A Thesis Presented to

The Faculty of Alfred University

CREATING A DEVICE TO MODEL THE PYROELECTRIC EFFECTS OF TOURMALINE

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I. ABSTRACT

Tourmaline is the crystalline form of the mineral aluminum borosilicate with 3m symmetry. Because tourmaline is a uniaxial polar crystal, it develops a spontaneous charge during a temperature change (pyroelectricity). Since the polar symmetry direction coincides with the long axis of tourmaline crystals, the two ends develop opposite charges. Consequently, a heated crystal suspended by a strand of thread is either attracted or repelled by a second heated crystal, due to the charges on the respective crystals. In this work, the crystals were heated by light sources of differing frequencies including; 650nm (red), 570nm (yellow), 510nm (green), and 475nm (blue) to create various charges. A device was created that demonstrates this effect. This device can be used to show the effects of pyroelectricity in a lab or classroom setting. Effects of the charged crystals were observed. Findings are presented in this work, along with the effects of humidity and ambient conditions on tourmaline's pyroelectric properties.

II. INTRODUCTION

Tourmaline is a complex borosilicate mineral that contains silicate (SiO_4) tetrahedral groups. The SiO_4 groups are arranged in silicate rings that are perpendicular to the c axis of the crystal; the c axis runs lengthwise along the natural needle-like morphology of tourmaline.[1] Tourmaline occurs naturally in rocks, gangues (material that surrounds minerals in an accumulation of ore), and riverbeds. The crystal is commonly recognized as a semi-precious gem used in the making of jewelry and comes in a variety of colors (from blue and green to pink or colorless) and crystals are often found with multiple colors.

In addition to its gemological uses, one interesting property that tourmaline possesses is pyroelectricity. Pyroelectricity is the ability of a material to have a temporary electric charge; after heat is applied, it becomes polarized. After heat is applied to tourmaline, it develops a temporary electric charge at opposite ends. The change in temperature changes the equilibrium position of the atoms in the crystal structure. In a macroscopic sense, one end of the tourmaline becomes very positive, and the other end of the tourmaline becomes very negative. This only occurs within a material when the material has opposite ends that are not symmetrically equal, which means the pyroelectric effect occurs at the ends of a polar axis. Coulombic attraction/repulsion can thus be developed with heating; if two like charges are close to one another, they will repel. If one positive charge and one negative charge are close to each other, they will attract each other. Tourmaline is a very classic example of a material with pyroelectricity. The device created for this work was created to display this property.

The setup was constructed so that not only could the experiment be conducted successfully, but the set-up could easily be constructed from materials that are readily available in hardware or local building supply stores. Tourmaline itself is readily available from non-scientific sources—it is reputed to have "magickal energy powers" and is easily purchased from purveyors of New Age supplies. In addition to demonstrating pyroelectricity, the finished device can also be used as a starting point for conducting simple experiments to initiate a discussion on the effects of lighting.

Four different color sources are used, and each color corresponds to a different wavelength. Different materials react differently to the color light that is introduced. A sample of the watermelon (named for the red & green color striations) tourmaline crystals used in this work are shown in Figure 1.

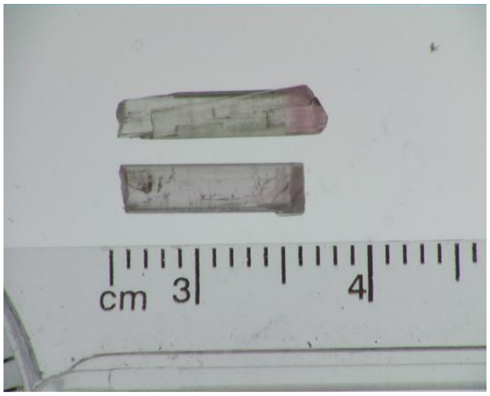


Figure 1. Examples of watermelon tourmaline crystals used.

They absorb yellow light the best, and thus the crystals heat most with yellow illumination. This absorption depends on the atoms and bonding within the mineral; hence, tourmaline with different dopants (i.e. colors) should preferentially absorb different energies.

Background

Tourmaline is a very complex aluminum borosilicate with the general formula of $XY_3Z_6Si_6O_{18}(BO_3)_3(OH,O,F)_4$ where: X is either Na^+ or Ca^{2+}; Y is Mg^{2+}, Li^+, or Al^{3+}; and Z is Al^{3+} or a combination of Al^{3+} and Mg^{2+}.[2] The variation in charges and anions, and consequent significantly variable stiochiometry, provides tourmaline with its vast assortment of colors. Tourmaline has 3m symmetry and is trigonal at room temperature. Most watermelon tourmalines are a form of Elbaite. Elba is a Mediterranean island in Tuscany that is well known as the place of

Napoleon Bonaparte’s exile. Watermelon tourmaline has the generic formula of $Na(Al_{1.5}Li_{1.5})Al_6(BO_3)_3Si_6O_{18}(OH)_4$.[2] Tourmaline’s pyroelectric properties have been known for centuries.[3,4]

History

Pyroelectricity was discovered by the Greeks about twenty-four centuries ago. Materials containing pyroelectric properties were originally believed to get their properties from the urine of a lynx. People also believed the stones to contain magical properties.[3] Some people nowadays still believe in those magical properties.[5] However, in 1756, Theodor Aepinus conducted the first scientific experiment to study the electrical properties of tourmaline. Aepinus’s results, that tourmaline had a positive and negative charge while being heated, were very controversial. Most scientists believed that both poles of the crystal were positively charged; they just contained different intensities. The nineteenth century saw more quantitative results in tourmaline pyroelectricity studies. Jean-Mothée Gaugain determined that pyroelectric properties were a function of the limits within which the temperature varies and the cross-sectional area of the tourmaline. Gaugain also discovered that pyrolelectricity occurred during cooling as well as heating. However, during cooling, the charges were reversed. In the twentieth century, the study of pyroelectricity led to the discovery of ferroelectricity. Ferroelectric materials also gain a charge while heated, but the polarization can be reoriented by applying a realizable external electric field.[3] The twentieth century and twenty-first century saw many applications for pyroelectricity. Pyroelectricity is used to measure small amounts of electromagnetic radiation fluxes and temperature changes. Practical examples include: movement detectors, pollution detectors, fire alarms, and thermal imaging. [6]

Fundamentals

Thermal, mechanical, and electrical properties are stored in crystals. The Heckmann diagram shows the relationships between these properties (originally created by Heckmann in 1925). An example of this diagram is shown in Figure 2.

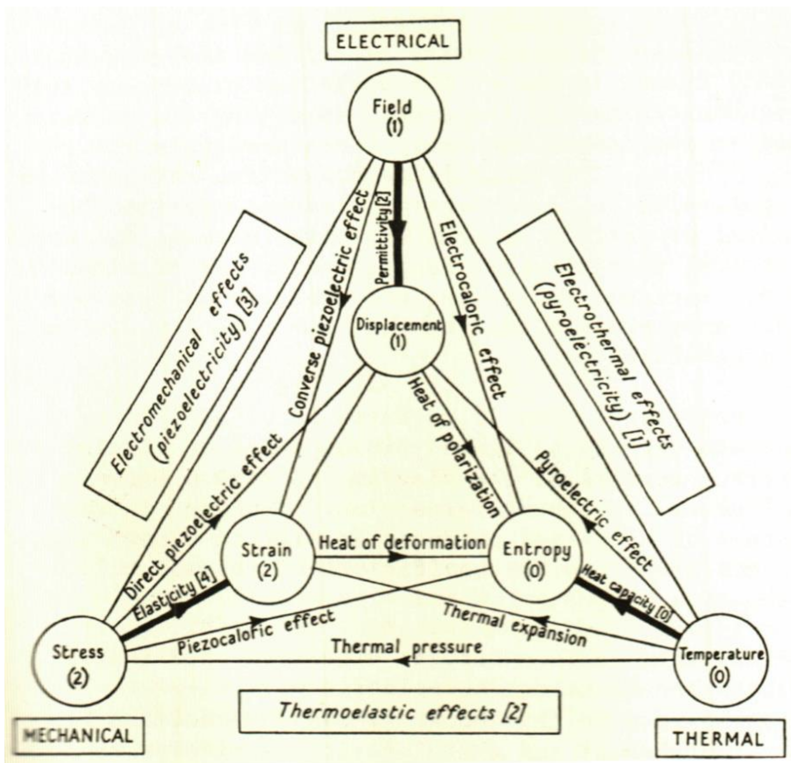


Figure 2. A Heckmann diagram showing relations among thermal, mechanical, and electrical properties of a crystal.

The lines in the diagram represent material properties and thus show that changes in one variable produce a change in another. For example, pyroelectricity occurs when there is a change in temperature which produces a change in displacement or electric field.[3] This correlation is known as primary pyroelectricity shown as “Pyroelectric effect” in the figure. Secondary pyroelectricity occurs when a change in temperature produces a change in strain which produces a subsequent change in displacement. Both primary and secondary pyroelectricity assume that there is uniform heating of the crystal. When non-uniform heating occurs, non-uniform stresses and strains are also present. Thus, the effect produced is called tertiary pyroelectricity.[7] Thus any increase in the temperature of a pyroelectric material results in development of a spontaneous charge—regardless of the method of heating.

Effects of Lighting on Materials

The consumer does not always consider the effects that the change in lighting has on materials. Some materials behave differently under different lighting conditions with paint and make-up being the most obvious. The change from incandescent to fluorescent lighting of various thermal colors can vastly alter the apparent color of either. Often lighting is not commonly thought about when preparing experiments. Factors such as humidity and sterility are controlled, but lighting is generally overlooked. A bulb that is created nowadays does not always behave the same as one that was created years ago—the spectral outputs and brightness can vary tremendously among various light sources. As lighting sources change the response of materials, some experimental results may change also. This tourmaline experiment can be used as an example of how measured material properties change with a change in lighting.

Outreach Demonstration

Many schools have outreach programs to get children and young adults interested in scientific fields. Alfred University is no exception. The tourmaline device created can be used as an outreach tool for a demonstration of pyroelectricity. The device is very visual and is also interactive. Many other experiments from the literature are dangerous and difficult to perform. This device is neither dangerous nor difficult to display. Different colored light sources can be used with the tourmaline to show that one will create greater changes than the others. Participants can hold a statically charged plastic rod or object, such as a comb, to show that the tourmaline is attracted to it. After the physical part of the demonstration is completed, ceramics and crystal structures can be discussed on a basic level. The crystal can be shown and the c axis can be pointed out. The c axis is the axis that goes along the length of the crystal. Because the c axis is the single axis of rotational symmetry, the poles that charge either positively or negatively can be easily located so that the tourmaline crystals can be hung effectively.

Also, pyroelectricity itself can be explained. Depending on the audience, piezoelectricity can also be mentioned. Piezoelectricity is the ability of a material to gain a temporary electric charge when pressure is applied to it, or, conversely to expand under applied electric field. Like pyroelectricity, piezoelectricity has many scientific and industrial applications, e.g., quartz timekeeping and frequency standards, ultrasonic welding, sonar, etc. Piezoelectric quartz also appeals to the New Age movement.

III. EXPERIMENTAL

Experimental Set-up

Watermelon tourmaline crystals, 1cm-3cm in length, 3mm-4mm in diameter, were used for all experiments purchased from healingcrystals.com.

1. Construction of the stand to suspend the crystals. See Figure 3 for details on construction.

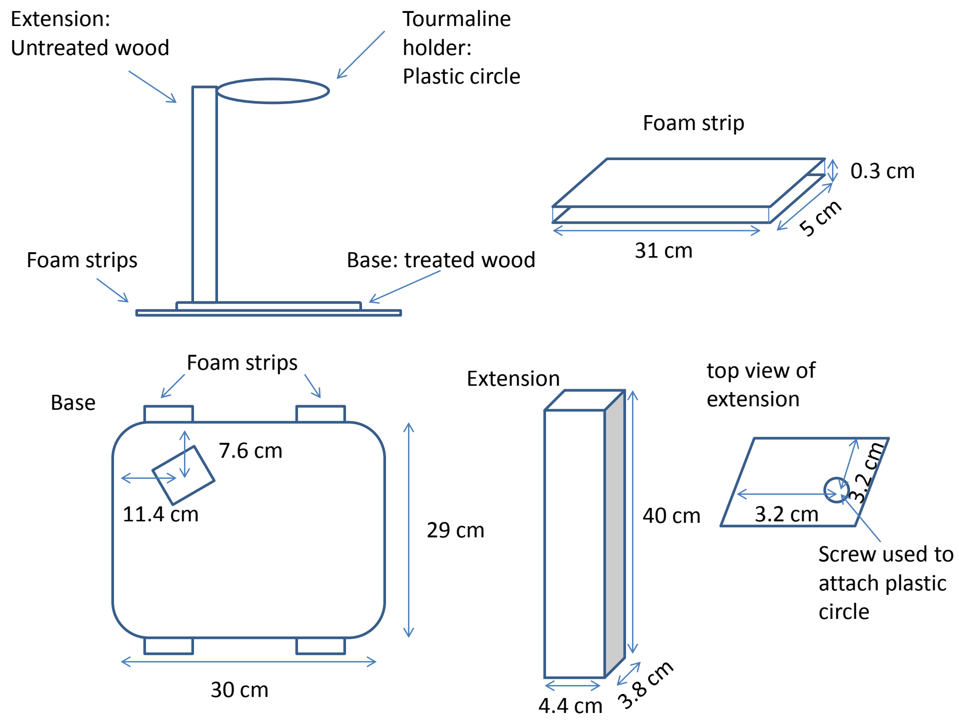


Figure 3. A graphic representation of stand created.

2. Tourmaline crystals were suspended from the central nodal point for easy motion. They were tied to nylon all-purpose regular weight sewing thread, with the diameter reduced in half, to minimize torsional resistance. .

3. The tourmaline crystals were hung on the plastic circle tourmaline holder as shown in Figure 4. The tourmaline crystals were all hung in the same horizontal plane.

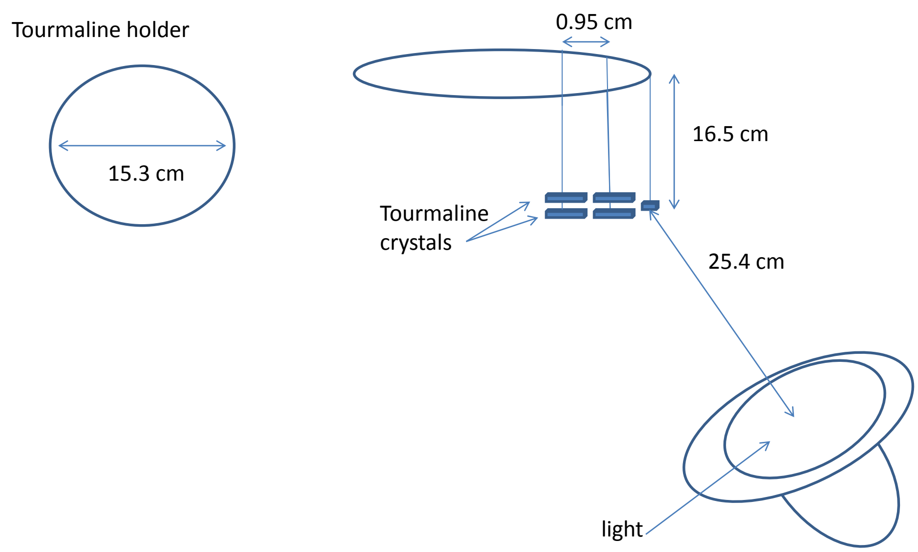


Figure 4. Assembly of the tourmaline crystals with the stand.

4. The device was set-up in a wind-proof box made out of cardboard. See Figure 5 for details.

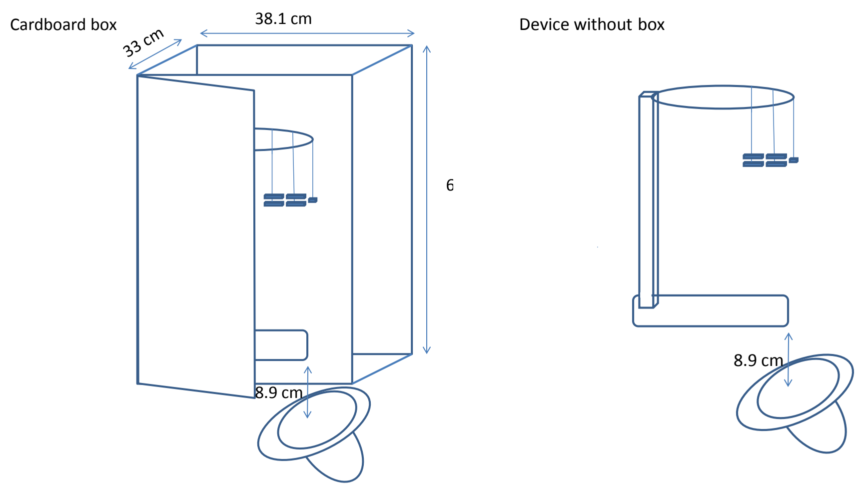


Figure 5. Completed device and construction of the wind-proof cardboard box used showing the light source at the bottom right.

5. Four different 85 Watt GE flood lights (red, yellow, green, blue) were used one at a time and placed in a 21.59cm light holder. The light was placed 8.9cm away from the edge of the stand's base.

The device was kept in a low humidity controlled room. A Craftsman 500 Degree Infrared Thermometer (4-500°F) was used to measure the temperature of the tourmaline crystals.

Experimental Procedure

1. A temperature baseline of the tourmaline crystals was measured at room temperature before each experiment with a different light source.

2. The temperature of the middle tourmaline crystal was measured over a time period of 200s in approximately 20s intervals from when the light was turned on. The laser function on the thermometer was used to verify that the temperature of the crystal was indeed the temperature being measured.

3. The rotation of the crystals was observed and recorded.

IV. RESULTS AND DISCUSSION

A temperature versus time curve was created from the data collected as shown in Figure 6.

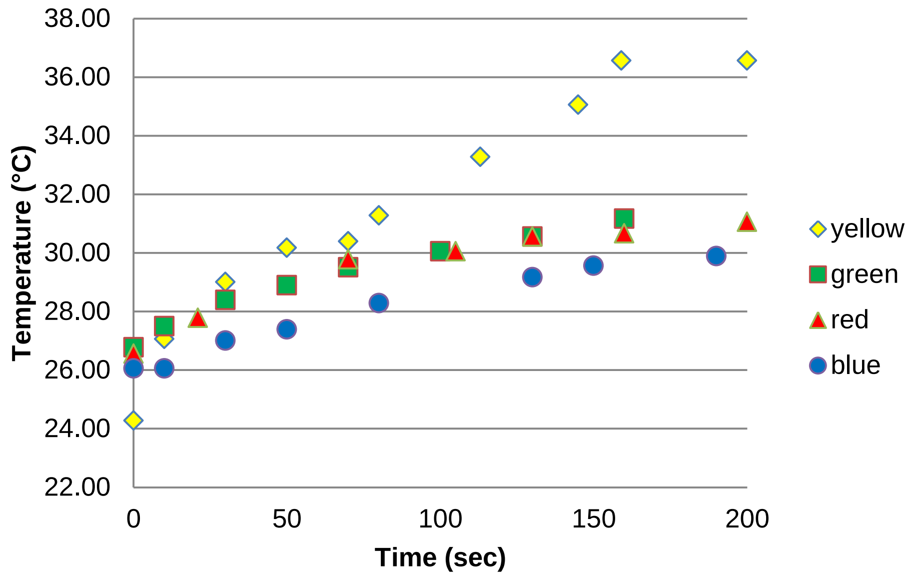


Figure 6. Temperature versus time curves for four light sources: 570nm (yellow), 510nm (green), 650nm (red), 475nm (blue).

When the different lights of varying wavelengths were shone on the tourmaline crystals, as illumination continued the temperatures of the crystals were measured and at a certain time, in this case, 80 seconds for the yellow light, the temperature of the crystals went up dramatically. The temperature rise correlated with the spin rate; crystals started to spin at a faster rate when yellow light was shone on them than it did for the red, blue, and green lights. With pyroelectricity dependent on temperature, the highest level of pyroelectricity is synonymous with the highest temperature produced by the yellow light shining on the tourmaline. The tourmaline crystals showed evidence of charging and discharging by rotating. Careful control of initial crystal position and illumination permitted the crystals to be stably oriented end-to-end and also metastably end-to-center.

Unexpected Result

The ambient temperature changed drastically during the second half of the spring semester. This caused an unexpected result in the movement of the crystals; the crystals would not spin at all when heat, in the form of light, was applied. This occurred even though the device was working fine the day before. An increase in humidity was causing the crystals to have a high conductivity and short out in the moist air.

V. CONCLUSIONS

The device was created successfully. The crystals do in fact rotate and align themselves when heated. It is possible to orientate the crystals perpendicularly.

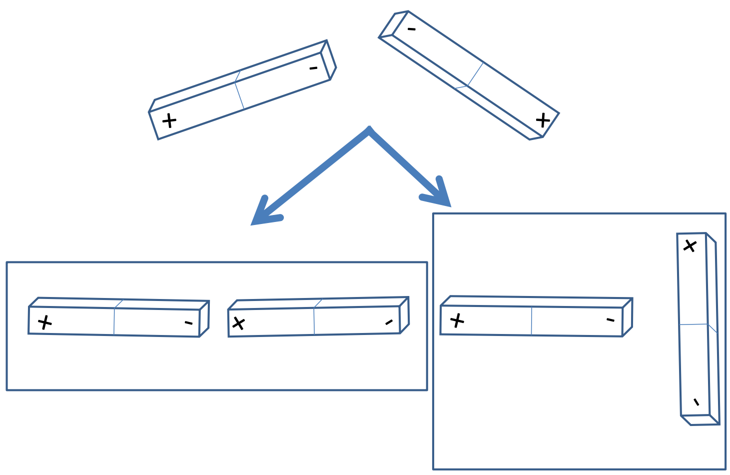


Figure 7. A schematic showing the top view of two possible outcomes for the orientation of the crystals after heating, aligned linearly and perpendicularly.

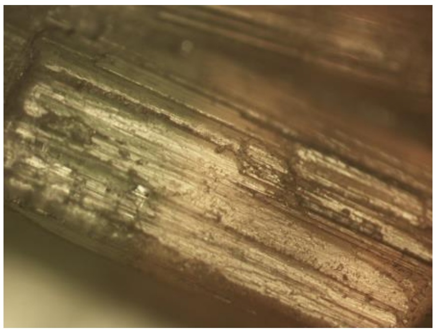
The device works best with a yellow light source. It should be used in relatively low humidity to prevent discharge through the moist air. Wind can affect the use of the device. Therefore, it is recommended to use the device in a box that will eliminate all outside air flow.

VI. SUGGESTIONS FOR FUTURE WORK

The tourmaline absorbed yellow light best. The results of the temperature versus time curve should be compared to the Raman absorption spectrum of the tourmaline used. A Raman absorption spectrum should show a large peak near 570nm. Other types of tourmaline (black, green, yellow-green, rose) should also be tested. Rose colored tourmaline (rubellite) is most likely to produce the greatest visual pyroelectric effects due to a high pyroelectric coefficient. Also, computational modeling of tourmaline could be completed to show what occurs inside the tourmaline as it is being heated. This would provide a powerful outreach tool by linking the centuries old pyroelectric effect with modern modeling. Very few literature sources included this type of modeling, and the ones that did include it, contradicted other sources.

VII. APPENDIX

The following are optical micrographs of the tourmaline used. Original magnification is listed.



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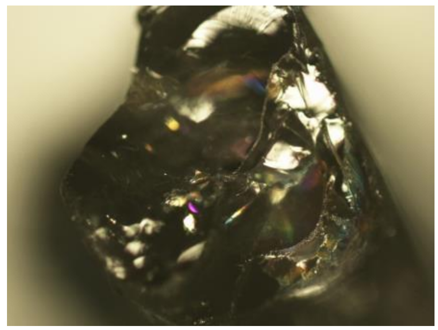

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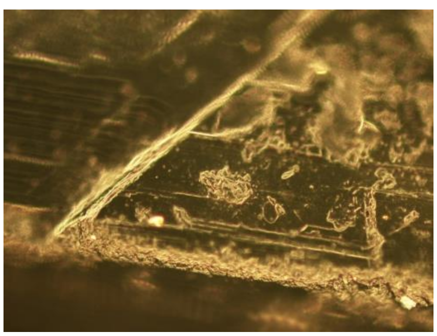
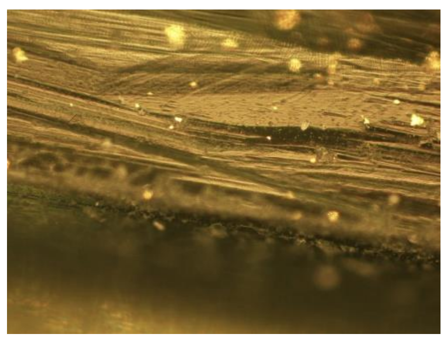


20x



20x

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