

## ACOUSTIC LOSS IN LANGASITE AND LANGANITE

Ward L. Johnson,<sup>1</sup> Sudook A. Kim,<sup>1</sup> and Satoshi Uda<sup>2</sup>

<sup>1</sup>National Institute of Standards and Technology, Boulder, CO 80305, U.S.A.

<sup>2</sup>Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577 JAPAN

**Abstract** – Resonant ultrasonic loss  $Q^{-1}$  in plano-convex unplated Y-cut disks of langasite and langanite was measured as a function of frequency and temperature with the aim of identifying dominant internal mechanisms that will degrade the performance of electronic oscillators. In both materials, the dependence on temperature is similar to that previously reported for langatate. An anelastic peak appears with maxima in the 150–280 K range at frequencies between 2 MHz and 14 MHz. The dependencies of this peak on temperature and frequency is consistent with a point-defect relaxation. The width of the peak is greater than that of a Debye peak, which indicates that the relaxation has a distribution of activation energies. The peak appears at higher temperatures in langasite than in langatate, and this may explain the lower room-temperature  $Q^{-1}$  reported thus far in langatate. Additional anelastic peaks appear at elevated temperatures. The peaks are superimposed on a component of the loss that increases monotonically with temperature according to an approximate Arrhenius expression.

**Keywords** – acoustic loss, anelasticity, langasite, langanite, langatate,  $Q$ , resonance, ultrasonic

### I. INTRODUCTION

The acoustic loss in langasite ( $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ), langanite ( $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ ), and langatate ( $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ ) at ambient temperatures has been found to vary significantly between specimens [1,2], even when material is taken from the same crystal boule. Systematic differences between the loss in langasite, langanite, and langatate also appear in published results, with langatate having the lowest product of  $Q$  and frequency reported thus far [1]. Only very limited information on the mechanisms responsible for these variations can be obtained from measurements of  $Q^{-1}$  performed at one temperature. To obtain more complete information, Johnson *et al.* [2] performed measurements on  $Q^{-1}$  of plano-convex (trapped-mode) Y-cut langatate disks as a function of temperature, frequency, and mechanical contact. A broad anelastic relaxation peak was observed with a maximum in the 150–240 K range at frequencies between 2 MHz and 18 MHz. This relaxation was found to cause significant loss at ambient temperatures. Johnson *et al.* also found that, for the geometry and supporting technique that were employed, damping from mechanical contact was insignificant for overtones 3 through 9 (6–18 MHz) in all specimens studied, consistent with theoretical calculations of vibrational trapping.

In the present work, we present measurements of  $Q^{-1}$  in langasite and langanite as a function of temperature and

frequency. These results are compared with previous measurements of  $Q^{-1}$  of langatate.

### II. SPECIMEN PREPARATION

A langasite specimen was fabricated from a crystal grown by Mitsubishi Materials Corporation<sup>1</sup> using the Czochralski method. The crystal boule had a diameter of ~100 mm and was pulled along the  $\langle 01-11 \rangle$  axis from an iridium crucible with a diameter of 160–170 mm. The growth atmosphere was argon with 2–4 vol. % oxygen. This level of oxygen provides a reasonable balance between the beneficial suppression of evaporation of gallium and the detrimental oxidation of the iridium crucible. The crystal had an orange tint. The homogeneity of elastic properties of similarly grown crystals was evaluated through measurements of the distribution of SAW velocities of wafers. These velocities had a standard deviation of ~100 ppm. A piece of the crystal was fabricated into a plano-convex Y-cut disk with a diameter of 14 mm. The spherical surface had a radius of 265 mm (2 diopter). The thickness at the center was 0.68 mm, which provided a fundamental trapped-mode frequency of 2.0 MHz. The methods of cutting, lapping, polishing, and cleaning the specimen are described by Smythe [3]. Final cleaning was performed with acetone followed by ethanol.

A langanite specimen was fabricated with the same geometry as the langasite specimen, using the same methods of cutting, lapping, polishing, and cleaning. The methods of crystal growth and the manufacturer were the same as those for the langatate studied by Johnson *et al.* [2]. The crystal was grown by Crystal Photonics<sup>1</sup> by pulling with the Czochralski technique along the  $\langle 01-10 \rangle$  axis ( $y$ -axis) from an iridium crucible with a diameter of 76 mm. Typical diameters of crystal boules grown by this method were 48–50 mm. The crystal had no color. The growth atmosphere was pure nitrogen to prevent oxidation of the iridium crucible. Gallium loss due to evaporation was compensated in the composition of the melt before the crystal growth.

### III. MEASUREMENT METHODS

Each specimen was supported near its edge on three sapphire spheres. Two noncontacting planar copper electrodes with diameters of 7.7 mm and a spacing of 2.75

<sup>1</sup> The identification of the manufacturer of the material is provided here for technical completeness and does not reflect an endorsement by NIST.

This work was partially supported by a grant from the United States Army Research Laboratory.

mm were placed on opposite sides of the specimen. Coupling to resonant vibrations was directly piezoelectric. A sinusoidal tone burst, 1–5 ms in duration, was used to drive the electrodes at a frequency close to an ultrasonic resonance of the specimen. Resonant vibrations of the specimen following excitation were detected through voltages induced on the electrodes.  $Q^{-1}$  was determined from the rate of exponential decay of the amplitude calculated from the magnitude of the components of the signal that were in phase and out of phase with the reference driving sinusoid [4]. The measurements were performed in a turbo-pumped chamber either under high vacuum or with a continuous flow of helium at 0.6–2.6 Pa, which provided thermal exchange. Before entering the chamber, the helium was passed through a titanium gettering furnace to remove oxygen.

The measurements of  $Q^{-1}$  versus temperature typically displayed a number of very narrow peaks, corresponding to “activity dips” [2,5] that are associated with coupling between vibrational modes. The number of such peaks varied between specimens and between resonant modes. To facilitate a more clear presentation of results, these peaks are deleted in the plots presented here.

#### IV. RESULTS

Measurements of  $Q^{-1}$  versus temperature  $T$  of the langasite specimen are shown in Fig. 1. The general form of the temperature dependence is similar to that reported for langatate [2,6]. Peaks in  $Q^{-1}$  are superimposed on a background that increases monotonically with increasing temperature. The background is also similar to that observed in quartz, which has been attributed to anelastic relaxation of alkali impurities [7].

In Fig. 1, the highest value of  $Qf$  at 300 K is  $1.4 \times 10^{12}$  Hz for the 14 MHz mode. This is an order of magnitude lower than the highest values of  $Qf$  reported by Smythe *et al.* [1] for langasite.

Fig. 2 shows the measurements of  $Q^{-1}$  of langasite plotted versus  $1000/T$  with the minimum  $Q^{-1}$  at each frequency ( $Q^{-1}_{\min}$ ) is subtracted. The temperatures of  $Q^{-1}_{\min}$  are near the lowest temperatures reached in the measurements ( $\sim 100$  K). The semilogarithmic scaling in Fig. 2 reveals two relaxation peaks superimposed on a background with an apparent Arrhenius form [proportional to  $\exp(-E/kT)$ , where  $E$  is the activation energy, and  $k$  is Boltzmann’s constant]. The shoulder of a third peak also appears to be present at the highest temperatures ( $1000/T < 1.6$ ). Each of the peaks appears at higher temperatures for higher frequencies, which is characteristic of anelastic relaxation mechanisms.

The straight line in Fig. 2 provides an approximate value for the slope of the Arrhenius background based only on a visual inspection of the relative levels of  $Q^{-1}$  at temperatures (near  $1000/T = 2.3$  and  $6.2$ ) that are away from the peak maxima. The activation energy corresponding to this line is 0.10 eV.

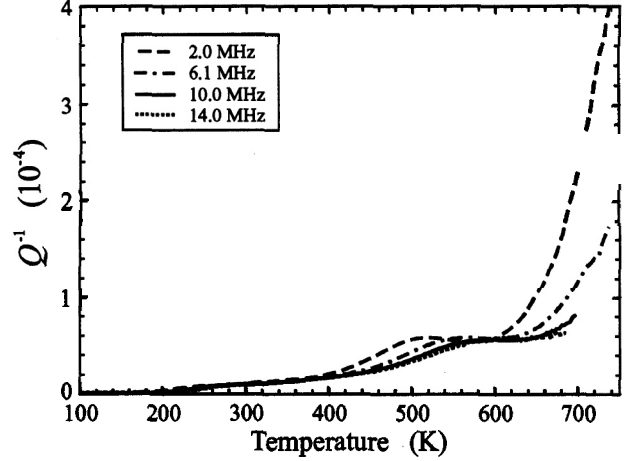


Fig. 1:  $Q^{-1}$  versus temperature of a langasite specimen.

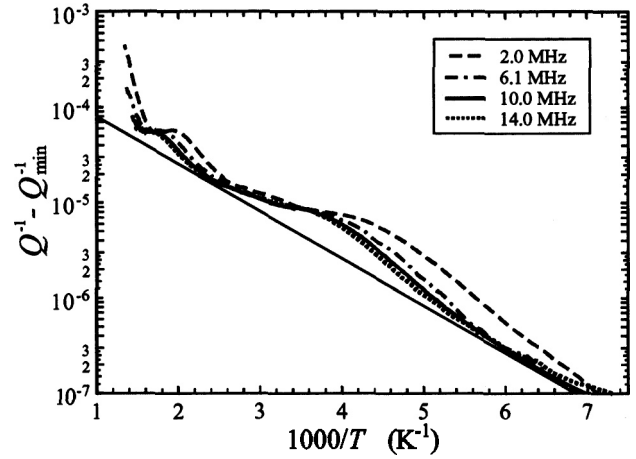


Fig. 2:  $Q^{-1}$  versus  $1000/T$  of a langasite specimen with the minimum  $Q^{-1}$  at each frequency ( $Q^{-1}_{\min}$ ) subtracted. The straight line has an Arrhenius form with an activation energy of 0.10 eV.

The results presented in Fig. 2 show that  $Q^{-1}$  at room temperature ( $1000/T \approx 3.3$ ) is dominated by contributions that are not intrinsic. The intrinsic Akhieser (phonon-phonon) contribution [8] is expected to increase relatively slowly with increasing temperature above room temperature and to be approximately proportional to  $f$  at all attainable temperatures. Considering that the observed Arrhenius background and peaks do not have these dependencies on  $f$  and  $T$ , the Akhieser contribution can be no larger than the subtracted values of  $Q^{-1}_{\min}$ , which are all approximately  $1 \times 10^{-6}$  and an order of magnitude smaller than the other contributions ( $Q^{-1} - Q^{-1}_{\min}$ ). Apart from the monotonically increasing background, the greatest contribution to the room-temperature loss shown in Fig. 2 is from the lowest-temperature anelastic peak.

The loss arising from an anelastic defect with a single relaxation time  $\tau$  has a Debye form [9]:

$$Q^{-1} = \frac{\Delta_0}{T} \frac{\omega\tau}{1 + \omega^2\tau^2}, \quad (1)$$

where  $\omega$  is equal to  $2\pi f$ , and  $\Delta_0$  is proportional to the concentration of relaxing defects. For point defects,  $\tau$  usually has an Arrhenius dependence on temperature:

$$\tau = \tau_0 \exp(U/kT), \quad (2)$$

where  $\tau_0$  is a constant. The maximum of a Debye peak occurs at the temperature where  $\tau = 1/\omega$ .

Fig. 3 shows values of the relaxation time calculated from the maxima of the lowest-temperature peak in langasite under the assumption that the dependencies of  $Q^{-1}$  on temperature and frequency follow (1) and (2). The approximate Arrhenius background (line in Fig. 2) was subtracted in determining the temperatures of the peaks. A least-squares fit of these data to (2) yields values of  $0.34 \pm 0.05$  eV for  $U$  and  $8.4 \times 10^{-15}$  s for  $\tau_0$ . Fig. 3 also shows values of  $\tau$  calculated from measurements previously reported [2] for langatate. For this langatate specimen,  $U = 0.25 \pm 0.03$  eV and  $\tau = 6.2 \times 10^{-14}$  [2]. For both materials, the values obtained for  $U$  and  $\tau$  are typical of point-defect relaxations.

The lower activation energy of the relaxation in langasite causes the peak to appear at higher temperatures than in langatate, thus increasing the relative contribution to the damping at room temperature. This difference may provide an explanation for the results of Smythe *et al.* [1], which show values of room-temperature  $Qf$  to be generally higher in langatate than in similarly grown and fabricated langasite.

The assumption of a single relaxation time for the low-temperature relaxation in langasite actually appears not to be valid. Fig. 4 shows the measurements at 6 MHz and 10 MHz with  $Q_{\min}$  and the approximate Arrhenius background (the line in Fig. 2) subtracted. The solid curves in this figure are Debye functions with the relaxation time derived from the least-squares fit shown in Fig. 3. The measured peaks are significantly broader than Debye peaks, which suggests that the relaxation has a distribution of activation energies. (This is most clearly seen from the measurements on the low-temperature side of the peaks. At temperatures above the peak maxima,  $Q^{-1}$  includes a significant contribution from the relaxation with maxima between 500 K and 600 K.) The low-temperature peaks measured in langatate also are broader than Debye peaks having a single relaxation time [2]. Therefore, the values presented in Fig. 3 for both materials only reflect dominant relaxation times of the distributions. A more complete analysis of these data would involve a least-squares fit to a superposition of loss mechanisms, including an Arrhenius background and relaxation peaks, with at least one peak having a distribution of activation energies. This type of analysis is not pursued here.

Measurements of  $Q^{-1}$  of langanite are shown in Fig. 5 along with previously reported measurements [2] on a relatively low-loss specimen of langatate (LGT17). Only data at 13.89 MHz are presented for langanite, because  $Q^{-1}$

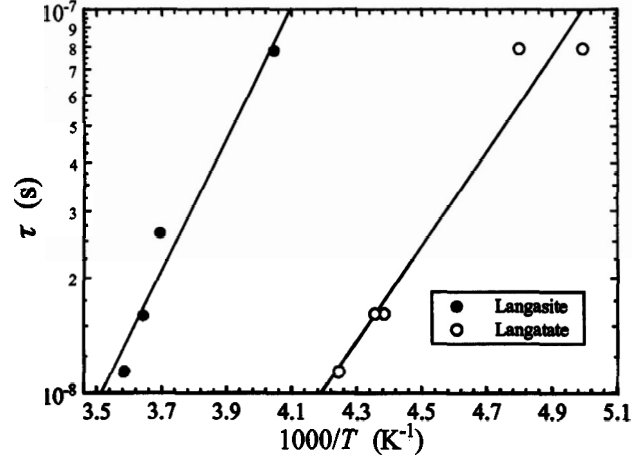


Fig. 3: Relaxation time  $\tau$  versus  $1000/T$  for langasite and langatate (specimen LGT7 [2]) determined from the temperatures of the maxima of the lowest-temperature peak under the assumption of a simple Debye relaxation (1) with an Arrhenius form (2) for  $\tau$ . The lines are least-squares fits with activation energies of  $0.34 \pm 0.05$  eV for langasite and  $0.25 \pm 0.03$  eV for langatate.

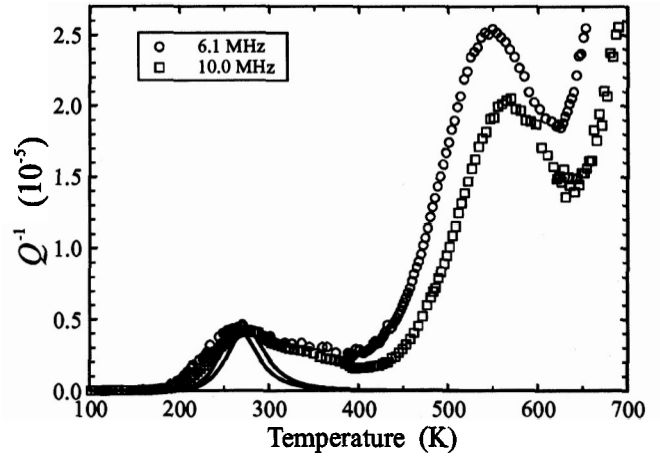


Fig. 4:  $Q^{-1}$  versus temperature in a langasite specimen with the minimum  $Q^{-1}$  at each frequency ( $Q^{-1}_{\min}$ ) and an approximate Arrhenius background (line in Fig. 2) subtracted.

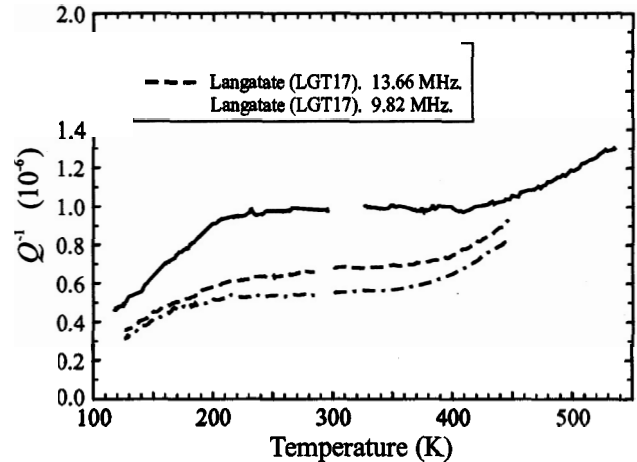


Fig. 5:  $Q^{-1}$  versus temperature of langanite and langatate (LGT17 [2]).

at other frequencies was dominated by mode coupling.

The forms of the temperature dependence of  $Q^{-1}$  of the two specimens shown in Fig. 5 are similar. They are consistent with a peak superimposed on a background that increases monotonically with temperature, as in langasite (Figs. 1 and 2).

The measured  $Q^{-1}$  of langanite near 300 K corresponds to a value of  $14.3 \times 10^{12}$  Hz for  $Qf$ , which is approximately equal to the median value for this overtone reported by Smythe *et al.* [1] for a set of langanite specimens having the same geometry as that employed here. The maximum  $Qf$  of langanite measured by Smythe *et al.* was  $21.5 \times 10^{12}$  Hz. The value of  $Qf$  at 13.66 MHz for the langatate specimen shown in Fig. 5 is  $20.1 \times 10^{12}$  Hz, which is 92 % of the median and 69 % of the maximum reported by Smythe *et al.* for this overtone in langatate.

## V. SUMMARY

A graphical summary of measurements of  $Q^{-1}$  of langasite (LGS) and langanite (LGN) is presented in Fig. 6 along with previously published results on three langatate specimens (LGT7, LGT9, and LGT17) [2,6]. LGT9 is a cylinder with a diameter of  $5.99 \pm 0.01$  mm and a length of  $15.97 \pm 0.01$  mm. Therefore, the vibrational patterns in this specimen have different symmetries than those studied in plano-convex specimens, and the 1.32 MHz mode (for which data are presented in Fig. 6) is not purely shear.

Fig. 6 illustrates common features of the temperature dependence of  $Q^{-1}$  of langasite, langanite, and langatate. In each material, there is evidence for an anelastic point-defect relaxation peak with a maximum in the 150–280 K range. The size of this peak varies between specimens. The difference in the positions of the peaks in langasite and langatate may provide an explanation for the higher room-temperature  $Qf$  reported for langatate [1]. The measurements of  $Q^{-1}$  in langasite also indicate the presence of a peak with a maximum just beyond the upper limit of the measured temperature range. A corresponding peak is completely visible in measurements on LGT9, which extend to higher temperatures. Another anelastic peak appears at intermediate temperatures in langasite. Thus far, this peak has not been observed in langatate or langanite.

None of the measurements show evidence for a significant intrinsic Akhieser [8] contribution to  $Q^{-1}$  (proportional to  $f$  and weakly dependent on  $T$  above ambient temperatures). Considering that the highest values of  $Qf$  reported here for langanite and langatate near 300 K (Fig. 5) are of the same order of magnitude as the highest published room-temperature values [1] for these materials, the lack of an obvious intrinsic contribution suggests that the maximum attainable  $Qf$  of these materials may be significantly higher than the values reported thus far.

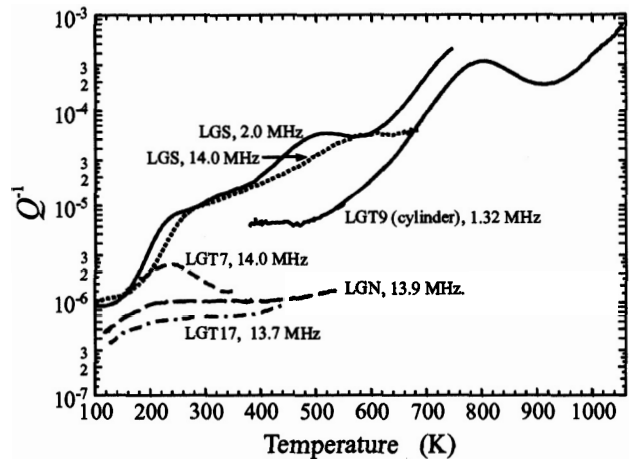


Fig. 6:  $Q^{-1}$  versus temperature of langasite (LGS), langanite (LGN), and three langatate specimens (LGT7, LGT9, and LGT17) [2,6].

## ACKNOWLEDGEMENTS

We thank Mitsubishi Materials Corporation for supplying and characterizing a langasite crystal and thank Robert Smythe of Piezo Technology, Inc., for helpful discussions.

## REFERENCES

- [1] R. C. Smythe, R. C. Helmbold, G. E. Hague, and K. A. Snow, "Langasite, langanite, and langatate bulk-wave Y-cut resonators," *IEEE Trans. Ultrason. Ferro. Freq. Contr.*, vol. 47, no. 2, 2000, pp. 355–360.
- [2] W. L. Johnson, S. A. Kim, D. S. Lauria, and R. C. Smythe, "Acoustic damping in langatate as a function of temperature, frequency, and mechanical contact," in *Proc. IEEE Ultrason. Symp.*, 2002, pp. 936–939.
- [3] R. C. Smythe, "Material and resonator properties of langasite and langatate: a progress report," in *Proc. IEEE Int. Freq. Contr. Symp.*, 1998, pp. 761–765.
- [4] W. Johnson, "Ultrasonic resonance of metallic spheres at elevated temperatures," *J. Phys. IV (suppl. to J. Phys. III)*, vol. 6, p. C8-849 (1996).
- [5] E. P. EerNisse, "Activity dips in FC-cut resonators from interaction with modes at twice the frequency," in *Proc. IEEE/EIA Int. Freq. Contr. Symp.*, 2000, pp. 331–333.
- [6] W. Johnson, S. Kim, and D. Lauria, "Anelastic loss in langatate," in *Proc. IEEE/EIA Int. Freq. Contr. Symp.*, 2000, pp. 186–190.
- [7] J. E. Ferris and J. J. Martin, in *Proc. IEEE Int. Freq. Contr. Symp.*, 1994, p. 115.
- [8] A. Akhieser, *J. Phys. (U.S.S.R.)*, vol. 1, p. 277, 1939.
- [9] A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).