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Elastic constants of barium fluoride from 300 to 1250 K

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We have determined all three independent adiabatic elastic constants of single-crystal cubic BaF_2, by an ultrasonic-pulse superposition technique, over the temperature range of 300 to 1250 K. Values of the compressibility, the ultrasonic anisotropy factor, and Cauchy-relation failure over this temperature range are obtained from C_{11}, $(C_{11}-C_{12})/2$, and C_{44}. The results are anomalous at the Faraday temperature of 1230 K for BaF_2 which is well below its melting temperature of 1550 K. A large decrease in C_{11} and a smaller decrease in C_{12} are observed near 1230 K, in addition to a nearly linear decrease in the elastic constants with temperature. C_{44} does not seem to deviate much from its general behavior near this temperature. Single-crystal BaF_2 is found to be approximately mechanically isotropic over the temperature range of 300 to 1200 K.

INTRODUCTION

Superionic conductors, sometimes called solid electrolytes or fast-ion conductors, are solid materials that display ionic conductivities that are typical of those found in molten salts. Based upon the structural considerations of superionic conduction, the superionic conductors can be divided into three classes.[1] The transition to a highly ionic conducting material is accompanied by a structural phase change in the crystal lattice for class I, but there is no structural change in class II associated with the increasing ionic conductivity and heat-capacity peak, while class III is characterized by a smoothly increasing ionic conductivity with no apparent transition, including no anomaly in the heat capacity. In class-II materials the conductivity increases more rapidly than in class-III materials, but not abruptly as in class-I materials, and exhibits a negative deviation from Arrhenius behavior at higher temperatures. This type of superionic conductor is said to undergo a diffuse transition,[1] which is also called the Faraday transition. Fluorites including BaF_2 are class-II materials. In the case of BaF_2 the fluorine sublattice becomes disordered at the transition temperature, while the complementary barium sublattice distorts negligibly. Thus there is no structural change in BaF_2. The diffuse transition temperature T_c is defined as the temperature well below the melting temperature at which a peak in the heat capacity occurs,[2,3] and at which the negative deviation from Arrhenius behavior occurs.[1,4] Associated with the peak in the specific heat and the behavior of the ionic conductivity in these materials are other anomalous properties, such as a softening of the lattice as measured by both Brillouin[5] and neutron[6] scattering.

Experimental observation of low-frequency acoustic-phonon coupling with mobile ions has been made in several superionic conductors. Graham and Chang[7] have reported sharp and narrow attenuation peaks for one ultrasonic shear mode and the longitudinal mode in [110] $RbAg_4I_5$ centered about the phase-transition temperature 208 K. Although the 208-K transition does not strongly indicate that it is a first-order transition, $RbAg_4I_5$ undergoes a crystallographic phase transition from a cubic to a trigonal space group.[8] The 208-K transition as well as the 122-K first-order phase transition both complicate the understanding of the ultrasonic attenuation that results from mobile ions in $RbAg_4I_5$.[9] Benguigui and Weil[10] have reported experimental results of sound velocity and dielectric losses of Ag_2HgI_4 in the vicinity of the phase transition at 324 K. The latter found anomalies only in the longitudinal sound modes. However, Ag_2HgI_4 is a class-I material like $RbAg_4I_5$ and undergoes a crystallographic phase transition from a tetragonal to a face-centered-cubic space group.[11] In this study the experimental effects of the disorder on the elastic constants of BaF_2 in the absence of a crystallographic phase transition using ultrasonic techniques are described.

THEORY

Owing to the symmetry of a cubic crystal the classical theory of elasticity[12] shows that there are only three independent elements in the elastic-constant tensor. Values of these elastic constants, C_{ij}, can be obtained from the relationship $C_{ij}=\rho v^2$, where ρ is the density and v is the velocity of sound. The crystals were cut along the [100] and [110] directions to allow measurements of two longitudinal and two transverse velocities. The relations of elastic constants to density and velocity used in this work were $\rho v_L^2=C_{11}$ and $\rho v_L'^2=(C_{11}+C_{12}+2C_{44})/2$, supplementing earlier work[13] which used the relations $\rho v_T^2=C_{44}$ and $\rho v_T'^2=(C_{11}-C_{12})/2$, where v_L is the longitudinal ultrasonic velocity of the wave propagated in the [100] direction, and v_L', v_T, and v_T' are the ultrasonic velocities of waves propagated in the [110] direction for the longitudinal wave and transverse waves polarized in the [001] and $[1\bar{1}0]$ directions, respectively.

The elastic constant C_{ij} is calculated from the pulse round-trip transit time Δt, and the crystal specimen's density ρ and length L, using the thermal-expansion-coefficient correction at any temperature T, and is given by the expression

$$C_{ij}=\frac{4\rho_0 L_0}{(\Delta t)^2}\exp\left[-\int_{T_0}^{T}\alpha(T)dT\right],$$

where ρ_0 is the density at $T_0=300$ K and is taken[5] to be 4.884×10^3 kg/m^3 for BaF$_2$, L_0 is the length of the crystal at $T_0=300$ K, and $\alpha(T)=d(\ln L)/dT$ is the thermal-expansion coefficient in units of K^{-1} and is taken[14] to be $\alpha(T)=9.0\times10^{-6}+3.8\times10^{-8}T-1.17\times10^{-11}T^2$.

EXPERIMENT

Two single-crystal specimens of fluorite-structured BaF$_2$ were obtained from Optovac, Inc.[15] The first crystal was cylindrical in shape, approximately 2 cm long and 2 cm in diameter, previously used for the first transverse ultrasonic measurements on fluorite fluoride materials above 800 K.[13] Backreflection Laue photography was used to orient this sample to within 2° of the [110] direction, and to identify the $[1\bar{1}0]$ and [001] directions for the shear polarization. The end faces were parallel to within 2 parts in 10^4. The second crystal was cylindrical in shape, approximately 1 cm long and 1 cm in diameter. Backreflection Laue photography was used to orient this sample to within 3° of the [100] direction. For the 3° misalignment, the relative percentage error in the longitudinal velocity is less[16] than 0.01%. The end faces of this sample were parallel to within 8 parts in 10^4.

The electronic equipment has been described previously.[17] Measurements of round-trip transit time of the ultrasonic pulse were made using the pulse superposition method[18,19] for the correct cycle-for-cycle overlap of two pulse echoes assuming the thin-bond limit. DuPont 9770,[20] a platinum and silver conductor composition ordinarily used to provide thick-film conductors for microcircuits, has been previously used as an effective acoustic bond at high temperature for compressional[14] and shear[13] waves. The transducers[21] used for longitudinal and transverse sound velocity measurements were a 10-MHz, 36° y-cut lithium niobate transducer and a 10-MHz, 41° x-cut lithium niobate transducer, respectively. The temperature was measured using a type-K Chromel-Alumel thermocouple with an Omega-CJ cold-junction compensator and a Keithley-171 digital multimeter. A Marshall furnace, Varian model 1023, was used in this work. The measurements were performed in a vacuum of approximately 4×10^{-3} Pa (3×10^{-5} Torr). The relatively small scatter of data of a particular run is an indication of the precision of the data. The estimated accuracy for the measured ρv^2 is approximately $\pm0.5\%$ near room temperature, increasing to $\pm0.7\%$ at high temperature due to possible thermocouple errors.

RESULTS

Figure 1 shows the temperature dependence of the measured quantities $\rho v_L^2=C_{11}$ and $\rho v_L'^2=(C_{11}+C_{12}+2C_{44})/2$. Figure 2 shows the temperature dependence of the three independent adiabatic elastic constants of BaF$_2$. C_{44} is taken from previously published results,[13] while C_{12} is experimentally derived from the previously published results[13] for $\rho v_T'^2=(C_{11}-C_{12})/2$ and the present measurements of C_{11}. Both measured quantities and the three independent adiabatic elastic constants exhibit a similar temperature dependence that is approximately linear over the temperature range 300—1040 K. From 1040 K to the highest temperatures for which velocity measurements could be obtained, there is a marked difference in the temperature dependence between C_{44} and the other quantities, $\rho v_L'^2$, C_{11}, and C_{12}.[22] While C_{44} has approximately the same temperature derivative from 300 to 1236 K, the temperature derivatives of the quantities $\rho v_L'^2$, C_{11}, and C_{12} are distinctly more negative above 1040 K. We obtain good consistency of the C_{11} values within experimental error, even though the specimens are of different orientations. The relative percentage difference of $C_{11}=\rho v_L^2$ and C_{11} derived from $\rho v_L'^2=C_{11}-\rho v_T'^2+C_{44}$ is 2% at 300 K, decreasing to less than 0.1% at 1000 K and increasing to 1.9% at 1144 K.

The present measurement of C_{11} and previous measurements[5,14,23–28] agree to within 1% at room temperature, except for the work of Gerlich,[24] Gerlich,[26] and Bergman,[28] which are 3.2%, 3.6%, and 2.5% lower, respec-

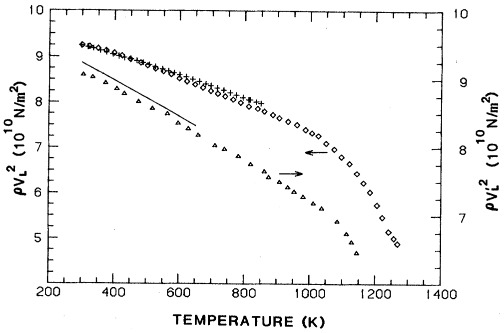

FIG. 1. Temperature dependence at 10 MHz of the measured quantities $\rho v_L^2=C_{11}$ (diamonds) and $\rho v_L'^2=(C_{11}+C_{12}+2C_{44})/2$ (triangles) is given. Previous temperature-dependent data are given for ρv_L^2 (crosses) (Ref. 14) and for $\rho v_L'^2$ (solid line) (Ref. 23).

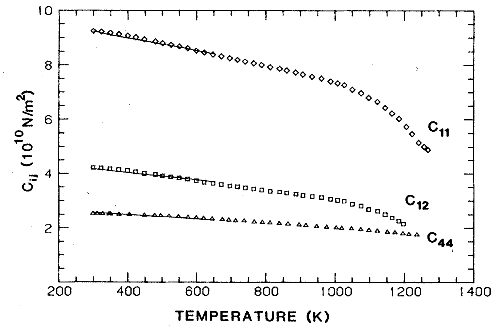

FIG. 2. Temperature dependence of the three independent adiabatic elastic constants C_{ij} at 10 MHz is given. Data for $C_{11}=\rho v_L^2$ (diamonds) are from the present work. Data for C_{12} (squares) are obtained by combining the measurements of $C_{11}=\rho v_L^2$ and $C_{11}-C_{12}$ of Ref. 13. Data for $C_{44}=\rho v_T^2$ (triangles) are from Ref. 13. Previous temperature-dependent data (Ref. 23) are given by the solid lines. The estimated accuracy of the calculated C_{12} is 3 times the relative percentage error estimated for a directly measured ρv^2.

tively, and agree to within 1.2% and 1.8% with Foster *et al.*[14] and Jones[23] at higher temperatures of 650 and 850 K, respectively. Agreement between present measurements, including those in Ref. 13, and previous measurements[23–28] at room temperature for $(C_{11}+C_{12}+2C_{44})/2$, C_{44}, and $C_{11}-C_{12}$ are within 2%, 1.8%, and 0.3%, respectively, except the work of Catlow *et al.*,[5] which is 3.7% for $C_{11}-C_{12}$, and agree to within 1.4%, 2.1%, and 0.1% with Jones[23] for $(C_{11}+C_{12}+2C_{44})/2$, C_{44}, and $C_{11}-C_{12}$, respectively, at 650 K. The agreement between the present measurements of C_{12} and previous ultrasonic measurements[23,25,27] is within 1.5% at room temperature, while the agreement with Gerlich[24,26] and Bergman[28] is less satisfactory.

DISCUSSION

Class-II superionic conductors—including BaF_2—have the fluorite structure. This structure consists of a face-centered-cubic arrangement of cations (Ba^+) with anions (F^-) occupying all the tetrahedral sites. Each cation is located at the center of a cube of eight anions and each anion is on the corner of a cube surrounded tetrahedrally by four cations. The anions are mobile with the cations forming an immobile fcc cage. The empty, body-centered positions serve as interstitial positions, giving the structure more sites than there are ions to fill them, and making it possible for the fluorite-structure materials to be good ionic conductors. As the temperature increases the anions begin to vibrate anharmonically, or are displaced in the direction of the empty body centers of the fluorite cube. The anions can thereby move through the tetrahedral faces into the octahedral interstitial positions. Shapiro[29] has performed neutron-scattering experiments on both BaF_2 and PbF_2 from low temperature, through T_c, up to the melting point. Interpretation of these neutron-scattering measurements shows that the fractional number of cations on the face-centered-cubic sublattice remains constant with temperature, while the fractional number of anions located at the equilibrium tetrahedral position decreases in the vicinity of $T_c \simeq 1230$ K for BaF_2. The difficulty in interpreting the anion-occupation sites at high temperatures in the work of Shapiro,[29] Thomas,[30] and Dickens *et al.*[31] is described by Shapiro and Reidinger[32] and Chadwick.[33] The effects of the mobile ions on the properties of BaF_2 begin well below T_c at approximately 1050 K,[3–5] resulting in the transition to a highly conducting solid electrolyte being diffuse. The more negative temperature derivative of C_{11} and C_{12} in the diffuse temperature range of 1050 K to above 1230 K, when compared to the temperature derivative below 1040 K, is associated with the development of relatively high disorder in the anion sublattice.[5] The behavior of the elastic constants below 1040 K is characteristic of the anharmonic contribution to the elastic constant.[34]

An explanation of different behavior of C_{12} and C_{44} from that of C_{11} has been given by analytical expressions for the elastic constants of a perfect fluorite lattice derived by Elcombe[35] and Kleppmann.[36] The results were based on a model of ionic potential as being due to both Coulomb and short-range forces. The changes in these forces with temperature yield canceling contributions to C_{12} and C_{44}, but additive contributions to C_{11}. However, the experimentally derived values of C_{12} do not seem to agree well with this picture, in which C_{12} should have a constant temperature derivative up to T_c, as C_{44} does.

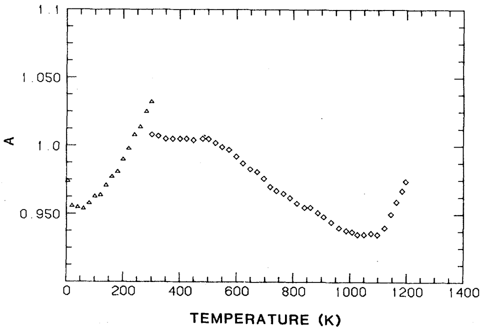

FIG. 3. Temperature dependence of anisotropy factor $A=2C_{44}/(C_{11}-C_{12})$ is given by data from this work (diamonds) and previous work (triangles) (Ref. 26).

Figure 3 shows the results for the elastic anisotropy factor $A=2C_{44}/(C_{11}-C_{12})$, while the adiabatic compressibility $\beta_s=3/(C_{11}+2C_{12})$ and the Cauchy relation failure $\Delta=C_{12}-C_{44}$ are given in Fig. 4. The values of the experimentally derived quantities given in Figs. 3 and 4 are obtained from both present and previous results.[13] Gerlich's[26] measurements of the anisotropy factor are also given in Fig. 3. The result shows that the anisotropy factor is close to unity over the entire temperature range of 300—1200 K, with a maximum percentage difference of 6.5% from unity near 1050 K. Single-crystal BaF_2 thus has the interesting property of being an approximately mechanically isotropic single crystal over a wide range of temperature. BaF_2 has the largest compressibility of any alkaline-earth fluoride at room temperature. The compressibility increases with temperature over the temperature range 300—1200 K. The positive temperature derivative of the compressibility increases significantly above 1050 K.

The ionic bond is predominant in the alkaline-earth fluorides. BaF_2 has a larger deviation from the Cauchy condition ($C_{12}=C_{44}$) than CaF_2 or SrF_2, but a smaller deviation than PbF_2 or CdF_2. Since the Cauchy condition

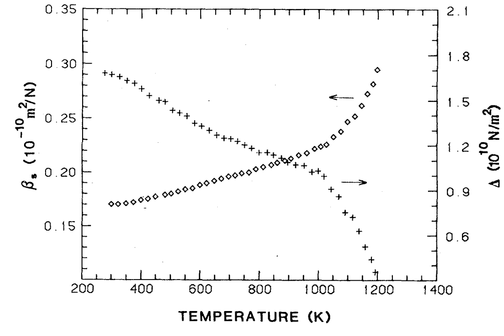

FIG. 4. Temperature dependence of adiabatic compressibility $\beta_s=3/(C_{11}+2C_{12})$ (diamonds) and Cauchy relation failure $\Delta=C_{12}-C_{44}$ (crosses) is given.

TABLE I. Cubic elastic constants, anisotropy factor $A=2C_{44}/(C_{11}-C_{12})$, compressibility $\beta_s=3/(C_{11}+2C_{12})$, and Cauchy relation failure $\Delta=C_{12}-C_{44}$ are given.

T (K)	C_{11} (10^{10} N/m^2)	C_{12} (10^{10} N/m^2)	C_{44} (10^{10} N/m^2)	A	β_s (10^{-10} m^2/N)	Δ (10^{10} N/m^2)
300	9.244	4.212	2.536	1.008	0.170	1.676
400	9.076	4.107	2.497	1.005	0.174	1.610
500	8.805	3.916	2.455	1.004	0.180	1.490
600	8.518	3.723	2.378	0.992	0.188	1.345
700	8.239	3.538	2.292	0.975	0.196	1.246
800	7.958	3.369	2.202	0.960	0.204	1.167
900	7.682	3.216	2.119	0.933	0.213	1.097
1000	7.358	3.040	2.026	0.938	0.223	1.014
1100	6.785	2.674	1.924	0.936	0.247	0.750
1197	5.856	2.157	1.802	0.974	0.295	0.355

results from the assumption of point charges at inversion centers,[37] the Cauchy condition failure (Fig. 4) indicates that BaF_2 has smaller covalent bonding than PbF_2 and CdF_2 and larger covalent bonding than CaF_2 and SrF_2 at room temperature. This covalent bonding, however, decreases with increasing temperature below the transition temperature, and near T_C the Cauchy relation failure decreases very rapidly.

Values of C_{11}, C_{12}, C_{44}, A, β_2, and Δ are calculated, assuming a linear relation between every two successive measurements, at 10 different temperatures, and are given in Table I.

CONCLUSIONS

The present study has provided new measurements of the adiabatic elastic constants as well as the mechanical parameters of barium fluoride up to 1250 K. These measurements demonstrate, that while the theories adequately explain the behavior of C_{11} and C_{44} near T_c, the behavior of C_{12} near T_c indicates shortcomings in the current theoretical explanations of lattice softening in fluorites near T_c. The elastic constants C_{11} and C_{12} and quantities derived from them exhibit a temperature dependence which is different above and below 1040 K. It is concluded that the mobile anions affect these ultrasonic properties in a broad range of temperature from 1040 K to the highest temperature reached in the present measurements, 1250 K. Further measurements of ultrasonic attenuation should provide interesting tests of theories of ion motion in solid electrolytes without the complicating factor of crystallographic phase transitions.

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