Specific heat of a Ferroelectric PZT Ceramic at the Morphotropic Phase Boundary

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Abstract—Ferroelectric ceramic materials have a wide range of applications because of their piezoelectric and pyroelectric properties. One of their most important physical properties is the specific heat. In this study, the specific heats of a series of lead-zirconate-titanate (PZT) compositions in the vicinity of the morphotropic phase boundary (MPB) were measured. The temperature range was from 1.8 to 300 K. It is believed that these are the lowest temperature measurements ever made on PZT. Differences between the specific heats of the different compositions were very small. However, the calculated Debye temperatures were slightly different. The results are useful in computing design parameters for technical devices.

I. INTRODUCTION

Knowledge of the specific heat of ferroelectric materials is important for both scientific and technological purposes. There have been relatively few publications on the specific heat of PZT at low temperatures. An exception is the work of Yarlagadda et al. who made measurements down to 23 K [1]. We were particularly interested in the vicinity of the morphotropic phase boundary (MPB), which is of special importance. It forms the intersection between the rhombohedral and the tetragonal phases as shown in Fig. 1 [2], and is the location of the recently observed monoclinic phase, illustrated in Fig. 2 [3]. The piezoelectric and pyroelectric properties are strongly enhanced at the MPB and those compositions are most frequently used in technological devices. The experimental technique, the materials studied, the specific heat results and calculations of the Debye temperature are given below.

II. MEASUREMENT TECHNIQUE

The specific heats were determined using the thermal relaxation technique as described by Lashley et al.[4]. A schematic diagram of the method is shown in Fig. 3. The test sample is attached to the platform by means of a thermal grease. A thin-film heater is attached to the lower side of the platform. The following equations describe the heat transfer processes in the apparatus where the symbols are defined in the figure:
Fig. 3. Schematic diagram of thermal relaxation technique. After [4].

The measurement procedure is as follows: Power is applied until \( T_p \) becomes constant. The derivative in the first equation is then zero permitting the calculation of \( K_1 \). The temperature is then allowed to decay to \( T_0 \). The time constant \( \tau \) is calculated. \( C_a \) is found by performing the measurement without the sample. Then \( C_x \) is found by measuring with the sample attached to the platform. The temperature is controlled by means of a He\(^3\) cryostat.

III. EXPERIMENTAL RESULTS

A series of samples were prepared with the compositions Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) with \( x = 0.45, 0.455, 0.465, 0.47 \) and \( 0.48 \). The stoichiometric reactants were mixed and ball milled for eight hours. They were then dried and pressed into pellets. The pellets were calcined at 850\(^\circ\)C for two hours and then ball milled for 12 hours. They were again pressed into pellets that were heated at 700\(^\circ\)C for one hour. Finally the pellets were sintered at 1220\(^\circ\)C for one hour and pulverized for the specific heat measurements.

The specific heat results for the full temperature range from 1.8 to 300 K are shown in Fig. 4. The range from 1.8 to 10 K is shown in Fig. 5. Compositional differences appear to be extremely small.

IV. DISCUSSION

The differences in the specific heats of the various PZT compositions in the tetragonal, rhombohedral and monoclinic phases are sufficiently small that they are almost masked by the experimental noise in the measurements. One way to distinguish them in the very low temperature region is by a computation of the Debye temperatures.

In 1912, Peter Debye proposed a model for the estimation of the phonon contribution to the specific heat of a solid [5]. The model treated the vibrations of the atomic lattice as phonons in a box. It predicted that the low temperature dependence of the specific heat would be proportional to \( T^3 \). The model has the following mathematical form:

\[
P = (C_a + C_x) \frac{dT_p}{dt} + K_1 (T_p + T_0)
\]

\[
T_p(t) = T_0 + \Delta T \exp(-t / \tau)
\]

where \( \tau = (C_x + C_a) / K_1 \)

\[
P = \left(\frac{T^3}{\Theta}\right) \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx
\]
TABLE I
HARMONIC-LATTICE EXPANSION OF SPECIFIC HEAT

<table>
<thead>
<tr>
<th>Composition</th>
<th>B₁</th>
<th>B₃</th>
<th>B₅</th>
<th>B₇</th>
<th>Θ ± Standard error (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(Ti₀.₄₅Zr₀.₅₅)O₃</td>
<td>5.429 x 10⁻⁴</td>
<td>3.453 x 10⁻⁵</td>
<td>-3.508 x 10⁻⁷</td>
<td>1.211 x 10⁻⁹</td>
<td>261.6 ± 0.4</td>
</tr>
<tr>
<td>Pb(Ti₀.₄₅₅Zr₀.₅₄₅)O₃</td>
<td>5.561 x 10⁻⁴</td>
<td>3.393 x 10⁻⁵</td>
<td>-3.371 x 10⁻⁷</td>
<td>1.132 x 10⁻⁹</td>
<td>259.5 ± 1.0</td>
</tr>
<tr>
<td>Pb(Ti₀.₄₆₅Zr₀.₅₃₅)O₃</td>
<td>4.875 x 10⁻⁴</td>
<td>3.504 x 10⁻⁵</td>
<td>-3.598 x 10⁻⁷</td>
<td>1.281 x 10⁻⁹</td>
<td>271.2 ± 0.3</td>
</tr>
<tr>
<td>Pb(Ti₀.₄₇Zr₀.₅₃)O₃</td>
<td>4.721 x 10⁻⁴</td>
<td>3.830 x 10⁻⁵</td>
<td>-4.573 x 10⁻⁷</td>
<td>2.025 x 10⁻⁹</td>
<td>274.1 ± 0.5</td>
</tr>
<tr>
<td>Pb(Ti₀.₄₈Zr₀.₅₂)O₃</td>
<td>5.094 x 10⁻⁴</td>
<td>3.888 x 10⁻⁵</td>
<td>-4.977 x 10⁻⁷</td>
<td>2.368 x 10⁻⁹</td>
<td>267.2 ± 0.5</td>
</tr>
</tbody>
</table>

low frequency expansion for the density of vibrational modes must be used [6-8]:

\[ D(\omega) = a_2 \omega^2 + a_4 \omega^4 + a_6 \omega^6 + \ldots \]  \hspace{2cm} (3)

The low-temperature specific heat is then given by

\[ C_v = \beta_3 T^3 + \beta_5 T^5 + \beta_7 T^7 + \beta_9 T^9 + \ldots \]  \hspace{2cm} (4)

All of the PZT data was fitted to the first four terms of Eq. 4 using linear regression and a weighting function of 1/C². A typical example is shown in Fig. 6 and the coefficients for all of the compositions are given in Table I. The low temperature limit of Eq. 2 is found by setting the upper limit of the integral to infinity giving

\[ C_v = \frac{12 \pi^4}{5} N k_B \left( \frac{T}{\Theta} \right)^3 \]  \hspace{2cm} (5)

The Debye temperatures were then found from the coefficient of the T³ term

\[ \Theta = \left( \frac{12 \pi^4}{5} N k_B \right)^{1/3} \beta_3 \]  \hspace{2cm} (6)

The number of atoms in a unit cell, N, was set equal to 5. The Debye temperatures as functions of PZT composition are shown in Fig. 7. The small differences between the compositions are now shown more clearly.

V. CONCLUSIONS

The temperature dependencies of the specific heats of a series of PZT compositions adjacent to the morphotropic phase boundary were measured. The temperature range was from 1.8 to 300 K. It is believed that this is the lowest temperature range ever studied for PZT. There were very small differences in the specific heats of the various tetragonal, rhombohedral and monoclinic compositions. The specific heats in the 1.8 to 10 K region were fitted to the harmonic-lattice expansion in the odd powers of temperature (except for the first power). The Debye temperatures were computed from the coefficient of the T³ term. The various compositions had slightly different Debye temperatures.

REFERENCES