

Hydrothermal Synthesis and Characterization of Titanosilicate ETS-10: Preparation for Research Integrated Inorganic Chemistry Laboratory Course

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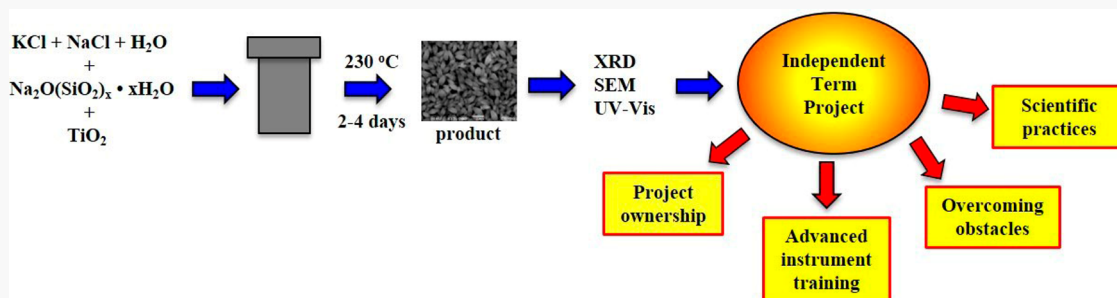
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ABSTRACT: Hydrothermal synthesis and characterization of titanosilicate ETS-10 was used as a means to prepare students for a research-focused independent term project as part of a 200-level descriptive inorganic chemistry course. Students spent the first 7 weeks of the course learning synthesis and characterization techniques that are common for metal oxide systems. In the second half of the semester, students led their own independent term projects as part of this research integrated laboratory course. All students successfully synthesized their materials and characterized their products independently. At the completion of the course, students submitted a journal-style report as well as presented their findings at a department poster session. The students were assessed through Student Assessment of their Learning Gains (SALG) surveys which showed enhancement in understanding and all-around research skills. The feasibility of learning advanced instrumentation that is not typically used in an undergraduate lab setting was demonstrated through this course.

KEYWORDS: Second-Year Undergraduate, Upper-Division Undergraduate, Inorganic Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Materials Science, Solid State Chemistry, Synthesis, UV-vis Spectroscopy, X-ray Crystallography

Chemists and educators agree on the importance of laboratory curriculums to accompany lectures. However, much of laboratory curricula are still “cook-book” style which rarely provides students with the opportunity to explore, nor prepares for how research is actually conducted. This also limits students’ ability to carry out their own independent project. This is particularly the case in undergraduate level inorganic courses for which much of the literature reports one- or two-week long experiments.^{1–5} However, to the author’s knowledge, there are no reports on a semester-long research-integrated laboratory curriculum for a 200-level descriptive inorganic chemistry course which prepares students for successful execution of an independent project. Thus, this article discusses a successful approach in implementing a semester-long, research-integrated curriculum for undergraduate students.

Engelhard titanosilicate ETS-10 is a zeolite-type microporous crystalline material⁶ with a framework consisting of a corner-sharing SiO₄ tetrahedra bridged to a TiO₆ octahedra through O atoms. This bridging results in a 12-membered ring structure with pores approximately 4.9 Å × 7.6 Å in size.⁷ The framework

of ETS-10 contains well-defined monatomic semiconductor ... Ti–O–Ti–O–Ti... chains, giving rise to a bandgap energy (E_g) in the range of ~3.8–4.03 eV,⁸ varying with the crystal quality as well as the method for the determination of the bandgap energy. ETS-10 has attracted much attention to be used in both traditional (e.g., catalysis,^{9,10} gas separation,^{11–14} adsorbent,^{15,16}) and advanced applications (e.g., photocatalysis^{17–20,27}) due to its inherent microporosity, pore regularity, and the presence of stoichiometric amounts of titanium in the silicate framework.

Similar to traditional zeolites, ETS-10 has been synthesized using a hydrothermal synthesis method. In general, the synthesis is prepared by mixing a Si-based precursor solution with a Ti-

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based precursor solution, resulting in a homogeneous white gel with pH ranging between 10.4 and 10.7. By controlling the synthesis compositions and crystallization conditions, ETS-10 products with a varying degree of crystal development, size, and morphology have been obtained, which can be used for its broad applications.^{21–25}

The laboratory course design described here involves the hydrothermal synthesis and characterization of titanasilicate ETS-10 using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and diffuse-reflectance (DR) UV–vis spectroscopy as a training tool for undergraduate chemistry students. This is part of a newly developed research integrated inorganic chemistry laboratory course. These techniques, although fundamental to chemistry and materials science, are not commonly used by undergraduate chemistry students. Therefore, the scope of this article details the training of undergraduate chemistry students on the synthesis and characterization of a well-established material so that the students can apply these techniques to their own individual term projects.

This research-integrated laboratory course was first developed as part of a 10-week summer research program where 12 students majoring in chemistry, biochemistry, or biology spent a fraction of their time being trained on hydrothermal synthesis and characterization using the techniques mentioned above. It was then implemented successfully as part of the core laboratory curriculum for a 200-level descriptive inorganic chemistry course at Simmons University in the Fall 2019 semester with 16 students enrolled in the course. Students in this course are typically juniors and seniors, with the occasional sophomore. Student majors include chemistry, biochemistry, environmental science, physics, and biology. The laboratory course was divided into two parts. Part I (7 weeks) focused on the training of the students on hydrothermal synthesis and characterization of titanasilicate ETS-10. Throughout this 7-week period students also learned how to critically review literature and do background research on the techniques to be used in lab for that given week as part of a prelab assignment. Articles and instrument techniques were discussed during the prelab lecture component. A general scheme of Part I laboratory experiments can be found in Figure 1.

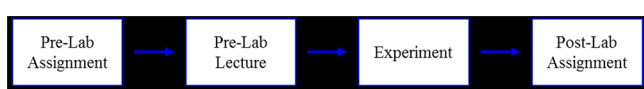


Figure 1. Flow-chart showing the outline of the components for each laboratory experiment. Details can be found in Table 1S of the [Supporting Information](#).

Part II (8-week period) focused on independent projects in which each student chose a material of interest to synthesize and characterize using the techniques learned in Part I. At the completion of the semester, students presented their findings through a formal journal-style report and a mini-poster-presentation session among other faculty and peers. This nontraditional laboratory course transitions students from a typical “cookbook-like” course to a more research-based course.

Pre- and postassessment surveys were given to students to assess the learning outcomes by ranking their knowledge in the synthesis and characterization techniques used in this course. The learning goals upon completion of the laboratory course were that the students are able to complete the following:

1. Design experiments and properly carry them out and have the ability to troubleshoot.
2. Properly record data and interpret results.
3. Independently use the XRD and identify the synthesized material from the XRD patterns.
4. Independently use the SEM and extract information from the captured images.
5. Independently use the diffuse reflectance UV–vis spectrophotometer and identify the absorption spectrum.
6. Effectively communicate findings through written journal-style reports and oral presentations.
7. Use modern library search tools (e.g., SciFinder) to retrieve scientific information about a topic.

■ EXPERIMENTAL SECTION

Overview

The course was divided into two parts. Laboratories for each week lasted about 3–4 h, including the prelab lecture component. Part I, a 7-week period, focused on the training of the students on hydrothermal synthesis and characterization of ETS-10. The laboratory class was divided into two groups; groups were then divided into pairs. One group synthesized ETS-10 using Degussa P25 as the Ti source, while the other group synthesized ETS-10 using anatase as the Ti source. It has been shown that the Ti source affects the size and development of the synthesized products. Therefore, through this investigation, the class was able to observe the effect of Ti source on their products. Students worked in pairs for this part of the laboratory course.

Part II, an 8-week period, focused on individual term projects. Students submitted a 2-page proposal by week 7 of the course. The proposal included the following: the material system of choice (inorganic); motivation behind choosing the system; synthesis technique along with a detailed procedure; a list of chemicals, glassware, and equipment required for the synthesis; hazards; and at least three characterization techniques to identify successful synthesis. Students were required to use only primary sources as references. The grading rubric can be found in section II-b of the [Supporting Information](#). By week 8, students were starting their individual term projects. Upon completion of their term projects (by week 13), students submitted a 10-page journal-style report, in addition to a poster. A mini-poster-session was held in week 14, and faculty and students were invited to attend. Attending faculty were given rubrics to informally assess the students’ poster presentations. Rubrics for the journal-style report and poster presentations can be found in section II-d and II-e of the [Supporting Information](#), respectively. A table detailing the week-by-week tasks for each laboratory experiment can be found in Table 1S of the [Supporting Information](#).

Hydrothermal Synthesis

P25 Synthesis. Hydrothermal syntheses of ETS-10 were carried out using a mixture with molar compositions of 3.4 Na₂O/1.5 K₂O/1.0 TiO₂/5.5 SiO₂/150 H₂O when using P25 as the Ti source.²⁴ Synthesis mixtures were obtained by mixing two precursor solutions: solution A containing NaCl, KCl, sodium silicate, and DI water; and solution B containing the Ti-source and DI water. A typical synthesis carried out by the students required 0.932 g of KCl (Sigma-Aldrich, >99.0%) and 0.858 g of NaCl (Sigma-Aldrich, >99.5%) dissolved in DI water and 4.815 g of N-brand sodium silicate (28.59% SiO₂, 8.88% Na₂O,

62.53% H₂O, PQ corporation) for solution A. Then, solution B was prepared by dissolving 0.338 g of P25 (76 wt % anatase, 25 wt % rutile, Degussa) in DI water and this was added to solution A. The resulting mixture was hand shaken for 5 min. The pH of the homogeneous white gel was adjusted to 10.6–10.9 using H₂SO₄. The mixtures were then transferred to Teflon-lined autoclaves and placed in the oven at 230 °C. Each student pair loaded two autoclaves per synthesis. After crystallization (2–4 days), the products were rapidly cooled to room temperature, filtered with DI water, and dried in air at ~75 °C. Samples synthesized using P25 were denoted “ETS-10_P25”.

Anatase Synthesis. Hydrothermal syntheses of ETS-10 were carried out using a mixture with a molar composition of 5.2 Na₂O/0.5 K₂O/1.0 TiO₂/5.5 SiO₂/113 H₂O when using anatase as the Ti source.²⁵ A typical synthesis carried out by the students required 0.326 g of KCl (Sigma-Aldrich, >99.0%) and 1.813 g of NaCl (Sigma-Aldrich, >99.5%) dissolved in DI water and 5.000 g of N-brand sodium silicate (28.59% SiO₂, 8.88% Na₂O, 62.53% H₂O, PQ corporation). A 0.349 g aliquot of anatase TiO₂ (Sigma-Aldrich, >99.8%) was then added, and the resulting mixture was hand shaken for 5 min. The pH of the homogeneous white gel was adjusted to 10.6–10.9 using H₂SO₄. The mixtures were then transferred to Teflon-lined autoclaves and placed into the oven at 230 °C. Each student pair loaded two autoclaves per synthesis. After crystallization (2–4 days), the products were rapidly cooled to room temperature, filtered with DI water, and dried in air at ~75 °C. Samples synthesized using anatase were denoted “ETS-10_anatase”.

Characterization

Each student characterized their synthesized products using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and diffuse-reflectance UV–vis spectroscopy. XRD patterns were collected on a Philips PW1729 X-ray powder diffractometer with a Cu K α source (30 kV, 35 mA) to determine the purity of the synthesized products. A JSM-5510 tungsten filament SEM was used to determine morphology, structure, topography, and size. An accelerating voltage of 10 kV and working distance of 6–10 mm using the secondary electron imaging mode were generally used. Diffuse reflectance UV–vis spectroscopy was employed to investigate the optical properties of the synthesized products. Spectra were recorded on a Cary 5000 UV–vis–NIR spectrometer equipped with a Praying Mantis accessory, bandwidth of 1.0 nm, and powdered Spectralon as a reference material.

HAZARDS

Sodium silicate is a known skin irritant, while sulfuric acid may cause severe burns if contacted with the skin. Additionally, KCl, NaCl, anatase, and P25 should be handled with care as they all belong to level 1 on the Health component of the Hazardous Materials Identification System (HMIS). Therefore, safety goggles, gloves, and lab coat must be worn at all times during the experiment. The hydrothermal process is carried out by heating an aqueous mixture in a closed container. Goggles and insulated gloves should be worn when handling the hot stainless steel autoclaves.

RESULTS AND DISCUSSION

Synthesis and Characterization of Titanosilicate ETS-10

Two titanium sources, P25 and anatase, were investigated by the student groups. Half of the class synthesized ETS-10 using P25, while the other half synthesized ETS-10 using anatase. The

crystallization temperature for all syntheses was kept constant at 230 °C, as well as pH of the final gel. Thus, the student groups were able to investigate the effect of the Ti source on the size, quality, and product purity of ETS-10.

When anatase was used as the Ti source, the molar composition resulted in nearly pure ETS-10 product as shown from XRD (Figure 2) and SEM (Figure 3). Products synthesized

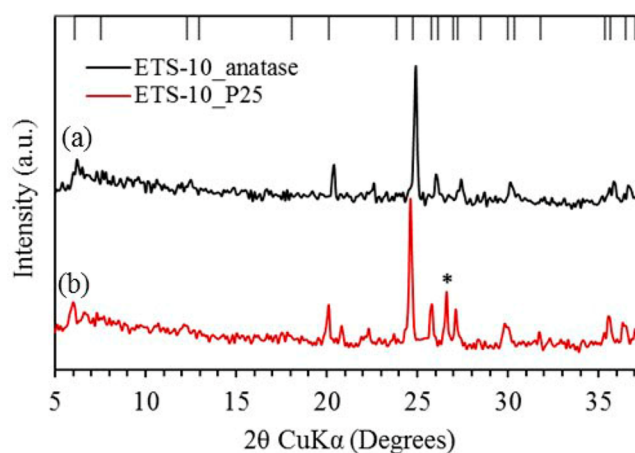


Figure 2. Representative XRD patterns from student reports of ETS-10 products hydrothermally synthesized using two different Ti precursors: (a) anatase; (b) P25. The tick-marks on the top of the graph correspond to ETS-10 reflections. The asterisk (*) indicates unreacted anatase phase.

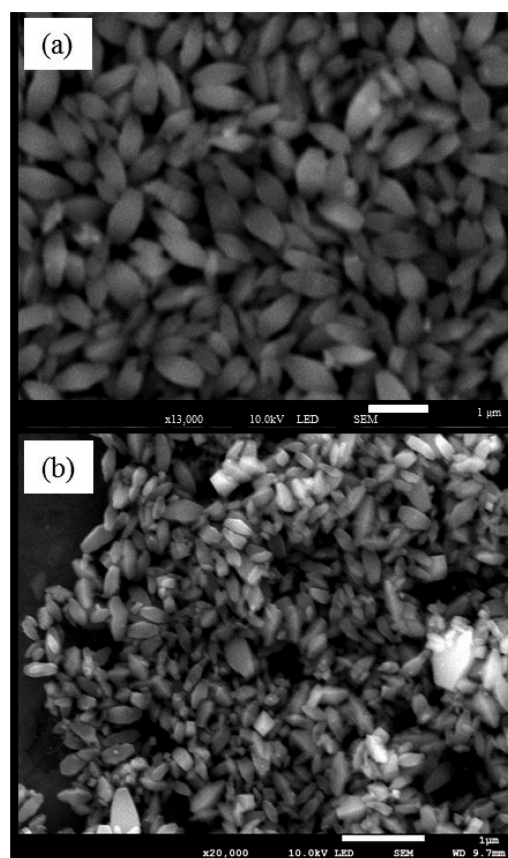


Figure 3. Representative SEM images from student reports of ETS-10 products synthesized from two different Ti precursors: (a) anatase; (b) P25.

from P25 as the Ti source resulted in ETS-10 product with some unreacted anatase as shown by XRD (Figure 2) and SEM (Figure 3). The XRD patterns of the final products synthesized using the two different Ti sources match very well with that of ETS-10 reported in literature.^{24,25} Characteristic ETS-10 reflections were observed as shown by the tick marks in Figure 2. This confirmed successful ETS-10 synthesis by all student groups. The shifts in the XRD reflections are attributed to sample displacement, and not to the unit cell. Students were also able to link the use of XRD to determine the unit cell. This correlated with the lecture topic on structures of solids (section IV of Supporting Information).

The students found that the morphologies of the products synthesized from the two different Ti sources were similar—typical truncated bipyramidal morphology (Figure 3). However, the students reported a difference in the average particle size as observed from SEM analyses. Products synthesized from P25 ($\sim 0.5 \mu\text{m}$, Figure 3b) were almost half the size of the products synthesized from anatase ($\sim 1 \mu\text{m}$, Figure 3a). Thus, there appears to be a trade-off between particle size and product purity for the molar composition investigated here. This trade-off will depend on that for which the application the ETS-10 product will be used. For example, the ETS-10_P25 product may be more beneficial than the ETS-10_anatase product for photocatalytic applications since surface area plays a big role in catalysis.

UV–vis spectroscopy (Figure 4) showed the distinct ETS-10 pattern with a broad absorption feature in the 200–300 nm

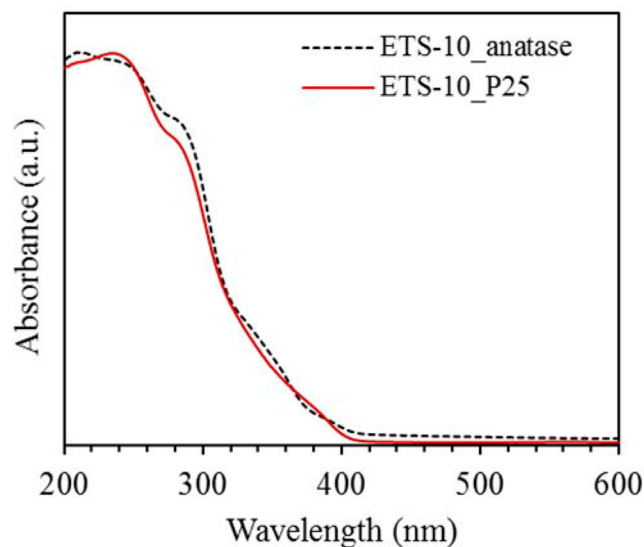


Figure 4. Representative UV–vis absorption spectra of ETS-10 products synthesized using two different Ti precursors, anatase and P25. The spectra were normalized by the intensity of the strongest band.

range. The band-edge for both products was found to be at ~ 350 nm. This is in agreement with prior reports on ETS-10.^{26,27} The band-edge corresponds to the electron transition between the $\text{O}(2p) \rightarrow \text{Ti}(3d)$ in the $\cdots\text{Ti}-\text{O}-\text{Ti}-\text{O}-\text{Ti}\cdots$ chains in the ETS-10 structure. Students were able to link the observation of this charge-transfer transition with their knowledge from lecture on semiconductors and band theory as reported in their Technique Pages on this topic.

Student Independent Term Projects

The first step of the independent term project was the submission of a 2-page proposal detailing the material system of choice and how to synthesize and characterize it. Through the proposal, students demonstrated the ability to retrieve scientific information about a topic, critically review articles and procedures, identify proper procedures, and regulations for safe handling and use of the chemicals, and use their knowledge from Part I to identify which characterization techniques would suit their material system the most. Students began working independently on their individual term projects once their proposals were cleared by the laboratory instructor (within a week from submission).

Students were given 8 weeks to follow an existing published synthesis procedure for any metal oxide material system, troubleshoot, characterize their synthesized product(s) using at least three techniques (e.g., XRD, SEM, DR UV–vis, FTIR, etc.), write a formal journal-style report, and assemble a poster for the mini-poster-session held in week 14. All students chose entirely different material systems than the ones they were trained on in Part I. Examples of some of the systems students chose can be found in Table 1.

Table 1. Examples of Materials Synthesized by Students for Their Independent Term Projects

Materials System	Synthesis Adapted from Reference No.
Hydrothermal synthesis of ZnO nanoparticles	28
Synthesis of CuO nanoparticles by green precipitation method	29
Hydrothermal synthesis Ag/Bi ₂ WO ₆	30
Hydrothermal synthesis of Magnetite (Fe ₃ O ₄)	31
Hydrothermal synthesis of ZrO ₂ nanorods	32
Synthesis of CuO–ZnO mixed metal oxide nanocomposite by coprecipitation method	33
Hydrothermal synthesis of hydroxyapatite	34
Hydrothermal synthesis of BiOBr flakes	35

Although the students were mostly independent during this 8-week period, they were required to send in progress summaries every week as a prelab assignment. This ensured students were on track to complete their projects in the allotted time. In Part I, students were required to submit “Technique Pages” for each lab week (rubric can be found in section II-a of the Supporting Information). In Part II, the students referred back to these “Technique Pages” to aid in the synthesis of their material system and/or characterization using the instruments learned in Part I. Through this approach, students were motivated from the beginning to take detailed notes on instrument background and operation. This also allowed for reinforcement of learned concepts and techniques, which increased retention of knowledge. Additionally, the instructor provided aid when needed. On week 12, students submitted a mini-laboratory-report discussing in detail their progress thus far. A rubric detailing the requirements of the mini-lab-report can be found in section II-c of the Supporting Information. The purpose of the mini-lab-report was to allow the students to summarize their findings in a concise manner, analyze their data, connect their findings with those found in literature, and ultimately submit a low-stake draft of their final term project report.

To address one of the learning outcomes stated above, a prelab lecture was designed to teach students how to present

Table 2. Pre- and Postsurvey Assessment Questions for Evaluation of Student Learning Outcomes after the Research Integrated Inorganic Laboratory Course

Question No.	Category	Survey Question
1.1	Understanding	Experimental inorganic chemistry synthesis.
1.2		Analysis of synthesis product purity using X-ray powder diffraction, and the background behind this technique.
1.3		Characterization using SEM, and the background behind this technique.
1.4		Interpreting the optical properties and oxidation states of the synthesized materials using UV-vis spectroscopy, and the background behind this technique.
2.1	Skills	Keep a clear, detailed lab notebook
2.2		Plan experiments using chemical reactions covered in this lab
2.3		Analyze and interpret experimental data
2.4		Integrate information from chemical references and knowledge from lectures to understand new reaction mechanisms
2.5		Troubleshoot experiments and/or modify procedures based on my knowledge of the chemistry taking place
2.6		Write clearly about experimental results
2.7		Work effectively with others
2.8		Identify resources to help me design and troubleshoot experiments
3.1	Attitudes	Enthusiastic about chemistry
3.2		Interested in discussing chemistry topics with friends or family
3.3		Interested in taking or planning to take additional classes in chemistry
3.4		Confident that I understand inorganic chemistry topics
3.5		Confident that I am ready to pursue faculty-supervised research
4.1	Integration of Learning	Connecting key ideas I learn in my classes with other knowledge
4.2		Applying what I learn in classes to other situations
4.3		Using systematic reasoning in my approach to problems
4.4		Using a critical approach to analyzing data and arguments in my daily life

their findings through a poster session. Week 13 of the laboratory course was allocated to poster formatting and presentation. By week 14, students presented their findings from their independent research projects during a department poster session. Faculty attending the poster session were provided with rubrics (see section II-e of [Supporting Information](#)) to provide feedback on the student presentations. Each student presented their poster to their peers and at least three faculty members.

Learning Outcomes and Student Survey

A survey, addressing the goals stated above, was created through the online program Student Assessment of their Learning Gains.³⁶ In week 1, prior to the start of the experiments, students were asked to rank the extent of their knowledge in regards to inorganic synthesis and characterization, and general research skills. The same survey was given to the students again upon completion of the laboratory course, in week 14. The survey was constructed to address four categories: understanding, skills, attitudes, and integration of learning (Table 2). The results of the surveys are shown in Figure 5.

Prior to this course, most students had self-identified as lacking knowledge in inorganic synthesis and materials characterization techniques ("Understanding" category, Figure 5). The self-identified understanding was significantly improved after the course as shown in Figure 5. The pre- and postsurvey responses regarding "Skills" showed the importance of prior experience in an academic lab setting (questions 2.1, 2.3, 2.6, and 2.7, Table 2 and Figure 5). This is in agreement with the fact that this course is intended for sophomores and beyond, although it has been historically taken by juniors and seniors. Additionally, the survey results also showed that students self-identified as improving their research skills upon completion of this course (questions 2.2, 2.4, 2.5, 2.8, 4.3, and 4.4, Table 2 and Figure 5). These results addressed one of the primary goals of a research-integrated laboratory course—to provide students with

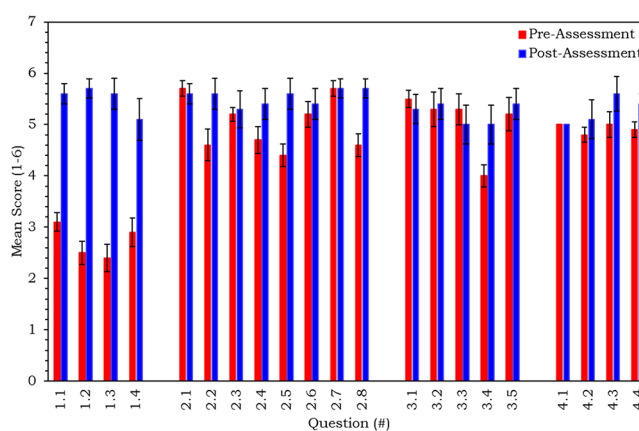


Figure 5. Results of the student self-assessment survey. For each question, the results of the precourse assessment are shown in the first bar (red, on the left), and the results of the postcourse assessment are shown in the second bar (blue, on the right). The students responded to the survey questions by ranking using a number scale from 1 to 6: 1 = "not applicable"; 2 = "not at all"; 3 = "just a little"; 4 = "somewhat"; 5 = "a lot"; 6 = "a great deal". The survey questions are summarized in Table 2.

research skills that will benefit them beyond the classroom environment. An increase in confidence in inorganic chemistry was also observed (question 3.4, Table 2 and Figure 5). The survey results also suggested that students were able to link the research-integrated laboratory experiments to concepts learned in the lecture component of the course, including band energy diagrams and unit cell structures.

Student feedback was extremely positive. Most students wrote in their final course evaluations that they thoroughly enjoyed learning new techniques and instrumentations such as XRD and SEM, while also leading their own research-based term projects. An excerpt from the written component of the course

evaluations stated that “the research-based term project we worked on for the majority of the semester was extremely educational in the fact that it simulated real lab conditions and encouraged us to be autonomous.” Additionally, throughout the term-projects students used other instruments they had previously used in other courses to further characterize their synthesized products. One student wrote in their final course evaluations that “I can now analyze and interpret data from instruments that I have not had to work with before including XRD and UV-Vis. I also learned how to analyze FTIR in a different setting outside of the organic chemistry lab.” This shows the ability of students to extend knowledge from one discipline of chemistry to another. The positive responses from the survey results implies that the learning objectives were achieved and that this research-integrated laboratory course design greatly enhances student learning.

CONCLUSION

This article describes a new approach to teaching a 200-level descriptive inorganic chemistry laboratory course. This work is the first reported for which hydrothermal synthesis of titanosilicate ETS-10 is used in an undergraduate laboratory course. Students were successful in synthesizing both ETS-10 and their term project materials. Application of this research-integrated approach to a 200-level course shows the ease and reproducibility of the techniques involved. Survey data and student reports also suggest that this research-integrated lab had a positive effect on students and provided them with skills that are easily translatable to beyond the classroom. Additionally, the survey data and assessment showed students as independent users of these advanced instruments. Students were also able to link concepts related to their data with ones learned in the lecture component of the course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemeduc.0c00165>.

(I) Lab schedule and corresponding assignments; (II) rubrics for techniques pages, project proposal, mini-lab-report, journal-style term project report, and poster presentation; (III) guidelines for proposal and term projects; (IV) a list of lecture topics and learning objectives; and (V) notes to the instructor (PDF, DOCX)

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Notes

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