$LiNbO_3$ composite oscillator for internal friction and modulus measurement at elevated temperatures

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(Received 22 November 1995; accepted for publication 19 February 1996)

We describe a longitudinal $LiNbO_3$ composite oscillator at 100–300 kHz to measure internal friction and Young's modulus of a small sample bar, which is directly heated in a furnace at elevated temperatures up to 800 °C. Resonant frequency, mechanical loss, and electric conductivity of a fabricated $LiNbO_3$ oscillator are measured as a function of temperature. The present method is successfully applied to $YBa_2Cu_3O_{6+x}$ wires with 1 mm diameter and 7 mm length at 30–800 °C. © *1996 American Institute of Physics.* [S0034-6748(96)00106-2]

Internal friction and elastic modulus anomaly are a sensitive probe of the motion of defects in solids. Specifically, they are useful for electrically conductive crystals which cannot be applied by dielectric loss measurement. Many methods have been used, and the choice is dictated by the desired temperature and frequency range of the measurement. The piezoelectric composite oscillator method using a composite bar of a quartz crystal and a specimen bar is one of the useful techniques for elastic measurement at 30–300 kHz. In its original form,[1–5] the specimen was excited into vibration at the resonant frequency by cementing it to one end of a quartz. A quartz crystal is used as a detector as well as the excitation of vibration of the composite bar. The modification of this method has been reported by Marx[6] and Robinson[7] in order to improve the accuracy of the measurement for internal friction in low-amplitude range. The advantages of a one-crystal technique using a quartz in a cryostat was described by Schwarz.[8] The technique using a simple composite bar is in practice very useful for the elastic measurement of a small specimen such as 5–10 mm length and 1–3 mm^2 cross-section area, achieved by less expensive apparatus. We applied this method to the study of the relaxation behavior of oxygen vacancy in single-crystal and polycrystalline ZrO_2–Y_2O_3 at moderate temperatures of 100–500 °C.[9,10] However, a measurement technique using a quartz crystal was limited by low and moderate temperature ranges, because a quartz oscillator loses the piezoelectricity above the phase transition of 573 °C. A multicomponent system with a buffer rod to avoid heat influence on an oscillator often need a complex ailment for a sample/oscillator composite, because of a large variation of modulus and internal friction in wide temperature range. Also, the homogeneous heat environment for a sample and an oscillator is not achieved in these measurements.

The system that we describe in this work is a simple one-crystal composite oscillator using a lithium niobate ($LiNbO_3$) crystal for high-temperature measurement. $LiNbO_3$ is a ferroelectric crystal of point group R_{3c} and transforms to paraelectric phase above 1210 °C. There has been literature on piezoelectric, elastic properties of $LiNbO_3$, and its application as a resonator.[11–14] For the measurement of Young's modulus, we need an oscillator with longitudinal mode in modified cube axes. In a practical procedure to make a resonator, we employed commercially available $LiNbO_3$ crystal wafers for surface acoustic wave (SAW) device application (Yamaju Ceramics, Japan). The piezoelectric-grade wafers were 1 or 2 mm thickness of 128° rotated-Y cut for a SAW filter in the MHz band. We fabricated a (YXl) 128° crystal oscillator with longitudinal vibration mode at frequencies of 200–300 kHz, whose dimension is 8–12 mm length and 1×2 mm cross section. The piezoelectric d matrix in the modified axes at room temperature was calculated using data in Refs. 11–14. Under an applied voltage to both faces of a present wafer normal to the modified y axis, the modified x direction along a long direction of a bar was proper in order to obtain pure longitudinal strain. The modified d value was calculated to $d_{21}=-1.34\times10^{-11}$ C/N. If one takes a strain S_3 (z axis), then $S_4\neq0$, so both longitudinal and stretching vibration are excited. The electrodes were coated with a platinum ink (Engelhard, NJ) followed by sintering–bonding of platinum wires at center positions on both surfaces of bars at 850–900 °C under a certain temperature schedule. The oscillators fabricated were further annealed at 900 °C for 30 min in air. The composite oscillator assembly in this work is illustrated as in Fig. 1.

The system to evaluate the resonance of both $LiNbO_3$ itself and a composite bar with a specimen consisted of an impedance analyzer (Hewllet Packard, HP 4192A), a personal computer with IEEE-488 interface (NEC-PC-9801, Japan), and a homemade electric furnace. The measurement procedure was the same as the evaluation of a piezoelectric resonator. 300 point sets of absolute admittance, phase shift, and applied frequency were recorded at resonance. A resonant frequency was graphically obtained from a plot of an admittance circle in a complex plane by the same manner as applied to an usual resonator. Figure 2 shows the plots of resonant frequency and mechanical loss versus temperature for longitudinal 200 kHz $LiNbO_3$ oscillator. There appeared to be a large loss peak and corresponding small nonlinear variation of the resonant frequency versus temperature at around 690 °C. There has rarely been a reference on such relaxation phenomenon to induce a large anelastic loss peak for $LiNbO_3$ at present temperature range. The influence of repeated heat treatment was not found on this peak. It is difficult to determine the origin of this relaxation in the present study, however we assume that it is due to a relaxation of a lithium ion or defect in a $LiNbO_3$ crystal. The dc conductivity of a $LiNbO_3$ longitudinal oscillator was also measured by a dc impedance from a circle in a Cole–Cole plot at various temperatures of 400–850 °C. The relation be-

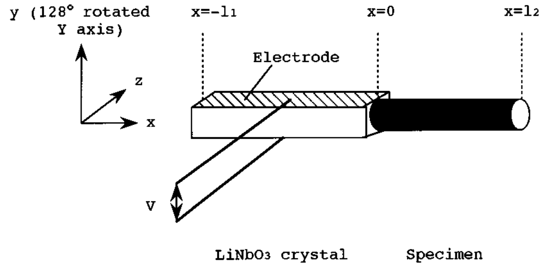

FIG. 1. $LiNbO_3$ composite oscillator.

tween σ and T was represented by an usual equation, $\sigma = \sigma_0 \exp(-H/RT)$, where $\sigma_0 = 6.71\times10^3$ S/m, and an activation enthalpy $H = 1.24$ eV.

Mathematic analysis of the piezoelectric resonance of a composite oscillator has been given by Read.[5] We used a technique of a one-crystal composite oscillator of a $LiNbO_3$ and a specimen in the measurement under a homogeneous heat environment at elevated temperature. The measured data for mechanical loss need be calibrated in order to reduce the damping of a used oscillator by the following equation:

$$Q_0^{-1} = (m_1 Q_1^{-1} + m_2 Q_2^{-1})/(m_1 + m_2), \tag{1}$$

where Q_1^{-1}, Q_2^{-1}, and Q_0^{-1} are mechanical loss (internal friction) of a resonator, sample, and composite bar, respectively. Solving the longitudinal wave equation for the system with the appreciate boundary conditions at $x = -l_1$ and $x = l_2$, using the continuity of the displacement and of the axial force at $x = 0$, one finds a relation between the resonant frequency f_0 of a composite oscillator, the free resonance f_1 of the piezoelectric crystal driver and f_2 of the specimen, and their respective masses m_1 and m_2,

$$m_1 f_1 \tan(\pi f_0/f_1) + m_2 f_2 \tan(\pi f_0/f_2) = 0. \tag{2}$$

Since the elastic constants of a oscillator crystal and a sample vary differently with temperature, a true match between f_1 and f_2 cannot be maintained over the temperature range of 30–800 °C. In order to minimize to mismatches between f_1 and f_2, $m_1 = m_2$ is desirable, as described by Schwarz.[8] However, this mismatch is indispensable to the composite-oscillator method applied in the wide range of temperature.

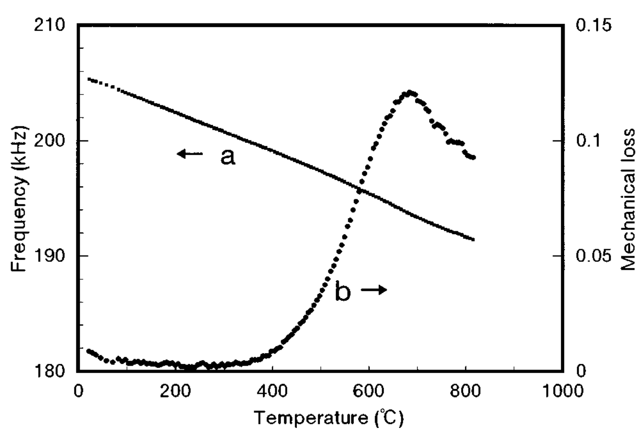

FIG. 2. Plots of (a) resonant frequency and (b) mechanical loss of a longitudinal 200 kHz $LiNbO_3$ oscillator vs temperature.

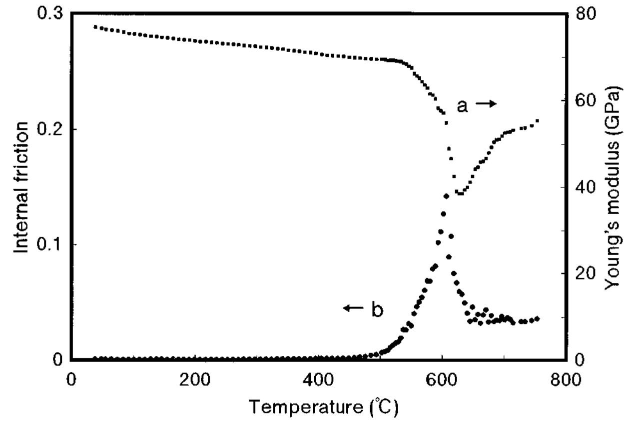

FIG. 3. Temperature dependence of (a) Young's modulus and (b) internal friction of $YBa_2Cu_3O_{6+x}$ wire annealed in flowing oxygen at 550 °C.

Kudo and Ozawa have proposed simple experimental equations to calibrate internal friction and f_0 measured using several oscillators having different resonant frequencies.[15]

Figure 3 shows an example measured using the present $LiNbO_3$ composite-oscillator technique at 200 kHz under directly heated environment in the furnace. Young's modulus and internal friction of $YBa_2Cu_3O_{6+x}$ annealed in flowing oxygen at 550 °C for 15 h are illustrated as a function of temperature up to 800 °C. The data were calibrated by Eq. (1) and experimental curves for correction.[15] Anelastic relaxation measurements for $YBa_2Cu_3O_{6+x}$ above room temperature have been carried out by several methods[16,18–20] as well as Marx's technique using a quartz and a buffer material.[17,21] It has been assumed that an internal friction peak above room temperature is due to the movement of oxygen defect between O1 and O5 sites in orthorhombic $YBa_2Cu_3O_{6+x}$. In Fig. 3, there is observed an internal friction peak at 590 °C, indicating relaxation of oxygen vacancy, and an anomaly of modulus due to the orthorhombic-to-tetragonal phase transition at around 633 °C.

[1] S. L. Quimby, Phys. Rev. **25**, 558 (1925).
[2] J. Zacharias, Phys. Rev. **44**, 116 (1933).
[3] L. Balamuth, Phys. Rev. **45**, 715 (1934); **46**, 933 (1934).
[4] R. C. Rose, Phys. Rev. **49**, 50 (1936).
[5] T. A. Read, Phys. Rev. **58**, 381 (1949).
[6] J. Marx, Rev. Sci. Instrum. **22**, 503 (1951).
[7] W. H. Robinson and A. Edgar, IEEE Trans. Sonics Ultrasonics **SU21**, 98 (1974).
[8] R. B. Schwarz, Rev. Sci. Instrum. **48**, 111 (1977).
[9] M. Ozawa, T. Hatanaka, and H. Hasegawa, J. Ceram. Soc. Jpn. **99**, 643 (1991).
[10] M. Ozawa and H. Hasegawa, J. Mater. Sci. **29**, 380 (1994).
[11] D. B. Fraser and A. W. Warner, J. Appl. Phys. **37**, 3853 (1966).
[12] R. T. Smith and F. S. Welsh, J. Appl. Phys. **42**, 2219 (1971).
[13] J. W. Burgess and M. C. L. Hales, Proc. IEEE **123**, 499 (1976).
[14] A. W. Warner, M. Onoe, and G. A. Cooquin, J. Acoust. Soc. Am. **42**, 1223 (1968).
[15] S. Kudo and M. Ozawa, Jpn. J. Appl. Phys. **28-2**, 184 (1989).
[16] B. S. Berry, Bull. Am. Phys. Soc. **33**, 512 (1988).
[17] J. L. Tallon, A. H. Schitema, and N. E. Tapp, Appl. Phys. Lett. **52**, 507 (1988).
[18] J. X. Zhang, G. M. Lin, Z. C. Lin, K. F. Liang, P. C. W. Fung, and G. G. Siu, J. Phys. Condens. Matter **1**, 6939 (1989).
[19] X. M. Xie, T. G. Chen, and Z. L. Wu, Phys. Rev. B **40**, 4549 (1989).
[20] J. R. Cost and J. T. Stanley, J. Mater. Res. **6**, 232 (1991).
[21] J. L. Tallon and B.-E. Mellander, Science **258**, 781 (1992).