SAWYER

TECHNICAL BRIEF

MEASUREMENT OF CURIE TEMPERATURE FOR $LiTaO_3$ QUALITY CONTROL

The recent increase in the use of Lithium Tantalate (LT) for Surface Acoustic Wave (SAW) radio frequency (RF) filters has generated renewed interest in its properties and uniformity. Prior to the 1960's, it was widely believed that most compounds had a specific composition. That is, crystals such as LT were believed to be $LiTaO_3$ with a perfect ratio of lithium to tantalum. Difficulty in precise chemical measurement was the main culprit in propagating this belief. The last forty years have seen drastic advances in analytical techniques such as mass spectrometry and microscopy which have shown that line compounds are the exception rather than the rule. Though we continue to refer to LT as $LiTaO_3$, in fact it is better represented using the composition formula $Li_{1-5x}Ta_{1+x}O_3$, where $0.00 < x < 0.008$.

The nearly 8% variation of lithium concentration with respect to tantalum concentration in an LT crystal influences every property of the crystal. Specifically, the SAW velocity, and thus the SAW filter center frequency, is a function of the specific lithium tantalate composition. Final device design and application dictate the allowable variation of SAW velocity and/or other critical properties. Whether the critical property of interest is temperature stability, insertion loss, wave velocity, frequency, or absorption, its value is likely coupled to the substrate composition.

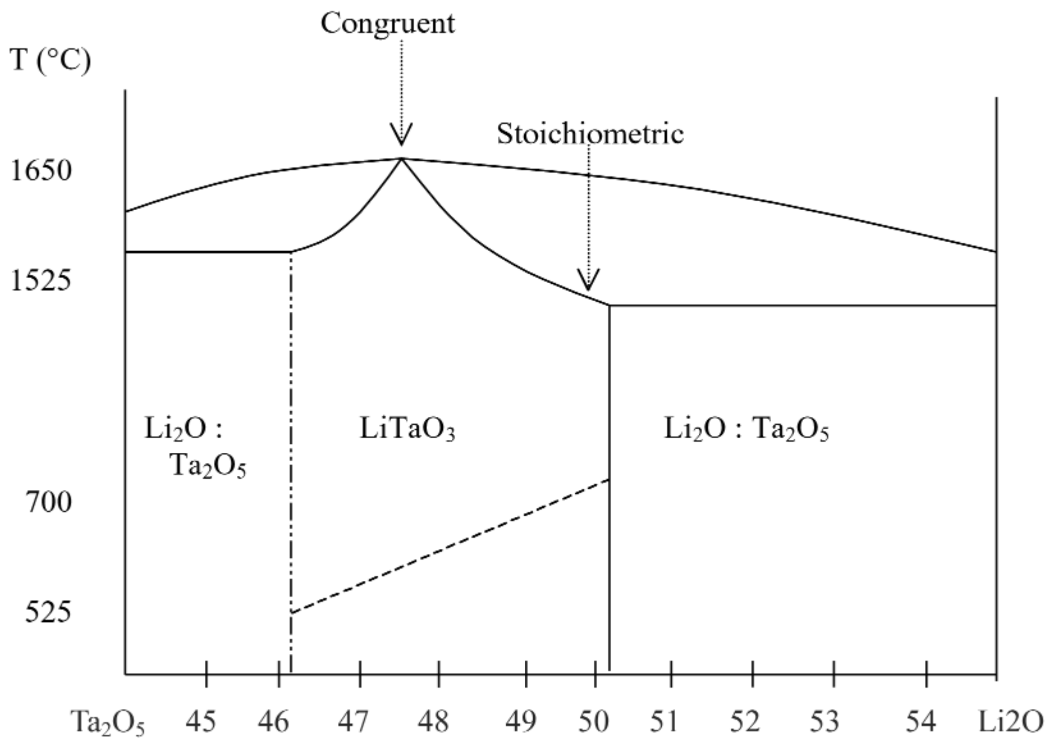
Crystal Growth and Uniformity

Crystal composition and its variation are controlled through the crystal growth procedure. By controlling crystal growth parameters and raw materials, crystal boules may be grown with minimal radial and translational composition gradients. Sawyer has dedicated significant resources to the continual improvement of our Czochralski growth equipment and processes. This controlled growth procedure guarantees the best possible wafer to wafer and across wafer homogeneity.

The LT phase diagram shows the relation between the crystal composition and the stable phase. The diagram shows the solid solubility region of LT, $Li_{1-5x}Ta_{1+x}O_3$, with $0.00 < x < 0.008$. Two compositions are highlighted on the diagram:

1) Stoichiometric crystals are represented by $x = 0$, (i.e. lithium to tantalum ratio is unity).
2) Congruent crystals are represented by $x \approx 0.006$.

The Czochralski crystal growth technique pulls a crystalline boule from a crucible of molten material. Because the congruent composition is solidified from a liquid of the same composition, the Czochralski method is the most effective method to reduce composition variations in LT. Thus, the majority of commercially available LT is supplied at or near the congruent composition.



Reporting Crystal Properties

In order to assure the commercial supply of LT with reliable composition, a precise, repeatable, and inexpensive method of measuring and reporting must be used to represent crystal properties that will result in predictable device behavior. The most obvious approach, direct chemical measurement of the crystal composition, remains imprecise, difficult, and expensive. As a result the industry has sought alternative measurements that can be used as proxies for direct measurement of composition. Due to its ease of measurement and its correlation to composition, Curie temperature has become the industry standard for specifying lithium tantalate.

Direct Chemical Analysis:

Chemical analysis is theoretically the ideal solution to this problem. In reality chemical analysis has been very effective for trace element analysis and for tracking contaminants, but has not been effective for measuring bulk composition. Sawyer uses the most accurate and reliable method for composition measurement, Inductively-Coupled Plasma - Mass Spectrometry (ICP-MS). Even this technique has a measurement error of +/- 0.5 mole %. The difficulties occur in a few areas: 1) The crystal must be dissolved, introducing measurement and contamination errors. 2) Constituent differences, lithium being very light and tantalum being very heavy, also add to measurement complexity. 3) Measuring the main constituents of a solution requires significant dilution, causing further increased contamination and measurement errors. The result is a measurement error of 1% which corresponds to a Curie temperature variation of 80 °C.

Proxy Methods:

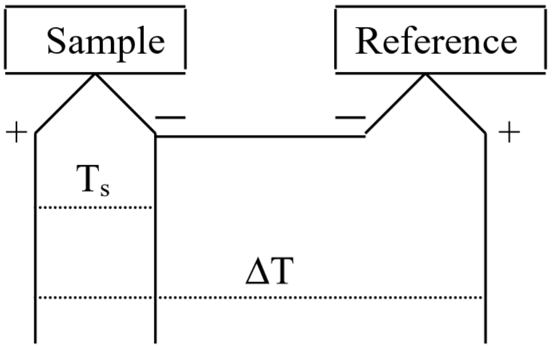
Due to the difficulties and expense involved in direct chemical measurement, the industry has identified other, more easily measured, properties that vary with and that can therefore be correlated to crystal composition.

Lattice Parameter: Lattice parameter is one property that varies with varying crystal composition and that has been used as a proxy for direct composition measurement. Though certainly a valid way to test the composition, the correlation to and the sensitivity to the composition and properties has not been openly established.

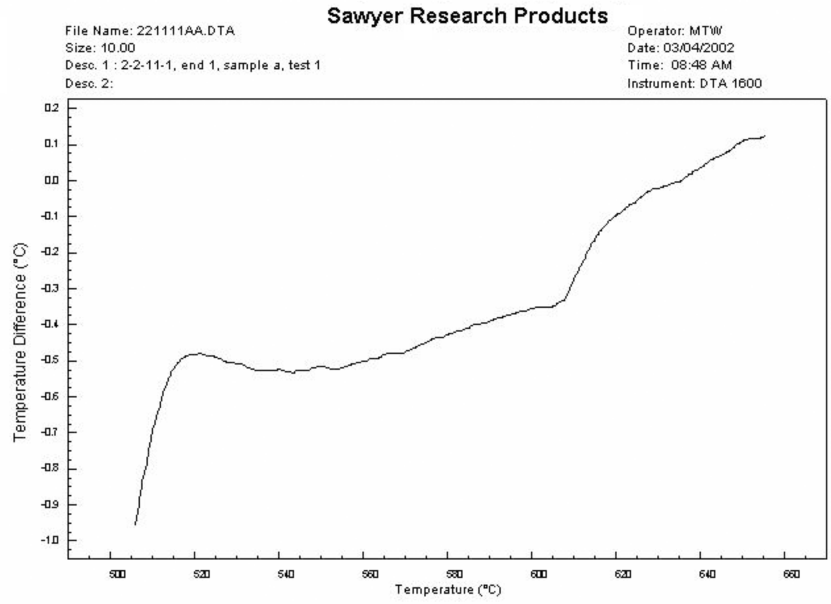
Curie Temperature: Another such material property is the Curie temperature which marks a phase transition, on heating, between the ferroelectric and the paraelectric states of the crystal. The Curie temperature varies from roughly 525 °C to 700 °C over the compositional range of solid solubility and has been superimposed on the phase diagram as the dashed line. Commercial SAW wafers are typically sold with Curie temperature specified at a fixed value between 599 – 608°C with a window of +/- 3°C. Two popular methods used to measure Curie temperature are the Capacitance Bridge and Differential Thermal Analysis.

Capacitance Bridge: Dielectric behavior of ferroelectric crystals results in a temperature dependence of the susceptibility. For crystals that follow the Curie-Weiss law, the behavior causes a maximum in capacitance near the Curie temperature. There are a few fundamental difficulties that make this measurement technique poor for production and quality control. 1) There is a strong frequency dependence of the maximum in capacitance. 2) The maximum in capacitance has a temperature hysteresis. 3) The magnitude of the temperature hysteresis has a frequency dependence.

Differential Thermal Analysis (DTA): The phase transformation that occurs at the Curie temperature causes a discontinuity in the crystal's heat capacity. DTA measures the temperature difference between a sample and an inert reference during identical heating in a furnace. By connecting the measurement thermocouples back to back, the resulting e.m.f. is proportional to the difference in temperature between the sample and the reference. This differential e.m.f. is constant as long as the sample neither absorbs nor emits heat, resulting in an increase in the measurement sensitivity of this technique. The discontinuity in heat capacity at the Curie temperature is reflected in a slope change in the plot of this differential e.m.f. at the Curie temperature.



Differential Thermal Analysis Schematic



Sample Differential Thermal Analysis Plot

Sawyer Standard Practice

Based on its reliability, repeatability, ease, and cost, Sawyer has selected DTA as its preferred method for measuring and reporting Curie temperature. Standard LT crystal wafers are supplied with Curie temperature of 605°C ± 3°. Though other methods or properties measurements are used, it appears that DTA is by far the most widely accepted and has become the default industry standard.

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