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Compact Low Power Infrared Tube Furnace for *in-situ* X-ray Powder Diffraction

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We describe the development and implementation of a compact, low power, infrared heated tube furnace for in-situ powder X-ray diffraction experiments. Our silicon carbide (SiC) based furnace design exhibits outstanding thermal performance in terms of accuracy control and temperature ramping rates while simultaneously being easy to use, robust to abuse and, due to its small size and low power, producing minimal impact on surrounding equipment. Temperatures in air in excess of 1100 °C can be controlled at an accuracy of better than 1%, with temperature ramping rates up to 100 °C/sec. The complete "add-in" device, minus power supply, fits in a cylindrical volume approximately 15 cm long and 6 cm in diameter and resides as close as 1 cm from other sensitive components of our experimental synchrotron endstation without adverse effects.

Introduction

X-ray powder diffraction studies of materials at extreme temperatures are conducted in multiple scientific communities from chemistry, materials science and engineering, to geophysics and mineralogy. Experiments utilize both laboratory x-ray sources and synchrotron beamlines the world over. A wide variety of heating schemes are utilized: radiation from IR lamps[1-3], bare filaments[4], hot furnace walls[5-9], or microwave resonators[10], as well as direct conduction through contact to hot surfaces[11] or gasses[12]. Many systems for performing these types of experiments suffer from two classes of limitations based on system design. Either the exact temperature of the sample under test is difficult to accurately and reproducibly obtain, or the system is large, making it both difficult to integrate into existing or multi-use diffraction experiments while also limiting temperature ramp rates.

In the first class of apparatus, samples are heated radiatively by a nearby possibly directional heater, either a focused IR lamp or a ceramic or metal heating element, or a microwave resonator. In these setups accurate determination of the sample temperature can be subtle and difficult. In many devices, including some commercial ones, temperatures are determined by placing a thermocouple near the sample that then receives similar radiative exposure from the heater. However, as described in detail in the next section, this strategy is inherently inaccurate and misleading as the actual sample temperature in such a geometry is determined by the emissivity of the sample and may have little to no direct relationship to that of the nearby thermocouple.

Other apparatus place the sample inside of an oven of some sort and allow the sample and temperature measurement device to come to thermal equilibrium with their surroundings. This strategy makes for accurate temperature determinations; however, typical ovens of this type can be quite large. The size makes for difficult integration with other parts of the experiment that may need to be in close proximity to the sample or are sensitive to heat. They require both large amounts of input power to heat, possibly large amounts of cooling power for the exterior, and due to the large mass are limited in achievable rates of temperature change.

Our solution to these issues is to radiatively heat by IR lamps a small tube, 2 mm outside diameter by 1 mm inside diameter, made of SiC and to place the sample under test inside this miniature "tube furnace". We achieve a sample and thermocouple environment inside the furnace where all objects reach thermal equilibrium for accurate

TABLE I. Tube furnace functional advantages.

Tube furnace feature	Advantages
Decoupling of IR heat absorption from sample properties and temperature measurement	• Pure samples may be studied without the need to add IR absorbers or diffraction temperature standards. • Accurate temperature measurements (±1-2%) possible with a simple thermocouple. • Simple and quick sample changes as no special sample preparation is needed.
Small size	• Easy to integrate into small spaces or crowded multi-use experimental apparatus. Entire device approximately the size of a small water bottle.
Small heated mass	• Temperature ramping rates in excess of 100K/sec. • Low power (150W) needed to reach maximum temperature (1100 °C) resulting in minimal active cooling needed to protect other nearby equipment.
SiC furnace material	• Extremely robust to abuse. • High thermal conductivity makes for large volume of constant temperature and thus easy and insensitive system alignment.

temperature determinations, while at the same time heating only a few 10s of grams of material. This second point makes for both a very low power device with minimal impact on surrounding equipment and one with the possibility for very fast temperature changes. Table 1 summarizes the features and advantages of our apparatus.

Temperature Determination Problems of some Existing Systems

As asserted in the introduction, heating set ups with small IR lamps or heaters in close proximity to the sample utilizing a separate thermocouple for temperature determination can be wildly inaccurate. Both the powder sample, typically residing in a small diameter glass capillary, and the thermocouple are in an environment where some small fraction of the 4π solid angle surrounding them is comprised of an extremely hot filament or heating element, in excess of 3000 °C in the case of IR lamp filaments, while the remainder is subtended by essentially room temperature objects. In some designs there may be some sort of heat shield as the major line of sight object, but this will still at best be at some small fraction of the intended sample temperature. What this means is that given the geometry of each setup, the equilibrium temperature reached by both the sample and the thermocouple are dominated by the emissivity of those materials.

Alternatively it is possible to embed a thermocouple inside the sample under test and have it come to thermal equilibrium with the sample material. However, with the extremely small diameter capillaries typically used, from 100 μm to 1 mm, this type of sample preparation is a challenge unto itself requiring both time and skilled hands as not only must the thermocouple fit, but one must take care that the surrounding powder sample completely

shields it from direct IR illumination. Avoiding the necessity of this type of sample preparation was one of the driving motivations of the development of our device.
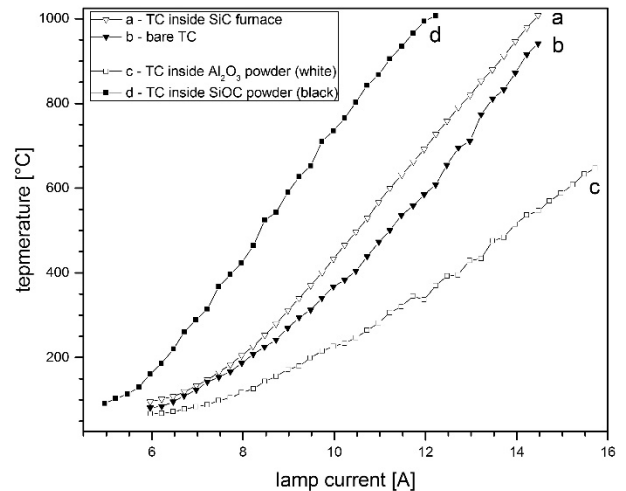

FIG. 1. Equilibrium temperatures of objects placed in direct line of sight of IR lamps. Temperatures are dominated by the emissivity of the objects.

Figure 1 compares the relative temperatures of two powder samples with wildly different emissivity prepared with miniature internal thermocouples as described in the last paragraph, a bare thermocouple, and the internal temperature of our device furnace when placed individually in identical positions in front of our IR lamps. The variation in response is obvious at all lamp currents and is particularly dramatic at 12 amps. At this irradiation level, the matte black SiOC powder reaches 1000 °C, the bright white Al_2O_3 powder is 350 °C, the bare thermocouple reads 575 °C, and the internal temperature of our furnace reaches 700 °C. Not only would a thermocouple merely in the vicinity of a sample be an inaccurate way of determining sample temperature, but if the sample were to undergo chemical or structural changes

that effect its emissivity during heating (unlike the two thermally stable samples shown here) the response of the sample to the lamps could not even be assumed to be proportional to that of the nearby thermocouple. Structural and chemical changes of an unknown nature are the most likely thing to be studied with this type of device, and thus compounding behavior in determining the sample environment during testing due to sample material properties is extremely undesirable.

SiC as Enabling Material

The difficulty of coupling IR radiation to low emissivity powders is well known in this experimental field and many practitioners have become accustomed to mixing good IR absorbers, such as platinum black, into their samples to increase the efficiency of heating and reach higher temperatures. Beyond issues of repeatability and difficulty, this strategy adulterates the pure sample and may lead to unintended or inhibited reactions of the now composite system. A similar problem exists with the mixing in of diffraction temperature standards as a means of determining temperature. This problem, coupled with our concerns detailed above regarding temperature determination lead us to the conceptual design idea of a dual walled sample container that would decouple the absorption of IR radiation from the specific emissivity of a given sample. The design of a reusable small tube into which the sample capillary could be placed from the top, and a thermocouple from the bottom, was realized after our acquisition of a proper tube material.

SiC, available commercially in small diameter tubes, was the enabling material for our conceptual design. The material properties of this ceramic (we used Hexology® SE grade from Saint Gobain Structural Ceramics[13]) are ideal for our application in a number of aspects. 1) SiC is of a dull grey/black appearance similar to graphite with an emissivity of 0.9 making it a very efficient absorber of IR radiation. 2) SiC is specified to be air stable to over 1600 °C. That is, it will not burn at the temperatures we wish to reach. 3) SiC has a reasonably high thermal conductivity of approximately 100 W/m-K meaning that the focused IR radiation from our lamps diffuses over a large area making for a stable zone of even temperature and reducing the temperature sensitivity of our set up to small alignment variations. 4) SiC hardness and fracture resistance is very high, typical of advanced ceramics, and is attractive for a robust apparatus. 5) Related to 3 and 4, the thermal shock resistance of SiC is exceedingly high, meaning it can survive extremely rapid temperature cycles and temperature gradients, also a necessary property both for experimental conditions we wish to reach and for robustness against system faults during use.

Design Details

Figure 2 shows the basic design details of the apparatus. Two short focal length, ~19 mm, IR lamps (Osram 64635HLX) are placed on either side of the vertically positioned SiC tube. Their native focal hot spot is of the order of a few cubic mm's but as described above, due to the thermal conductivity of the SiC, we achieve an approximately 4 mm long hot spot along our furnace where the internal temperature does not vary more than a few percent. Orthogonal to the axis of the two lamps, two holes have been drilled into the SiC to allow X-rays into and out of the furnace without creating a line of sight between the sample and the lamps. The choice to include these holes was made to prevent both absorption and X-ray diffraction from the thick walled SiC and, in the case of absorption, is necessary due to the low energy X-rays (15-35 keV) utilized at our facility. This choice diminishes the ideal sample environment of having as close to 4π solid angle around the sample being at the equilibrium temperature of the furnace, but we have found that the effect is small and can be at least partially accounted for in our temperature calibration. Finally, a thermocouple is inserted through the bottom of the tube and placed as close to the sample as possible without having it interfere with the X-rays.

For alignment and integration into our diffraction endstation, the apparatus is mounted in two pieces that are able to be aligned separately. The SiC tube is mounted on top of a slightly larger diameter alumina tube through a Macor (machinable ceramic) adaptor. This provides sizable thermal insulation, even over the short 3 cm length of alumina, of the very hot SiC from our standard baseplate to which the alumina tube is mounted. We use a water cooled mounting plate to ensure that our sample alignment motor stack remains at room temperature and does not experience drift due to temperature changes. A small "C" shaped bracket is also mounted to the baseplate which reaches out and above the top of the SiC tube furnace and is used to hold and align the glass capillaries that contain the samples to be measured. The IR lamps, and a simple co-axial cylindrical heat shield, with cut outs for the SiC, capillary, and X-rays, are then mounted separately and moved into position surrounding the SiC.

Alignment for experiments proceeds as follows. The "C-shaped" bracket is manually adjusted to place the sample capillary roughly centered and at the proper height inside the SiC tube. Our precision motor stack, optics, and beamline diagnostic tools are employed using our standard procedure to align the sample (and accompanying SiC tube) on our focused x-ray beam within μm accuracy. Finally, the lamp system is adjusted to ensure that the lamp focus is optimally placed on the SiC both laterally and at the proper height. As mentioned earlier, this alignment is not particularly sensitive due to the spreading of the hotspot by the SiC thermal conductivity. Once the first lamp alignment is done, many samples may be placed in the setup each with its necessary fine adjustments to the x-ray beam, but no further lamp adjustments are required.
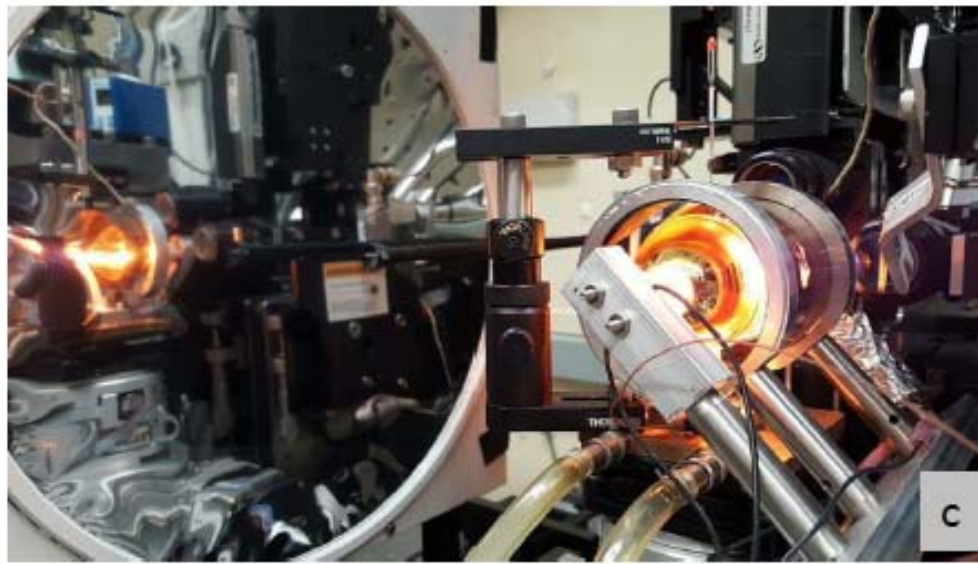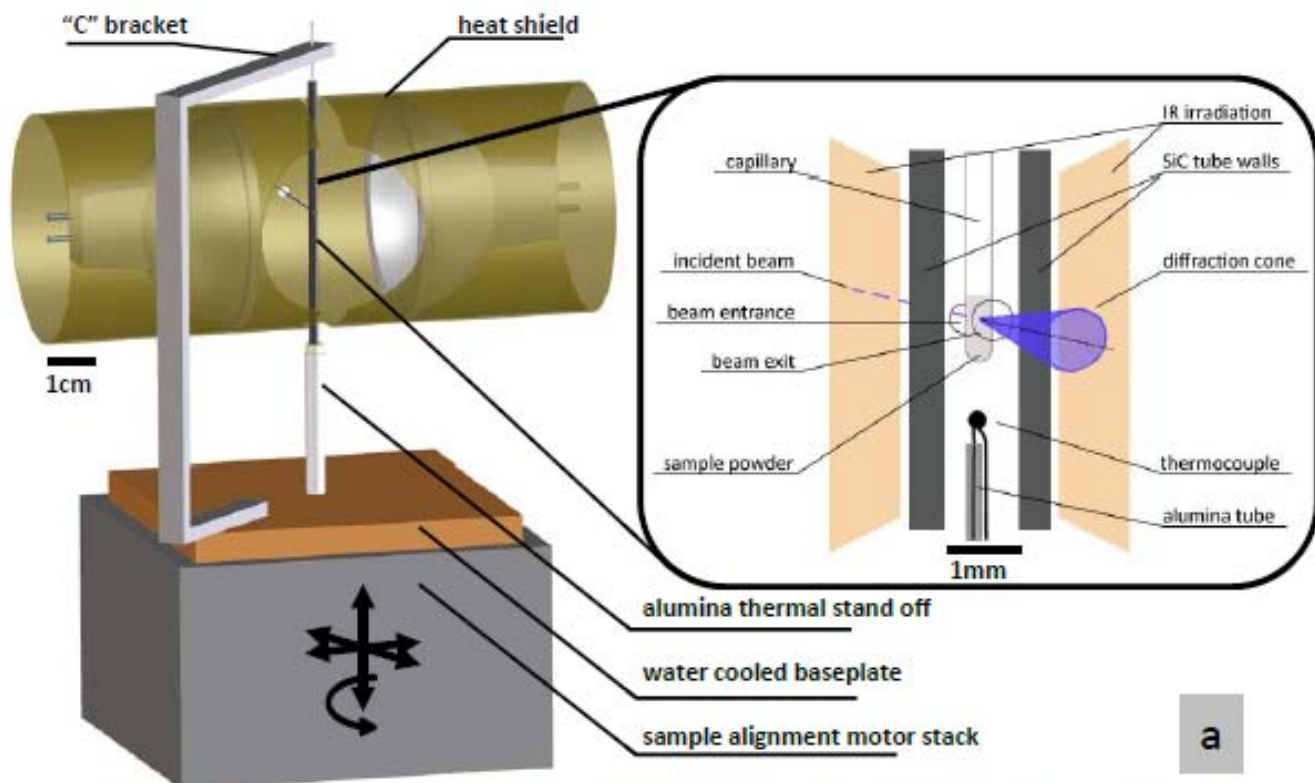
FIG. 2. Device images. (a) A simplified CAD drawing and schematic showing the major components of the device and their relative orientations when assembled. (b) Close up photograph of the actual device as seen from a view looking upstream from the detector towards the x-ray source. (c) Wider angle photograph showing the device in operation at its position nestled into our crowded experimental endstation. On the left of the image is a reflection in the detector faceplate where the hot furnace can be seen glowing, on the right the lamp holder apparatus can be seen in close proximity to various optical components related to other aspects of the endstation.[photo credits: LS and CMB]

Temperature Performance/Calibration

Lamp power, and thus sample temperature, is controlled remotely through a PID loop in our experimental control software using the thermocouple as input. Careful tuning of loop parameters is needed, as in all such control systems, for optimal performance but our system proves no more difficult to tune than others. Reported furnace temperatures can be controlled to a stability/precision of better than 1 % over the range of 50°C to more than 1200 °C, the maximum temperature attempted thus far with our apparatus. Our device does not easily

control temperatures in the 20-50 °C range due to issues with extremely low lamp power; however, such temperatures are easily reached through other means.

A temperature of 1200 °C can be reached while applying a total power of 150 W to the lamps. At this power the lamp mounting bracket reaches approximately 85 °C at its hottest point and can easily reside in close proximity to other parts of our experimental apparatus with no need for further effort to mitigate adverse effects beyond avoiding direct contact. Several times during operation we have experienced control system failures that turned the lamps on to full power instantaneously while the furnace was cold or had the lamps turn off completely while the furnace was at temperature. In all instances the SiC survived the thermal shock while our temperature monitoring recorded temperature changes of as much as 1000 °C over the course of a few seconds. These instances demonstrate the inherent very fast time scales of our low mass furnace, and our robustness to operator and system errors.

Calibration of the reported temperature was carried out by placing a second thermocouple in the sample position of the furnace, and measuring this temperature along with the control thermocouple. The two temperatures were in very good agreement (within the reported 1 % accuracy of our simple thermocouples) at temperatures up to 700 °C with the sample position reading slightly lower than the control thermocouple, increasing to roughly a 2.5 % difference at the hottest temperature measured. We attribute this discrepancy to the holes punched in the SiC furnace walls at the sample position for X-rays, and the line of sight to cooler surfaces that those holes present.
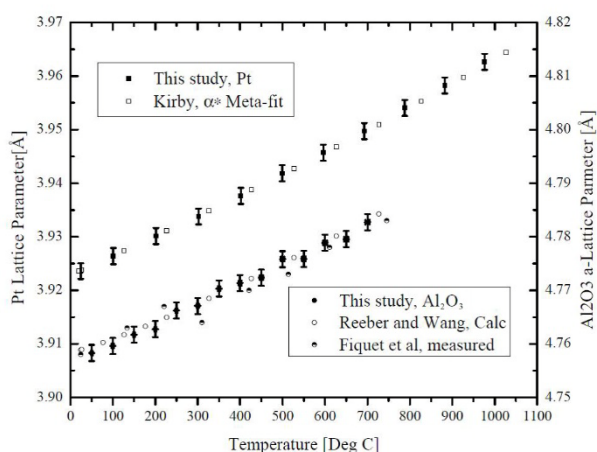

FIG. 3. Experimental and literature lattice parameters of alumina and platinum derived from Rietveld refinement of X-Ray patterns acquired at temperatures up to 1000 °C.

We performed two separate diffraction experiments with samples of vastly different emissivities, one with platinum (Sigma-Aldrich), one with a NIST Al_2O_3 corundum standard[14], and compared the measured crystalline lattice parameters as a function of temperature (adjusted with our temperature calibration above) to the literature. The lattice parameters of Pt and α-Al_2O_3 were determined from the Rietveld refinement of X-ray patterns by using Fullprof program[15]. Our measured platinum lattice parameters are compared to lattice parameters calculated from the paper by Kirby[16] that derives an analytic thermal expansion coefficient, α^*, based on a fit of 5 data sets. Our measured Al_2O_3 a-lattice parameters are compared to both first principal calculations from Reeber and Wang[17], and prior x-ray diffraction results from Fiquet et al[18]. Results are plotted in Figure 3 showing that the accuracy of our temperature measurement is very good along with our previously demonstrated precision.

Application Example

The device was utilized to characterize the thermally induced decomposition of metastable indium oxyhydroxide (InOOH) into metastable corundum-type indium oxide polymorph (rh-In_2O_3)[19,20] and its further transformation to stable bixbyite-type c-In_2O_3 at elevated temperatures. This work stands in continuation with our research of transformation pathways in the In-O system[12,21]. A quartz capillary filled with solvothermally synthesized phase-pure and nanocrystalline InOOH sample powder was placed into the device and heated up to 950 °C with a ramp rate of 40 K/min. In-situ x-ray diffraction was performed in angle-dispersive mode, a focused monochromatic beam (27 keV – 0.45920 Å) with 50µm spot size was used. The diffraction patterns were collected by a flat panel detector (Perkin Elmer XRD 1621) every 15 s with offline correction for dark image. The diffraction patterns were further processed with Fit2d and Origin software.
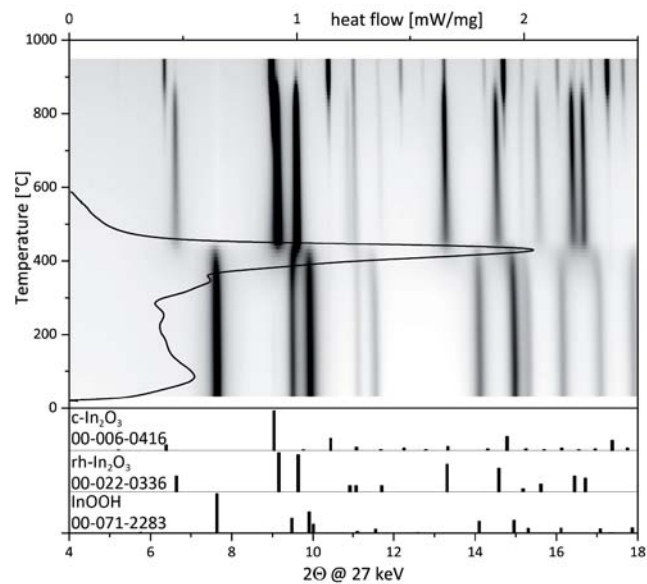

FIG. 4. Contour plot of in-situ PXRD pattern series and overlaid DSC data of InOOH to rh-In_2O_3 to c-In_2O_3 transformation.

The resulting pattern series is shown as a contour plot in Figure 4, dark areas denote high intensity crystalline

reflections, light areas background intensity. Up to 400 °C all reflections can be assigned to InOOH, above 400 °C clear changes in the diffraction pattern indicate a phase transition from InOOH to rh-In_2O_3 without any transient intermediate crystalline phases; the conversion is completed at around 440 °C. A second change in diffraction patterns appears at 775-920 °C and can be identified as a rh-In_2O_3 to c-In_2O_3 metastable to stable polymorph transition. Additionally, the structural changes upon heating InOOH as observed by x-ray powder diffraction were characterized up to 600 °C by Differential Scanning Calorimetry (DSC) (STA 449C Jupiter using α-Al_2O_3 as a reference) applying the same heating rate and gaseous environment (artificial air). In Figure 4 the x-ray data is overlaid with the resulting DSC heat flow data. The exothermic DSC peak position and structural transformation as evidenced by XRD shows good agreement between the two techniques and further confirms our system accuracy.

Applications and Future Development

The current and potential applications of our device are numerous. Beamline 12.2.2 of the Advanced Light Source is used to study materials at extreme conditions, most prominently both powder and single crystal materials at high pressure and ambient as well as elevated temperature through the use of Diamond Anvil Cells (DACs). The ability to expand our ambient pressure powder diffraction capabilities to include elevated temperature enhances our program by providing a means to easily and robustly reach extreme temperatures that are difficult to reach with DACs, and whose temperatures are much easier to interpret[22-24]. Current and potential users span our user base of geologists, geophysicists, materials scientists, chemists, and engineers.

The application example above was conducted with a modest temperature ramping rate and was not particularly focused on probing kinetics. However, our device's wide range of temperature control from static to ramp rates in excess of 10° K/sec is well suited for such studies. If combined with fast X-ray detectors, one could in principle probe sub-second kinetics.

We are currently in the prototype stages of upgrading our device with the ability to control the gaseous environment around the sample. We envision very enthusiastic interest in this upgrade for applications in catalysis, materials synthesis, and MOFs to name just a few areas.

Acknowledgements

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