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CASE STUDY

EP21ARHT: Fabrication of a High-Energy-Resolution Diced Quartz Spherical Analyzer for RIXS

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Fabrication of a High-Energy-Resolution Diced Quartz Spherical Analyzer for RIXS

Researchers at the Argonne National Laboratory document their achievement of a novel, diced spherical quartz analyzer for use in the spectroscopic method of resonant inelastic X-ray scattering (RIXS). The RIXS analyzer requires high-quality, single crystal materials, usually silicon, for their construction. Here, a novel construction technique using single crystal quartz and acid-resistant Master Bond EP21ARHT is summarized leading to an analyzer with an unprecedented energy resolution of 10.53 meV at the iridium (Ir) L3 absorption edge.[1]

Application

Resonant inelastic x-ray scattering (RIXS) is a powerful and emerging technique used by physicists, material scientists, and chemists to study the electronic states and material properties of matter. This resonant scattering technique probes the valence electrons, providing measurements of both the energy and momentum transfers.[2] An example of where RIXS is used is the investigation of low energy magnetic excitations in superconductors, an area of research with intense focus.[3] Requiring a high intensity, tunable x-ray source, RIXS experiments are performed on-site at large particle accelerators directly at the beamline.[2]

RIXS involves a three-state, photon-in-photon-out process.[2] From the initial state, an x-ray is absorbed leading to the excitation of a core-level electron to a higher-energy, empty valence state. This intermediate state with a core-hole is highly unstable; an electron from a higher-level occupied valence state then fills the core-hole with concomitant emission of a photon. See ***Figure 1*** for a diagram. With the ability to probe both occupied and unoccupied electronic states, the technique of RIXS provides superior insights relative to other x-ray spectroscopy techniques like x-ray absorption spectroscopy (XAS) and x-ray photoelectron spectroscopy (XPS).[2] Further, the technique provides element and orbital specificity while allowing for great flexibility in sample preparation.

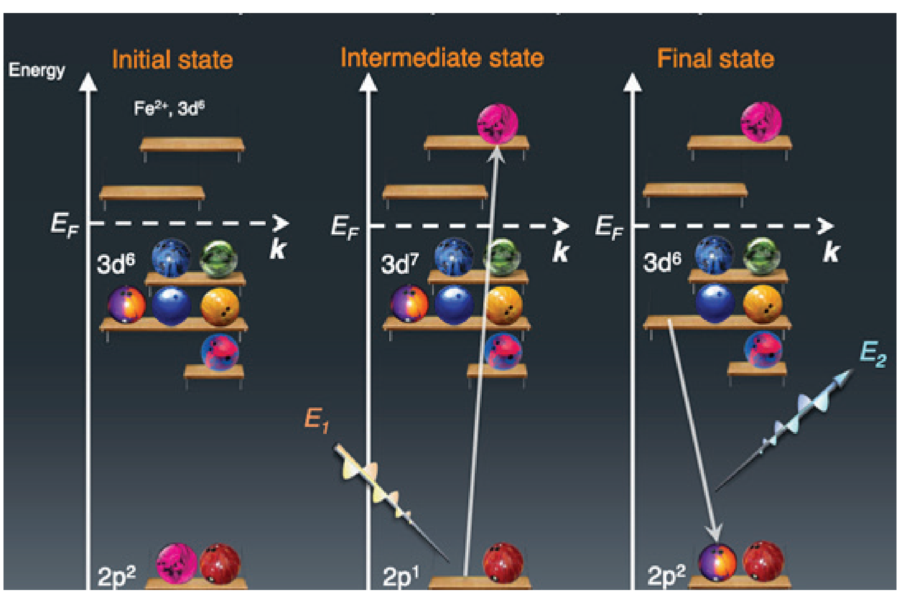


Figure 1. Visual representation of the photon-in-photon-out process of RIXS. An x-ray is absorbed (E_1) by the initial state leading to promotion of an electron from the core-level to an unoccupied, valence state. An electron from an occupied state then fills the core-hole with emission of a photon (E_2) of a differing energy.

Image: Dr. Ignace Jarrige, Brookhaven National Laboratory.[2]

In RIXS, the sample is irradiated with x-rays of a specific wavelength. As it is a low-yield process, a high intensity x-ray source that is tunable to a specific wavelength is necessary; the wavelength is chosen to resonate with the x-ray absorption edge of the element of study.[2] The scattered photons are first filtered and focused via a crystal analyzer and then subsequently measured on a 2-D detector array.[3] Due to the availability of high-quality, single-crystals as well as an established set of fabrication techniques, silicon is the material of choice in the construction of crystal analyzers employed in RIXS.[1] The crystal analyzer is a highly critical component as it will dictate what elements and absorptions edges can be studied as well as influencing the efficiency, throughput, and resolution of the technique. Due to its high crystal lattice symmetry, silicon provides a limited number of reflections that are near backscattering thus limiting the energy resolution and utility of the RIXS technique.

In order to overcome the limitations of silicon crystal analyzers and to allow for the analysis of a more diverse range of elements and absorption edges, significant efforts are underway to use other materials with lower lattice symmetries such as sapphire, quartz and lithium niobate. Unfortunately, currently available sapphire and lithium niobate crystals lacks the uniformity and quality needed for use in RIXS. The researcher at Argonne National Laboratory used commercially available quartz of suitable quality along with an acid-resistant Master Bond EP21ARHT two-part epoxy to construct a crystal analyzer for use in RIXS.

Key Parameters and Requirements

High-quality silicon boules are readily available commercially, and as they are used extensively in industry, advanced fabrication techniques such as cutting, polishing, bonding, and etching are well established.1 Quartz, contrarily, has a less established toolkit when it comes to fabrication techniques. Further, material properties such as a low thermal conductivity and a large, anisotropic linear thermal expansion complicate the construction of highly-sensitive, analytical equipment such as the crystal analyzers used in RIXS. A low thermal conductivity makes temperature control difficult, and a high degree of thermal expansion may create strain that adversely affects the analyzer performance. Strain relief techniques for quartz are less developed, and the higher thermal expansion requires greater thermal stability in the device.

Relative to the standard silicon, the thermal conductivity of quartz is approximately 15 times lower. This poses a technical challenge; tight temperature control is critical for maintaining a high degree of resolution, and the presence of even a small temperature gradient will adversely affect the resulting energy spectrum. Purposefully changing the temperature of the analyzer surface in a controlled fashion can be used to scan or sweep the analyzer energy; thus, thermal control of the system is critical for maximizing analyzer performance. As will be discussed, the assembly consists of the diced quartz bonded to a silicon backing wafer with Master Bond EP21ARHT. In addition to requiring hydrofluoric acid resistance to stand up to the etching process, adhesive choice may also influence the thermal performance of the overall assembly. In this case, two dissimilar materials—quartz and silicon—are bonded together. Master Bond epoxies can be formulated to cover a wide coefficient of thermal expansion (CTE) range as well as a wide thermal conductivity range. The device outlined in this scientific publication could potentially be optimized for better thermal stability via consultation with Master Bond's experienced engineers and formulators. Excess strain present in the quartz material has a deleterious effect on resolution—an improved adhesive system designed to minimize strain, minimize thermal stresses, and/or efficiently transfer heat, may offer performance improvements. Further, a carefully optimized epoxy, when joining two dissimilar materials, can provide benefits in thermal management and device longevity.

An overview of the RIXS process is as follows: a focused and narrow bandpass incident beam is generated from the beamline source using a high-resolution monochromator and a KB mirror. The approximately 10 μm x 40 μm sized beam strikes the sample, and the scattered radiation is filtered and focused by the spherical crystal analyzer onto a 2-D detector. ***Figure 2*** shows a simplified schematic of the scattering and collection process along with the spherical crystal analyzer.

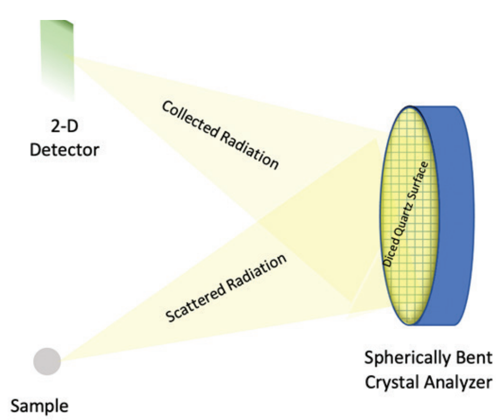
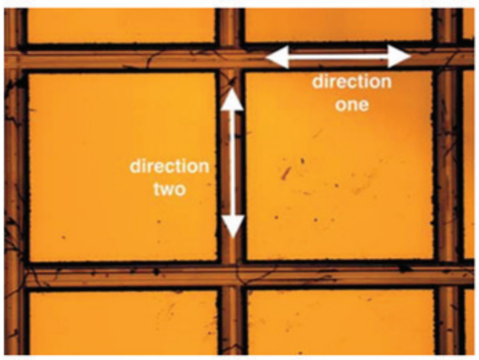


Figure 2. Simplified visual diagram of the sample, the scattered radiation, the spherically bent diced analyzer, the collected radiation, and the 2-D detector. The diced surface of the analyzer is composed of quartz.

The multi-step fabrication process is shown in ***Figure 3***.[1] To summarize, 2 mm thick and 25 mm diameter quartz wafers were sliced from a single, high-quality α-quartz ingot. The surfaces were polished and subsequently etched in hydrofluoric acid (HF) to remove any residual strain from the surfaces that result from cutting and polishing. Residual strain is detrimental to the performance and the resolution capabilities of the crystal analyzer. The quartz wafer was temporarily bonded to a silicon support wafer using wax; the surface of the quartz was then diced to within 0.25 mm of the backwall to form pixels. The quartz-silicon assembly was then re-etched in HF. As HF acid will not etch the silicon backing wafer, only the quartz was etched in this process. Further, the etching is anisotropic such that the surface of the quartz pixels etched at a faster rate than the sides.

To complete the dicing process, the diced surface of the quartz wafer was bonded to a 0.5 mm thick silicon support wafer using Master Bond EP21ARHT, a two-part epoxy with exceptional resistance to acids as well as strong adhesion to a variety of substrates including metals, glasses, and ceramics. The adhesive must resist the HF acid used in the etching process. Of further benefit, Master Bond EP21ARHT has high temperature resistance and has low linear shrinkage upon cure—low shrinkage upon cure serves to minimize stresses within the bond-line that are critical for bonding fragile materials such as the finely diced quartz. After removal of the wax and the first silicon backing wafer, the quartz was diced all the way through to form the final pixels, and subsequent HF etching processes were then performed. Finally, the assembly was bent and bonded to a concave-Plano glass lens of a 2 m radius to form the final spherical crystal analyzer.



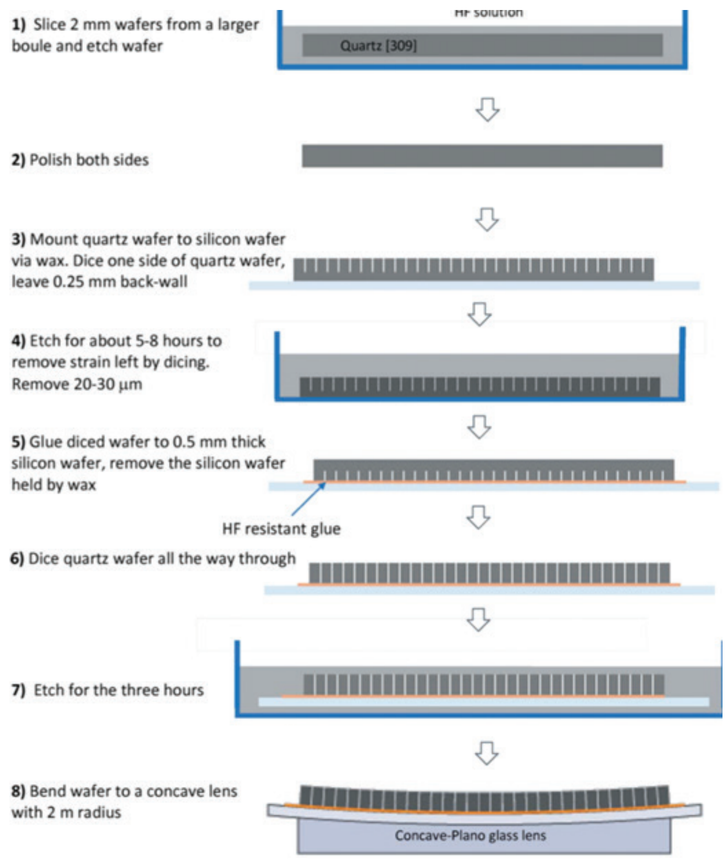


Figure 3. Visual summarization of the fabrication steps employed to construct the spherical crystal analyzer from a single large boule of quartz. The fabrication process used Master Bond EP21ARHT, an acid resistant epoxy, to successfully bond the diced quartz onto a silicon support wafer. Shown on left, quartz pixels after first dicing.[1]

Results

The researchers successfully produced a diced quartz spherical analyzer for use in resonant inelastic x-ray scattering (RIXS) spectroscopy. The construction used Master Bond EP21ARHT, a two-part acid resistant epoxy, to bond the diced quartz analyzer surface to a silicon support layer. Their experimental results demonstrated an unprecedented resolution of 10.53 meV at the Iridium L3 absorption edge (11.215 keV). This resolution is measured as FWHM—full width at half measure—narrower resolution improves the accuracy and specificity of an analytical technique enabling greater and more high-quality information to be gleaned from such experiments. See ***Figure 4*** for a summary of their analytical results and resolution determination. Efforts such as these, pioneering the use of crystal analyzers other than silicon, seek to expand the capabilities of the powerful RIXS technique.

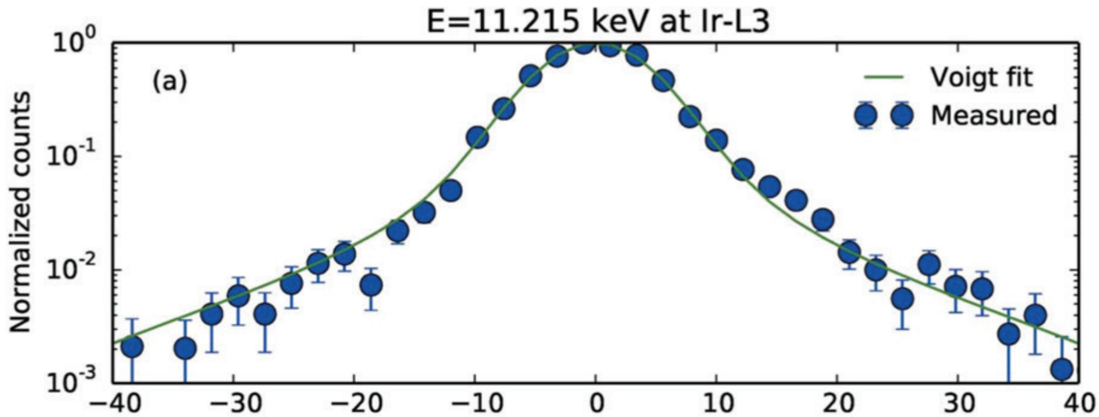


Figure 4. Spectral resolution function in $Sr_3Ir_2O_7$ at the Ir L_3 absorption edge (11.215 keV) with Voigt fit. Resolution determined to be 10.53 ± 0.1 meV at FWHM (full width at half measure).[1]

This prototype quartz crystal analyzer achieved the expected energy resolution; however, it is still a prototype proof-of-concept device. Further work is still needed to improve the fabrication process and to increase the size of the crystal analyzer. Master Bond EP21ARHT was found to successfully bond the quartz to the silicon backing wafer, and the adhesive was found to be HF resistant. However, the experimenters did note some acid incursion between the bond-line—this could potentially be improved via more careful degassing of the epoxy prior to application, the method of pressure application, changes to the cure schedule, modification of the adhesive application method, or additional surface preparation. Master Bond EP21ARHT was selected primarily for its acid resistance in this project; however, additional consultation with the Master Bond engineering team could result in a more rigorously designed adhesive application and curing schedule to further improve the capabilities and robustness of the RIXS spherical crystal analyzer.

References

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[2] Jarrige, I. Resonant Inelastic X-ray Scattering (RIXS). Brookhaven National Laboratories. Presented by Ignace Jarrige, PhD, at Columbia University, November 2015. Accessed: 04/15/2023. URL: https://www.bnl.gov/nsls2/userguide/lectures/lecture-8-jarrige.pdf

[3] Soleil Synchrotron. Resonant inelastic x-ray scattering (RXIS) at very high resolution. Accessed: 04/15/2023. URL: https://www.synchrotron-soleil.fr/en/news/resonant-inelastic-x-ray-scattering-rixs-very-high-resolution