ from the ultrasonic-attenuation data of Fig. 3 above the transition temperature are given with the solid line as a first-order least-squares fit of the data whose slope represents the Arrhenius activation energy of the mobile anions in BaF_2.

$(3\times10^{-5}$ Torr) or by the limitations of the transducer bond and furnace in the case of BaF_2. Measurements at different frequencies well above T_c have been reported elsewhere for CdF_2,[31] but not in a pure shear mode direction as was available in PbF_2.

DISCUSSION

If we assume that the maximum disorder of the anion sublattice occurs above the diffuse transition temperature and if the ultrasonic attenuation and the elastic constant were measured above this temperature, then one can obtain the relaxation rate $R(T)$, from Eq. (1), or

$$R(T)=\omega_k^2 T_c(\rho/C)^{1/2}/\alpha T \tag{3}$$

as a function of temperature T (ω_k, T_c, ρ, and C were defined earlier).

The temperature variation of the relaxation rate $R(T)$ of PbF_2 given in Fig. 4 was obtained by using the longitudinal ultrasonic-attenuation measurements above the transition temperature in Fig. 1. The temperature dependence of the relaxation rate for BaF_2 given in Fig. 5 was

obtained by using the longitudinal ultrasonic-attenuation measurements above T_c in Fig. 3.

Equation (2) predicts that the slopes of the solid lines in Figs. 4 and 5 represent the Arrhenius activation energy for the motion of mobile anions. The relaxation-rate measurements for PbF_2 above T_c in Fig. 4 show clearly a change in slopes corresponding to different Arrhenius activation energies while the relaxation-rate measurements for BaF_2 do not exceed T_c sufficiently to show such an effect. The Arrhenius activation energies obtained from Figs. 4 and 5 are given in Table I along with values above T_c reported in the literature. The Arrhenius activation energies above T_c from these ultrasonic measurements generally agree within experimental error with activation energies reported in the literature.[6,7,32-35]

The Arrhenius activation energies above T_c are clearly identified as being associated with ionic motion more complicated than vacancy or interstitial migration.[7,8] The present results support the interpretation of Azimi et al. that the Arrhenius activation energy near T_c is due to the onset of the transition since the present measurements are bulk measurements which would presumably not be affected by surface oxidation.

TABLE I. Arrehenius activation energies (eV) for anion motion in nominally pure cubic PbF_2 and BaF_2 above the diffuse transition temperature T_c.

| | Temperature limit | | | Activation energy (eV) | | Reference |
	T_1 (K)	T_2 (K)	T_3 (K)	$T_1 < T < T_2$	$T > T_3$	
PbF_2	670	720	770	1.60	0.25	7
			715	1.80±0.03		32
				1.78	0.3	33
			723		0.2±0.02	34
	711	769	769	1.94±0.23	0.33±0.28	present work
BaF_2				2.2±0.1		6
	1111	1250		2.1		35
	1222	1257		2.39±0.11		present work

A sharp increase in the ultrasonic attenuation associated with the longitudinal velocity propagating along the [100] direction in a β-PbF$_2$ crystal was reported[36] below ~ 800 K. This is in excellent agreement with the present ultrasonic-attenuation measurements. Unlike the ultrasonic bond used by Smolenskii et al.,[36] the present ultrasonic bond (DuPont 9770) used in this work to couple the transducers to the fluorite crystals allowed us to perform ultrasonic attenuation measurements at temperatures higher than the transition temperatures. Nevertheless, it is found that the ultrasonic-attenuation peaks for both PbF$_2$ and BaF$_2$ occur at temperatures higher than the diffusion transition temperatures which are specified by the heat-capacity and ionic-conductivity measurements.

The lack of an ultrasonic-attenuation peak for a pure shear mode demonstrates an absence of coupling between the mobile ions and pure shear strains which indicate that the mobile ions are being redistributed among energetically inequivalent sites.[21]

CONCLUSIONS

The present study provides the first measurements above the diffuse transition temperature of the longitudinal and transverse attenuation in PbF$_2$ and the longitudinal ultrasonic attenuation in BaF$_2$. The ultrasonic attenuation peaks observed near the diffuse transition temperature are associated only with the ionic conductivity saturation rather than in combination with crystallographic phase transitions. The Arrhenius activation energies for PbF$_2$ and BaF$_2$ extracted from the ultrasonic-attenuation measurements and fluctuations of local-site populations are indicative of anion motion more complicated than simple-anion Frenkel motion and are associated with redistributions among energetically inequivalent sites.

ACKNOWLEDGMENT

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