CONTENTS

The Effect Of Peroxyacetic Acid Treatment At Elevated Temperature Onto The Indonesian Coal Microstructure
Mohd Azlan Mohd Ishak, Khudzir Ismail and Ahmad Faris Ismail

Enhancement Of L-Phenylalanine Production By Aminoacylase-Chitosan Complex
Pat M. Lee and Kong-Hung Lee

Effects Of Oxygen Content And Pr Substitution On Vibrational Anharmonicity Of ErBa$_2$Cu$_{3}$O$_{7-5}$ Superconductors
Ahmad Kamal Yahya, Mohd Hanapijah Mohd Yusoff and Roslan Abd-Shukor

$^{63}$Co and $^{88}$Y True Coincidence Summing Correction By Simulated Total Detection Efficiency Of Gamma-Ray Spectrometry System
Ahmad Saat

Passive Mode-Locking In Single Tapered Diode Laser
Mohd Kamil Abd Rahman

The Functional Properties Of Alcalase Produced Threadfin Bream (Nemipterus Japonicus) Protein Hydrolysate
Normah I, Jamilah B, Nazamid S and Yaakob CM

Improved Properties Of Oil Palm Trunk (OPT) Laminated Veneer Lumber (LVL) Through The Inclusion Of Rubberwood Veneers
Kamarulzaman Nordin, Hashim W. Samsi, Mansur Ahmad and Mohd Ariff Jamaludin

The Integration Of Plantation Crops With Timber Species In Malaysia
Ahmed Azhar Jaafar, Norman Kasiran, Suhami Muhammed and Wan Hanisah Wan Ismail

Modeling Stand Volume Of Rubber (Hevea Brasiliensis) Plantations In Malaysia Using Landsat TM
Mohd Nazip Suratman, Gary Bull, Don Leckie, Valerie LeMay and Peter Marshall

Predicting The Life Of Textile Materials As Automotive Car Seat Fabrics
Mohamad Faizul Yahya and Abbas Deghami
EFFECTS OF OXYGEN CONTENT AND Pr SUBSTITUTION ON VIBRATIONAL ANHARMONICITY OF ErBa$_2$Cu$_3$O$_y$ SUPERCONDUCTORS

Ahmad Kamal Yahya$^a$, Mohd Hanapiah Mohd Yusoff$^a$ and Roslan Abd-Shukor$^b$

$^a$Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.
$^b$School of Applied Physics, Universiti Kebangsaan Malaysia, 43000 Bangi, Selangor, Malaysia.

*Corresponding author: Tel: +603-5544 4613 Fax: +603-5544 4562 email: akamalh@hotmail.com

ABSTRACT

The temperature dependent ultrasonic longitudinal and shear velocities propagated at 10 MHz in superconducting (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{6.9}$ ($x = 0.0, 0.1$ and $0.2$) and non-superconducting ErBa$_2$Cu$_3$O$_{6.9}$ were used to evaluate effective Gruneisen parameters ($\gamma_{\text{eff}}$) for both modes. The elastic behavior of (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{6.9}$ ($x = 0.0, 0.1$ and $0.2$) deviates from lattice anharmonicity theoretical curve generally above 160 K. Shear elastic response for less oxygen ErBa$_2$Cu$_3$O$_{6.9}$ is described by purely anharmonic effects throughout the temperature range of 80 K - 220 K. Deviation of elastic response for the longitudinal and shear modes from vibrational anharmonicity curves is oxygen-related and may be due to a phase transition involving oxygen ordering. The calculated effective Gruneisen parameters for (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{6.9}$ ($x = 0.0, 0.1$ and $0.2$) for both longitudinal and shear modes were found to increase with Pr content, indicating increasing anharmonicity. The influence of Pr substitution on BCS electron-phonon coupling constant and its relationship to vibrational anharmonicity is discussed.

Keywords: anharmonicity, Gruneisen parameter, superconductor

1. INTRODUCTION

Lattice vibrational anharmonicity is responsible for many different properties of solids as lattice modes in a real crystal are never completely harmonic. At low temperatures, anharmonicity contributes considerably to the magnitude of the elastic modulus of solids and in the absence of a relaxation...
process or phase change in the material, elastic moduli and sound velocities in solids increase with decreasing temperature. A means of assessing the anharmonic contribution to the temperature dependence of the velocity of sound for solids with normal acoustic phonon spectra was given by Nava et. al.\textsuperscript{1}. In this model, the change in sound velocity is given by

\[ \Delta v/v = -\frac{TC_v}{2\rho v} \tilde{\gamma}_e \]  

where \( v \) is the sound velocity, \( \rho \) is the mass density, \( C_v \) is the specific heat per unit volume, and \( \tilde{\gamma}_e \) is the effective Gruneisen parameter. The specific heat \( (C_v) \) in the equation above is given by

\[ C_v = \left( \frac{n}{V} \right) (3N_Ak_B) \left[ 3 \left( \frac{T}{\Theta_D} \right) \int_0^{\Theta_D} \frac{x^4 e^{-x}}{(e^x - 1)} dx \right] \]

where \( N_A \) is the Avogadro's number, \( k_B \) is the Boltzmann constant, \( n \) is the mole number and \( V \) is the volume of the sample. The change in velocity \( (\Delta v/v) \) can be fitted to this theoretical model using eq. (1) if values of \( \Delta v/v \) at two different temperatures along with Debye Temperature \( (\Theta_D) \) of a material are known. Anharmonic contribution to lattice vibration can be estimated from the computed value of the effective Gruneisen parameter \( (\tilde{\gamma}_e) \) which can be calculated from the equations above.

On the other hand, elastic studies using ultrasonic waves on certain high temperature superconductors have revealed peculiar features in the temperature dependent velocity profiles. Elastic anomalies between 200 K to 230 K which is usually accompanied by a velocity hysteresis was observed during warming and cooling cycles in the RE123\textsuperscript{1-3}(RE-rare earth), Bi-2212\textsuperscript{5} and Bi-2223\textsuperscript{6} superconductors. These elastic anomalies and velocity hysteresis have been attributed to a phase transition involving oxygen ordering in the materials\textsuperscript{7}. Previous reports have shown that in the presence of such a phase change, the elastic moduli and sound velocities originating at lower temperatures deviate from lattice vibrational anharmonicity with increasing temperature\textsuperscript{6,8}. Near the temperatures of the phase transition, lattice anharmonicity no longer dominates the magnitude of the elastic moduli of the high-temperature superconductors. Theoretically predicted temperature dependent elastic behavior of a material is useful to determine magnitude of deviation from lattice anharmonicity-dominated elastic behavior to phase-transition dominated elastic behavior. It may also be used to compare effect of oxygen content and chemical doping on elastic properties in the lattice anharmonicity-dominated region\textsuperscript{6}. In addition, the effect of anharmonicity on the electron-phonon coupling can be evaluated from calculated values of
Gruneisen parameter ($\gamma_{\text{eff}}$) and BCS electron-phonon coupling constant ($\lambda$). This would be of particular interest because the effect of anharmonicity on electron-phonon coupling in high temperature superconductors is relatively unknown.

This paper reports the influence of vibrational anharmonicity on temperature dependent longitudinal and shear ultrasonic wave velocity measurements in superconducting (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{6.9}$ ($x = 0.0, 0.1$ and $0.2$) and non-superconducting ErBa$_2$Cu$_3$O$_{6.3}$. The ErBa$_2$Cu$_3$O$_{7.5}$ is chosen because it is isostructural to the widely studied YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors$^9$--$^{11}$. Another interesting fact is that the effect of Pr substitution on anharmonicity can be easily analyzed, as oxygen content does not change appreciably with Pr content$^{12}$. Results of electrical measurements and structural investigations using powder X-ray diffraction are also discussed.

2. EXPERIMENTAL DETAILS

The (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{6.9}$ ($x = 0$, 0.1 and 0.2) samples were prepared by mixing appropriate amounts of high purity (≥99.99 %) Er$_2$O$_3$, Pr$_6$O$_{11}$, BaCO$_3$ and CuO powders. The materials were ground in a mortar and then calcined in air at around 900 °C for 48 hours with several intermittent grindings and oven cooled. The powders were then pressed into pellets of ~12.5 mm diameter and 3 mm thickness. The pellets were heated at the same temperature for 24 hours and cooled to room temperature at 40 °C per hour. Non-superconducting ErBa$_2$Cu$_3$O$_{6.3}$ sample was prepared by reheating the ErBa$_2$Cu$_3$O$_{6.9}$ sample at around 900 °C and quenching it immediately in liquid nitrogen. Details on the preparation of the samples have been reported earlier$^7$.

Electrical resistance (d. c.) measurements were carried out using the four-point-probe technique with silver paint contacts. The samples were also examined by X-ray powder diffraction with CuK$_\alpha$ radiation using Siemens D 5000 diffractometer. The ultrasonic velocity was measured using a Matec 7700 system which utilizes the pulsed-echo-overlap technique. The sample was bonded to a quartz transducer using Nonaq stopcock grease. The longitudinal and shear velocity measurements were performed at 10 MHz in an Oxford Instrument liquid nitrogen cryostat model DN 1711 and the temperature was varied at a rate of about 1 K/min during warming and cooling. Ultrasonic velocity data collected during sample heating was used for computations of the effective Gruneisen parameters and theoretical anharmonicity curves.

3. RESULTS AND DISCUSSION

Powder X-ray diffraction patterns (not shown) showed all samples to be single phased 123. The density, porosity, zero-resistance transition temperature ($T_c$ zero), onset transition temperature ($T_c$ onset), and lattice parameters of the various samples
are shown in Table 1. Temperature dependent electrical resistance measurements showed that (Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9} with x = 0, 0.1 and 0.2 exhibited metallic normal state behavior with T_c zero of 92 K, 85 K and 73 K, respectively. The quenched ErBa_2Cu_3O_{6.3} sample was non-superconducting with measurement conducted at temperatures to as low as 15 K. The oxygen content of the superconducting and non-superconducting ErBa_2Cu_3O_{7.8} samples was estimated using results of lattice constant versus oxygen content variation of Maletta H. et. al. The Pr substituted samples were also estimated to have an oxygen content of O_{6.9} since they were prepared under the same conditions and low Pr substitution was reported not to affect the oxygen content appreciably. The longitudinal and shear velocities, Debye temperature (θ_D) measured at 80 K, effective Gruneisen parameter (γ_eff) and BCS electron-phonon coupling constant (λ) are given in Table 2. A brief discussion of ultrasonic propagation in polycrystalline ceramics has been presented earlier.

Ultrasonic velocity measurements on the samples revealed different elastic response with temperature. Superconducting ErBa_2Cu_3O_{6.9} (Figure 1(a)) and (Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9} (Figure 3(a)) showed thermal longitudinal velocity-hysteresis between cooling and warming. Non-superconducting ErBa_2Cu_3O_{6.3} showed monotonic shear and longitudinal velocity change with temperature (Figure 1(b) and Figure 2(b)). Figures 1 to 4 show the temperature dependence of the shear and longitudinal wave velocity changes, for all samples together with the curve-fitted lines calculated using equation (1). Equation (1) have been fitted to the experimental data for both modes in the samples assuming γ_eff is temperature independent using θ_D values given in Table 2 and the magnitudes of two selected data points. The data points selected are boundary points of regions that give a high correlation (99.2 %-99.9 %) between the theoretical curves and the experimental data.

For superconducting ErBa_2Cu_3O_{6.9}, the ultrasonic velocity for both modes (Figure 1(a) and Figure 2(a)) is dominated by vibrational anharmonicity below 160 K. Above 160 K, ultrasonic velocity for both modes deviates very much from anharmonicity theoretical curves. A step-like anomaly indicating a pronounced lattice stiffening was observed for the longitudinal mode at around 230 K during heating and at around 205 K during cooling (Figure 1(a)). The step-like anomaly has been suggested to be due to a phase transition involving oxygen ordering and has been discussed in detail elsewhere. From the magnitude of deviation from the idealistic behavior, the elastic response of ErBa_2Cu_3O_{6.9} may be strongly influenced by the phase transition creating an anomalous region above 160 K.
Table 1. Physical parameters measured for various samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Tc onset (K)</th>
<th>Tc zero (K)</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErBa₂Cu₃O₆.₉</td>
<td>5.62</td>
<td>19.8</td>
<td>94</td>
<td>92</td>
<td>3.813  3.879  11.632</td>
</tr>
<tr>
<td>ErBa₂Cu₃O₆.₃</td>
<td>5.54</td>
<td>19.8</td>
<td>-</td>
<td>-</td>
<td>3.856  3.856  11.767</td>
</tr>
<tr>
<td>(Er₀.₉Pr₀.₁)Ba₂Cu₃O₆.₉</td>
<td>5.86</td>
<td>17.9</td>
<td>89</td>
<td>85</td>
<td>3.813  3.887  11.629</td>
</tr>
<tr>
<td>(Er₀.₉Pr₀.₂)Ba₂Cu₃O₆.₉</td>
<td>5.75</td>
<td>19.5</td>
<td>77</td>
<td>73</td>
<td>3.817  3.879  11.625</td>
</tr>
</tbody>
</table>

Table 2. Experimental and computed values of physical parameters of various samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>v₁ (ms⁻¹)</th>
<th>v₂ (ms⁻¹)</th>
<th>θD (K)</th>
<th>γeffₗ</th>
<th>γeffₛ</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErBa₂Cu₃O₆.₉</td>
<td>4440</td>
<td>2705</td>
<td>375</td>
<td>7.98</td>
<td>5.28</td>
<td>0.65</td>
</tr>
<tr>
<td>ErBa₂Cu₃O₆.₃</td>
<td>4306</td>
<td>2533</td>
<td>351</td>
<td>5.99</td>
<td>5.54</td>
<td>-</td>
</tr>
<tr>
<td>(Er₀.₉Pr₀.₁)Ba₂Cu₃O₆.₉</td>
<td>4598</td>
<td>2790</td>
<td>387</td>
<td>8.64</td>
<td>5.48</td>
<td>0.61</td>
</tr>
<tr>
<td>(Er₀.₉Pr₀.₂)Ba₂Cu₃O₆.₉</td>
<td>4660</td>
<td>3120</td>
<td>428</td>
<td>9.29</td>
<td>6.60</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Note: The longitudinal and shear velocity values are corrected for porosity as in ref. 7.
Figure 1: Temperature dependence of longitudinal wave velocities of (a) superconducting ErBa$_2$Cu$_3$O$_{6.9}$ and (b) non-superconducting ErBa$_2$Cu$_3$O$_{6.3}$. Fits of equation (1) to curve (a) and curve (b) are shown by the solid and broken lines, respectively.

Figure 2: Temperature dependence of shear wave velocities of (a) superconducting ErBa$_2$Cu$_3$O$_{6.9}$ and (b) non-superconducting ErBa$_2$Cu$_3$O$_{6.3}$. Fits of equation (1) to curve (a) and curve (b) are shown by the broken and solid lines, respectively.
For nonsuperconducting ErBa$_2$Cu$_3$O$_{6.3}$ the shear velocity curve (Figure 2(b)) showed an approximately linear temperature dependence and is in good agreement with the curve based on lattice anharmonicity model by Nava et. al. (eq. (1)). This indicates that shear elastic response for oxygen reduced ErBa$_2$Cu$_3$O$_{6.3}$ is dominated by purely anharmonic effects throughout the temperature range of 80 K - 220 K. However, for the longitudinal mode, lattice anharmonicity dominates below 170 K. Above 170 K, the longitudinal velocity deviates from the theoretical curve.

For (Er$_{0.9}$Pr$_{0.1}$)Ba$_2$Cu$_3$O$_{6.9}$, the ultrasonic velocity for the longitudinal and shear modes as shown in Figure 3(a) and Figure 4(a) respectively, are dominated by vibrational anharmonicity below 160 K, above which, both velocities start to deviate from theoretical curves. Because Pr substitution of 0.1 in (Er$_{0.9}$Pr$_{0.1}$)Ba$_2$Cu$_3$O$_{6.9}$, does not cause large difference in the percent change of velocity and the velocity hysteresis compared to superconducting ErBa$_2$Cu$_3$O$_{6.9}$, the deviation from theoretical anharmonicity curves at temperatures above 160 K for both modes is probably caused by a similar oxygen ordering process $^7, 13$.

On the other hand, for Er$_{0.8}$Pr$_{0.2}$Ba$_2$Cu$_3$O$_{6.9}$, the longitudinal velocity deviates from anharmonicity theoretical curve starting at around 190 K (Figure 3(b)). The temperature dependence of the longitudinal velocity in Er$_{0.8}$Pr$_{0.2}$Ba$_2$Cu$_3$O$_{6.9}$ exhibited a monotonic behavior with no elastic anomalies. Suppression of elastic anomalies and oxygen ordering with Pr$_{0.2}$ substitution may have enhanced longitudinal acoustic mode anharmonicity and caused deviation from theoretical curve to start at a slightly higher temperature. However, the shear velocity starts to deviate from the vibrational anharmonicity curve at around 160 K (Figure 4(b)).

The values of $\gamma_\sigma$ is substantially larger than $\gamma_\phi$ for all samples (Table 2). This indicates that in these samples, the longitudinal acoustic mode anharmonicity is larger than the shear mode anharmonicity. A similar observation was observed in Y-123$^6$ and Gd1113$^8$. In addition, we observed that both $\gamma_\sigma$ and $\gamma_\phi$ increase with increase of Pr content. However, oxygen depletion causes a decrease in the value of $\gamma_\sigma$ but an increase in the value of $\gamma_\phi$. This is different from previous report$^6$ on Y123, where both $\gamma_\sigma$ and $\gamma_\phi$ increase with increasing oxygen content. These results are not due to the changes in oxygen content of the Pr substituted samples since previous reports showed no appreciable change in oxygen content when Pr is substituted$^{12}$.

Standard BCS theory$^{14}$ in the weak coupling limit where $T_c \sim \theta_D e^{-\Delta/k_B}$ predicts that an increase in $\theta_D$ would accompany by an increase in $T_c$ but this is not observed in the Pr substituted samples. However, our observation of a decrease...
in $T_c$ following an increase in $\theta_d$ with increasing Pr content is not in contrast to the BCS theory as our results (Table 2) showed that the computed BCS electron-phonon coupling constant ($\lambda$) decreased with Pr substitution. Our results also show that the decrease in $\lambda$ which indicates weakening in electron-phonon coupling with Pr substitution is accompanied by an increase in vibrational anharmonicity, which is indicated by the effective Gruneisen parameters $\gamma_s$ (Table 2). It was previously reported that in phonon-mediated superconductors, the presence of lattice anharmonicity does not enhance superconducting transition$^{15}$. As such, based on our results, it is possible that lattice anharmonicity may be detrimental to electron-phonon coupling in (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{6.9}$ high-temperature superconductors.

![Figure 3: Temperature dependence of longitudinal wave velocities of (a) (Er$_{0.9}$Pr$_{0.1}$)Ba$_2$Cu$_3$O$_{6.9}$ and (b) (Er$_{0.8}$Pr$_{0.2}$)Ba$_2$Cu$_3$O$_{6.9}$. Fits of equation (1) to curve (a) and curve (b) are shown by the solid and broken lines, respectively.](image-url)
Figure 4: Temperature dependence of shear wave velocities of (a) \((\text{Er}_{0.9}\text{Pr}_{0.1})\text{Ba}_2\text{Cu}_3\text{O}_{6.9}\) and (b) \((\text{Er}_{0.8}\text{Pr}_{0.2})\text{Ba}_2\text{Cu}_3\text{O}_{6.9}\). Fits of equation (1) to curve (a) and curve (b) are shown by the broken and solid lines, respectively.

4. CONCLUSION

In conclusion, effective Gruneisen parameters \((\gamma'_s)\) have been computed from ultrasonic velocity data for \((\text{Er}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7.5}\) to evaluate lattice vibrational anharmonicity. Deviation of elastic response for the longitudinal and shear modes from vibrational anharmonicity curves was found to be oxygen-related. Pr substitution caused \(\gamma'_s\) for both longitudinal and shear modes to increase and electron-phonon coupling constant \((\lambda)\) to decrease. This indicates that an increase in anharmonicity weaken the electron-phonon coupling in the material and causes lowering of the superconducting transition temperature.
ACKNOWLEDGEMENTS

A. K. Yahya and M. Hanapiah would like to thank BRC, Universiti Teknologi MARA for the Mathcad software used for computations.

REFERENCES


system” Supercond. Sci. & Technol. 6, 678-684.

