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American Association for Crystal Growth

Volume 3, Issue 1, Spring 2025

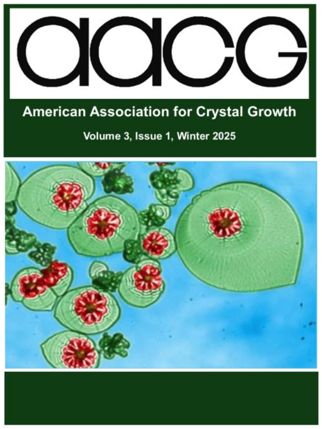
Letter from the Editor

I hope you enjoy this issue of the AACG newsletter! We are always on the lookout for content to include in the next newsletter. If you have ideas of interesting people we should interview, news from your business or local AACG chapter, companies we should profile, technical contributions or anything else you'd like to see included, please reach out to me. Our intent is to release at least one issue per year, but we would love to put out more issues if we have content to run. We welcome any feedback or contributions from our readers!

AACG Newsletter Editor

AACG Executive Committee Member

Kevin Schulte



ON THE COVER: From ACCGE-20 / OMVPE-17, held in Big Sky, Montana, USA, in 2015, "The Flowers That Be" was a winning entry by Elias Nakouzi, Physical and Computational Sciences Directorate at PNNL. The AACG Photo Contest happens at every ACCGE/OMVPE.

About the photo: This image was acquired while at the Department of Chemistry and Biochemistry in Florida State University working with Oliver Steinbock. These materials are "biomorphs" which form life-like morphologies from simple inorganic reaction, specifically amorphous silica and crystalline barium carbonate precipitation. No organic additives, proteins, or other biomolecules are needed. The trick is that the silicate species downsizes the carbonate crystals to the nanoscale, which results in nanorod that self-organize into complex architectures.

Membership in the AACG is open to everyone with a professional interest in crystals, thin films, crystal growth, epitaxy, and characterization.

Our membership includes **engineers, scientists, educators, technologists, marketing representatives, and students.** All share a strong interest in one or more facets in the field of crystal growth and epitaxy.

Annual membership benefits include discounted conference registration, annual newsletters, important career and conference announcements, and **connection** to the global crystal growth community.

Stay informed:

- Membership
- Conference News
- Community Announcements
- Career Opportunities

www.crystalgrowth.org

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Shanthi Subramanian, Coherent, Incorporated

President's Corner

As a crystal grower, you probably cringe when someone asks you the question "So, what do you do for a living?"

If you're like me, you think to yourself "Okay, here we go…" Then you pause, take a breath, and answer that you are a crystal grower – that you grow crystals for a living. This usually elicits a blank stare, an awkward silence. a confused expression, perhaps references to Crystal Meth, etc. Then you launch into your standard spiel about single crystals, why they're important, how they're widely used in computers, cell phones, supermarket scanners, solar cells, PET scans, etc., and then shift to the particular crystals you grow, what they are used for, how you grow them. Even while you're speaking you watch their attention wane, they look at their watch, for someone else to talk to, and you realize you should have kept it short and simple - just said you were an engineer.

The beauty of attending an American Conference on Crystal Growth is that you are finally among your own! You can share your passion about crystal growth with kindred spirits, and "geek-out" to your heart's content with like-minded souls who will listen with enthusiasm, ask probing questions, tell of common experiences, offer technical insights, and share war stories. Ours is a rare and exotic profession, so it is a great relief to find camaraderie and fellowship in the AACG community.

Our most recent conference, ACCGE-West-28, is our smallest and most intimate meeting – best suited for these interactions - and last years' was a huge success. 92 attendees (a new record) met at the rustic Stanford Sierra Camp Conference in Fallen Leaf Lake, CA on June 9-12, 2024. The highly successful fund-raising efforts of the organizing committee enabled an unprecedented injection of youth into the meeting, making it possible for 10 post-docs, 12 grad students, 16 undergrads, and even 7 high school students to attend! 38 oral presentations and 18 poster presentations facilitated stimulating scientific exchange in the mornings and evenings, freeing up afternoons for hiking, water sports, long walks, and talks in glorious surroundings around the camp. The registration fee for ACCGE-West always includes all sessions, lodging, recreation and meals, so look for announcements about ACCGE-West-29 in June of 2026.

Our next national meeting, the 24th American Conference on Crystal Growth and Epitaxy (ACCGE-24)– co-located with the 22nd US Workshop on Organometallic Vapor Phase Epitaxy (OMVPE-22), will be held at a spectacular new venue in the Pacific Northwest: Skamania Lodge in Stevenson, Washington, July 13-18, 2025. The conference features a broad range of crystal growth topics, more than a dozen symposia ranging from theory and modelling to manufacturing and applications. The Abstract Deadline (March 18th) is rapidly approaching (click here to Submit an Abstract) and be sure to take advantage of Early Bird Registration by May 16! Please note that booking your room at the **conference hotel** before you register earns you an additional **$300 registration fee discount** (Book a Room). I cannot emphasize enough how important it is to stay at the conference hotel. In order to cover the very high cost of conference facilities provided by the hotel, the AACG must guarantee that our attendees will book a minimum number of total room nights: failing to do so results in enormous penalties for the organization (since we have to pay for each of those unused room nights, which quickly adds up!). In previous years – notably at the International Conference on Crystal Growth in Salt Lake City in 2007 – AACG was nearly bankrupted due to a large number of attendees staying at other local hotels instead of the conference hotel. So I urge you to book your room at the conference hotel, both to greatly enhance your conference experience and to save the AACG from potential disaster!

Of course, none of these conferences would be possible without the dedication and relentless efforts of our members who volunteer their time and talents, their expertise and their connections, to make them a reality. The AACG has existed for over 60 years due to the outstanding contributions of many faithful executive committee members, officers, and administrators, but arguably none have done more for the group than Vince Fratello.

Vince has been the heart and soul of the AACG for as long as I can remember (and I have been active for 35 years!), and as he enters into retirement we want to gratefully acknowledge the enormous impact he has had on our organization and on the crystal growth community as a whole. This is essentially the official Vince Fratello issue of the AACG Newsletter. (Not the ”memorial issue,” since he is still with us, and we expect him to remain active in the AACG for many more years even in retirement.) So please take time to enjoy the Vince’s featured interview with our Newsletter Editor, Kevin Schulte, which highlights his amazing career in crystal growth, as well as a technical paper on “**Indifferent Points in Perovskite Solid Solutions”** (perhaps the first journal-quality paper ever published in the AACG Newsletter) which showcases Dr. Fratello’s deep understanding of thermodynamics. Vince was able to extract incredibly exotic and technologically important magneto-optics and piezo-electric crystals from phase diagrams that would frankly reduce most crystal growers to tears!

I hope you’ll be inspired by Vince’s story, and follow his example of scientific achievement, active involvement, and dedicated involvement in the crystal growth community.

In your service,
Pete Schunemann, D. Eng,
Sr. Director of Crystal Growth, Onsemi
AACG President

Summers with ACCGE West Section Meeting at Fallen Leaf Lake, CA

It is a brisk 65-degree F morning, the lake water is a balmy 50-degree F—the world around is still, with occasional clapping of the lapping waves at the lake shore, the morning sunlight gleams over the pine tree tops and over from the Eastern edge of the Sierra Nevada Mountain range, shimmering every now and then off the lake surface. These are the ideal conditions that begin each day at the ACCGE West Meeting at the Stanford Sierra Camp, Fallen Leaf Lake in the South Lake Tahoe region of California. The organizers of the meeting past and present deliberated on the planning for the meeting and converged on the importance of outreach and inclusion were priorities the West Meeting needed to place front and center to prepare the next generation of crystal growth scientists and engineers.

The 28th ACCGE West Meeting began on June 9th, 2024 and a number of "firsts" were achieved as it kick-off'ed. Firstly, a record number of attendees were in attendance. It was indeed the first meeting to have a record 92 attendees; of those it was also a first to include a contingent of 6 high school students and 2 chaperones from the Tracy Unified School District (1 additional high school student, not affiliated with the Tracy school, presented a poster in the poster session). The attendance of these high school students were made possible by the successful fundraising activities of co-organizers and staff of the meeting. This included lead sponsors by Blue Planet Systems Corporation and the National Science Foundation, as well as both Lawrence Livermore and Pacific Northwest National Labs, and industrial contributions from Mesta Electronics and GHO Ventures, making the total more than any other year raised to fund the meeting and its activities. As a result, the financing of the attendance of 10 postdoctoral scholars, 12 graduate students, and 16 undergraduate students were possible with use of these funds. A sample of the meeting activities included poster sessions and poster awards. This year there were 5 graduate students and postdoctoral scholars who were recognized by their peers for best research poster and poster presentation, all prizes were generously provided by sponsors. This year we introduced a new session emphasizing the connection between the environment and energy. This research strand was anchored by a plenary lecture by Brent Constantz, Ph.D. on creating a circular material economy at the gigaton-scale to address the looming climate change problem and was a hit with the audience. Additionally, a commitment by Blue Planet Systems Corporation will ensure these prizes and new sessions will be available for subsequent ACCGE West meetings for the foreseeable future.

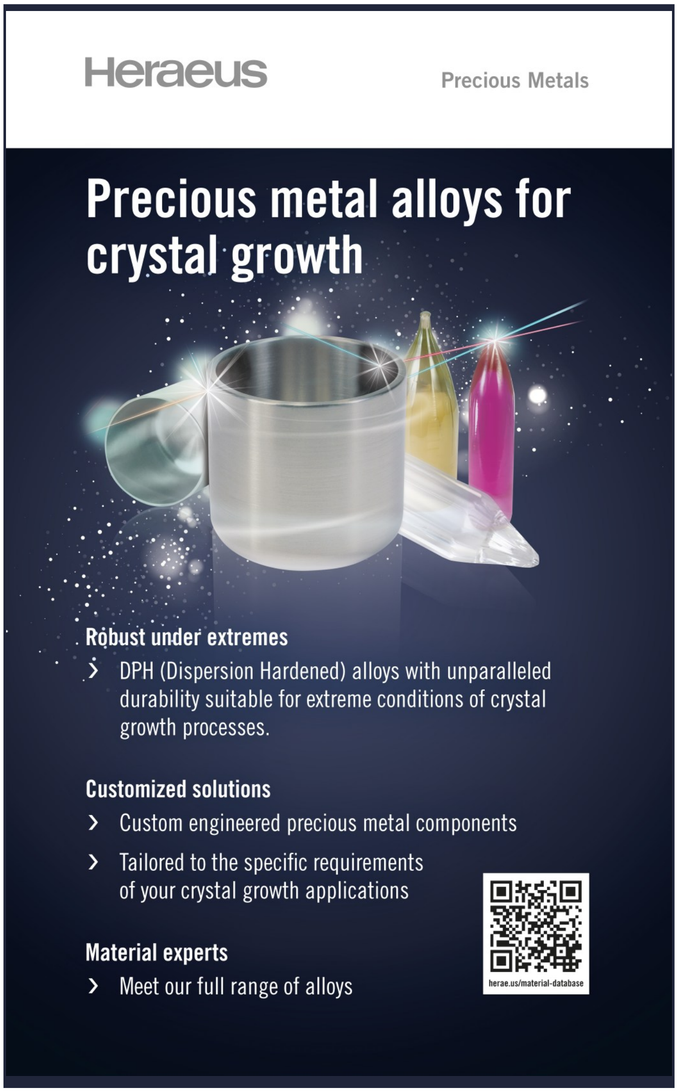
With each passing day, another successful session of the ACCGE West Meeting concludes and the camp is filled with a hive of bustling outdoors activity from ACCGE attendees. Discussions of research results and poster presentations continued and filled the serene atmosphere on the hiking trails around the camp with the traditional guided tour of Mt. Tallac after lunch on the first day of the meeting. For those that wanted to indulge in the watersports of Fallen Leaf Lake, kayakers, paddle boarders, and sailors were readily taking advantage of the picturesque calm waters and the warming days available to lake go'ers every day of the meeting. And just like that the day passes and we gather to break bread and share anecdotes of the day in the camp cafeteria. The later evening session of the meeting concludes around the fire pit to discuss and revel in challenges accomplished earlier in the day. A tradition of the ACCGE West meetings is the late-night star gazing tours organized by the Stanford Sierra Camp staff where we hear the tales of how the constellations Ursa Major and Minor formed from Callisto's tragedies with Zeus and Artemis. (Not too long ago, the Greeks and Romans thought that these constellations were composed of crystalline elements, where the constellations are assigned due to resemblances to properties of crystals). It is an appropriate way to wind down the meeting with these astronomical observations—a similar route to dissolution and recrystallization process—to reset our "appetites and imaginations" for the next ACCGE West Section Meeting.

Above: *Activities at ACCGE West Section Meeting throughout the day. (A.) Poster session included 18 poster presenters, with 1 presenting his high school summer research, (B.) Talks included plenary, invited, and individual contributors with a total of 38 presenters during the entire meeting, with some attendees coming as far as France, while others came as close as from the Bay Area and Merced, (C.) Hikes in between the sessions were made possible by the scheduling of "free-time" during the afternoons, (D., E.) Talks spanned the morning and evenings, (F.) Rustic accommodations and time allowed for outdoor activities for everyone.*

We acknowledge the support of the Stanford Sierra Camp and ACCGE staff for creating an accommodating atmosphere and environment for another year of wonderful lectures and posters at Fallen Leaf Lake. The organizers also would like to thank Morgan Marshall and the entire staff at the Stanford Sierra Camp for the exemplary service and accommodation provided during the meeting. We acknowledge the use of drone photos from Mr. Jason Marmon, an attendee of the meeting. We expect to exceed both funding and attendance by high school, undergraduates, and graduate students in the following years to come at ACCGE West Meetings with beautiful Fallen Leaf Lake as a backdrop again.

Co-organizers of the 28th AACGE West Meeting

Jong Seto, Arizona State University
Moneesh Upmanyu, Northeastern University



Stevenson, Washington
USA

July 13-18, 2025

ACCGE-24
OMVPE-22
Washington, USA

24th American Conference on Crystal Growth & Epitaxy (ACCGE-24)

and

22nd US Workshop on Organometallic Vapor Phase Epitaxy (OMVPE-22)

Plenary Speakers

David Kisailus

Henry Samueli Faculty Excellence Professor and
Kavli Fellow of the National Academy of Sciences
Director, Materials and Manufacturing Technologies Program
University of California, Irvine

"Synthesis of Multiscale High-Performance Biological Composites"

Joan Redwing

Distinguished Professor and
Director of 2D Crystal Consortium MIP
Pennsylvania State University

"Epitaxy of 2D van der Waals crystals - from fundamentals to applications"

Darrell Schlom

Tisch University Professor
Department of Materials Science and Engineering
Cornell University, USA
Leibniz-Institut für Kristallzüchtung, Germany

"Suboxides MBE Rocks!"

Submission & registration now open!
https://www.crystalgrowth.org/skamania25

Sessions & Session Chairs

Biological & Biomimetic Materials

David Kisailus, UC Irvine

Bulk Crystal Growth

Peter Schunemann, Onsemi
Kevin Zawilski, BAE
John Frank, Luxium Solutions

Characterization Technique for Bulk & Epitaxial Crystallization

Michael Dudley, Stony Brook
Xianrong Huang, ANL
Sakiko Kawanishi, Kyoto University

Fundamentals of Crystal Growth

Moneesh Upmanyu, Northeastern University

Modeling of Crystal Growth Processes

Talid Sinno, University of Pennsylvania

OMVPE (III-V, III-N)

Luke Mawst, University of Wisconsin
Andy Allerman, Sandia

Semiconductors: Advanced Growth Techniques & Technology

Nathan Stoddard, Lehigh University
Ryan Lewis, McMaster University

Semiconductors: High-speed Electronics, Optoelectronics, and Photovoltaic Materials (III-V, III-N, Narrow)

Luke Mawst, University of Wisconsin
Theresa Saenz, NREL
Kevin Schulte, NREL
Ryan France, NREL

Semiconductors: Ultra-wide Bandgap Semiconductors (SiC, Ga2O3, III-N)

Michael Dudley, Stony Brook
Balaji Raghothamach, Stony Brook
Sriram Krishnamoorthy, UCSB
Shailaja Rao, Wolfspeed

ML/AI in Crystal Growth

Chair TBA

Reduced Gravity Crystal Growth

Ching-Hua Su, NASA

Symposium on Detector Materials: Scintillators & Semiconductors

Chuck Melcher, University of Tennessee
Edgar van Loef

Symposium on Epitaxy of Complex Oxides (incl. Ferroelectric Crystals & Textured Ceramics)

Ho Nyung Lee, ORNL

7th Symposium on 2D and Low Dimensional Materials (incl. BN)

Kevin M. Daniels, University of Maryland
Cheng Gong, University of Maryland
Soaram Kim
Daniel Pennachio, US Naval Research Laboratory (NRL)
Jimmy Kotsakidis, University of Maryland
Siddha Pimputkar, Lehigh University

Conference Organizers

View full committee

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Conference Co-Chair:
Balaji Raghothamacahar
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OMVPE Chair:
Andy Allerman
Sandia National Laboratory

Program Co-Chair:
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University of Maryland
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Stevenson, Washington
USA

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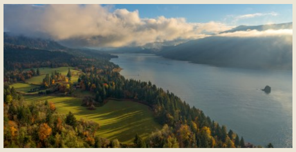
OMVPE-22
Washington, USA



Wednesday Afternoon Tours

The Conference is pleased to offer three types of tours for attendees including all costs of transportation, guide fee, arrangements, permits, bottled water, snacks, and staging from Skamania Lodge. Because of limits on transportation, there will be two sets of 2.5 hour tours. The first set of tours will depart at 12:15 and return at 2:45. The second set of tours will depart at 3:00 and return at 5:30 (times approximate depending on technical sessions). The following options are available:

Waterfall Tour $130

The waterfall tour will include 620’ Multnomah Falls, one of the tallest year-round waterfalls in the United States and the most visited natural recreation site in the Pacific Northwest. Permits are required to park in the lot and visit the falls in the summer, so this guided tour is the best choice. Multnomah Falls Lodge has a public Visitor Center, snack bar, gift shop, adjacent accessible restrooms, and a restaurant on the second level. For the physically active, there is a climb from the Multnomah Falls Visitor Center up a steep trail to the historic Benson Bridge. Beyond the bridge, those seeking a more rigorous experience can continue to the top of the cliff and take a short spur trail to a small viewing area at the very top of the falls. The total distance to the top of the falls and back is 2.4 miles and around 600’ of elevation or the equivalent of 60 flights of stairs on uneven, steep terrain. Sturdy footwear is required past the bridge. Other Gorge attractions will be added as time permits. The second tour will be aimed at those who want to hike the full distance to the top of the falls but may get fewer other attractions. Multnomah Falls is a 20 minute drive from the conference venue.

Winery Tour $150

The winery tour will offer a scenic drive through the Gorge to a premier local vineyard & winery for tastings (cost includes $20 venue fee). "A World of Wine in Forty Miles" is the motto for the Columbia Gorge Winegrowers. Straddling the mighty Columbia River, the Columbia Gorge Growing Region includes the fertile soils of both Washington and Oregon. From the marine influenced climate of Underwood Mountain to the arid, dry land of the Eastern Gorge, from Albarino to Zinfandel, the grapes and wines of this unique region are a spectacular selection of sweet whites and luscious reds. The wineries span the Columbia River Gorge National Scenic Area through 40 miles of peaceful, open roads running through double mountain views of Mt. Hood and Mt. Adams. Many Columbia Gorge wineries sit just a half hour scenic drive from Skamania.

Nature Tour $130

The nature tour would offer a guided nature walk to waterfalls &/or vistas, including discussion of flora & fauna, history, geology, etc. Inside the Columbia Gorge National Scenic Area is a wondrous natural paradise tucked away from the rest of the world. Ancient volcanoes created basalt flows that are now the majority of the rocks in the Gorge. The flows are arranged in horizontal sheets, each representing a volcanic eruption. The Columbia River snakes through this spectacular canyon on its westward journey before joining the Pacific Ocean. Nowhere else on earth exists such a wonder of desert and forest, cliffs and waterfalls, sun and rain. It’s the only place in the world where a mighty river crashes through an entire mountain range. With the highest concentration of waterfalls in the nation, stumbling upon a magnificent rush of fresh falling water is easier to discover than you think. The area’s basalt cliffs, oak woodlands, and sweeping meadows offer an amazing variety of wildflowers.

Early-Bird Registration

Early-Bird Registration is now open, and ends May 16, 2025.

- Regular and Post Doc Registration include a digital copy of the conference proceedings and a ticket to the banquet.
- Regular, Post Doc, Grad Student, Retiree, One-Day, and Accompanying Person Registration include daily continental breakfast, coffee breaks, and receptions.
- Retiree, Grad Student, One-Day, and Accompanying Person tickets do not include a digital copy of the conference proceedings or a banquet ticket.
- Banquet tickets will be available to purchase.

Staying at the Conference Hotel? Receive a $300 registration discount.

Attendees who stay at the conference hotel will receive a $300 discount. Please use the coupon code HOTELDISCOUNT at checkout and then email a PDF receipt to aacg@comcast.net.

Early Bird Rates before & after $300 conference hotel discount

Early-Bird Regular Registration .... $1400 USD ($1100 USD after $300 discount)

Early-Bird Post-Doc Registration .... $1250 USD ($950 USD after $300 discount)

Early-Bird Grad Student Registration .... $1050 USD ($750 USD after $300 discount)

Early-Bird Retiree Registration .... $900 USD ($600 USD after $300 discount)

Early-Bird One-Day Registration .... $750 USD ($450 USD after $300 discount)

Early-Bird Accompanying Person Registration .... $750 USD ($450 USD after $300 discount)

Interview with Vince Fratello

Vince Fratello has had a distinguished career in crystal growth and a long track record of service to our Association. As he enters a well-deserved retirement, we wanted to sit down with him and discuss his lengthy career in crystal growth and his role in the Association. We also discussed the inspiration for his technical article that appears in this edition of the Newsletter. This interview is edited for length and clarity.

American Association of Crystal Growth: Let's start at the beginning. Where did you grow up and how did you get into crystal growth?

Vince Fratello: Well, I grew up on the West Coast. My dad was a merchant seaman and so, although I was born in Seattle, I lived in 10 different places by the time I was 10. Then my mom got tired of it, and I grew up the rest of the time in a small town on the Oregon coast. When I was five years old, I decided that I wanted to be a physicist working in a big industrial think tank. But you know, that's sort of a big, big goal and my small town school was a small pond. Then the summer between my junior and senior year in high school, I got to go to a summer science training program at Western Michigan University and that was huge.

AACG: How did you end up at Western Michigan?

VF: I have no idea how I found out about it or how I got into it. It was a program done by the NSF and the National Research Council. I don't know why they chose Western Michigan in particular for it, but it was a great program. It was 50 kids from all over the country. We all did the math program and then half were in physics and half were in chemistry. We all did a did a lab course as well. I was sort of shocked when I came out on top in both the physics and the lab course because these were people that had had two years of calculus and things like that, and I'd had none of that.

AACG: What came next?

VF: That really opened up a lot for me, so I applied and got into Caltech as an undergraduate, and it was the perfect place for me. My crystal growth journey started right there. When I did my senior project, it was on grain size of permalloy films. I had the opportunity to work in a lab under Pol Duwez, who had invented the splat quenching method for making metallic glasses and other metastable phases. He trained me up to be the main operator and analyst in X-ray crystallography, so he didn't have to do it all. I worked there for three years, which gave me a head start on grad school. I ended up working for Dave Turnbull at Harvard in my graduate work, mainly on kinetics. The topic of my thesis was the effect of pressure and hydroxyl content on the crystal growth kinetics of fused silica. So, there I was, back at crystal growth again.

AACG: Then you started your career?

VF: When I was at Harvard, there was a guy from the National Bureau of Standards (now NIST), Hal Raveche, who was doing an adjunct professorship at Harvard, and he liked me. He basically wired up a post doc for me. It was a time when a lot of places weren't hiring, and so there were not a lot of interviews for permanent jobs. It was great, but almost immediately after that, Bell Laboratories started recruiting me. I had only been at NIST for 13 months, but you know that when Bell Labs makes that offer you can't refuse, what with Bell Labs being Bell Labs and the 60% salary increase.

AACG: Did you ever have designs on academia?

VF: Not really. The Harvard assistant professorship always had the reputation that 1-in-50 got tenure, and I watched that academic merry go round. My friend Frans Spaepen, when he finally did get tenure, he said, "For many years I've occupied a special chair here at

Harvard, it's called the ejection seat!” And then, working at a government lab, when [President] Reagan was elected, his first impulse was to fire everybody above a certain level and put in political loyalists, but he was told basically, no, you can't do that. People have to have a certain competence in what they're doing. So government did not look so attractive. All of those things said to me, “I'd like to go to industry.” I felt it would be more stable; what did I know?

AACG: So then you went to Bell Labs?

VF: Yeah. I started at Bell Labs in the magnetic bubble program, growing thin garnet films for magnetic bubble memory. Then, as we say, we got caught between a RAM and a hard disk. When you say, “well, this is the only technology that can do this,” pretty soon silicon sort of creeps in on you.

AACG: Yeah, it seems to be the case in a lot of different fields that silicon always wins. I've never heard of magnetic bubble technology. What was the concept there?

VF: So, the concept was that if you grow these thin magnetic garnet films, the magnetic garnets are ferromagnetic, and you can grow them with a perpendicular magnetic anisotropy so that they have a mixture of up and down serpentine domains that look like a plate of spaghetti. If you now apply a magnetic field, the opposite domains will shrink down until they become this stable small round bubble domain, and that that round domain can be manipulated around a shift register or any number of things. So it was a truly non-volatile type of memory. That was very valuable for the space program. For example, even after the program at Bell Labs got cancelled, the Western Electric factory continued making these memories for some years just to supply an inventory for the space program so that they would have that over the long term.

AACG: You were also working with liquid phase epitaxy (LPE)?

VF: LPE was really my sweet spot and when we were done making these thin magnetic garnet films we said to our management, “you know, the Japanese are using these now to make magneto-optic isolators.” They're basically a one-way light valve that only allows light to go forward, but not to come back to the laser and cause reflections, feedback and noise. But they said no, we're happy with the yttrium iron garnet ones we've got. Then a couple years later, they came back to us and said, you know, the Japanese are working on these thick films and how come you aren't working on that?

So I was put on that problem and after about two years we had caught up to where the Japanese researchers were. The Japanese program was all done mainly at one university, and it was promulgated from there out to various companies in Japan. We had to stat from scratch. They published some, but the nature of these things is you never publish everything, so there are about six different scientific breakthroughs you have to make in order to make this a practical process, and if you miss one, you can't do it. We independently developed that process, and then then we took another step. To make these magneto-optic materials work, they apply a magnetic field and there's this big magnet there that has to have a pretty good size field. That puts it out of bounds for a number of locations close to the laser. We found this thermodynamic trick. Some people would call it magnetic, but we called it thermodynamic, wherein if you lower the saturation magnetization of the material and magnetize it, it will not demagnetize because the free energy required to overcome the creation of the domain wall is greater than the driving free energy and so it's stays magnetized. We called it latching.

The crystal we were growing was a thick film, bismuth-doped rare-earth magneto-optic garnet. It's grown by LPE, but it's got to be anywhere from 300 to 500 microns thick, so you're now sort of challenging your no-

tion of epitaxy when your substrate and your film are of similar thickness.

That was at that time the business unit was outsourcing the making of the isolators. We were working still in the basic research arm of Bell Labs, supplying the crystals, and they were going out to our customers and coming back into the business unit. At the time the AT&T breakup occurred, we were part of Lucent Technologies in Murray Hill, which was the corporate headquarters and so where everybody wanted to be. They were about to kick us out to put the public relations people in our space. We used to say that the rugs were marching towards us because the labs all had tile floors and when they put in any administrative functions, they put in rugs, of course. But we were supplying these latching crystals outside and we were the only ones that knew how to do it. Our customer who was making the devices invited us to come out to Lucent Optoelectronics business unit to talk about capacity. The Optoelectronics marketing guys drew one of these hockey stick curves, and they said, “Can you meet this ramp?” And I said, “We're going to have to put in more capacity.” That went over everybody's head except somebody way down at the end of the table who had supply line management. She said, “Well, can you do that?” I said, “Oh no, we have no space.” She went white as a sheet because the whole business plan for the business unit depended on this one component because it was in everything. All of a sudden the rugs came to a screeching halt.

They gave us a whole building in Reading, PA, and we had roughly 100 furnaces at the peak. We were making 12 million devices a year, and at the beginning of 2001 I said okay, nobody can say that we are limiting the growth of the company. But within six weeks I knew that we were all screwed, because everybody had suddenly discovered that the whole capacity was over overblown and then the telecom crash occurred. I laid off everybody that worked for me and laid off myself and joined some friends who had previously begun a startup company named Integrated Photonics the next day. We were still doing thick film Faraday rotators, but of the more traditional kind that required magnets since Bell Labs had abandoned that market.

My friends had split off during the big boom because it was a very stressful time, and they said that they didn’t want to work in that environment anymore. In those days you could get money on the basis of a back of an envelope business plan. They broke ground on a building, and they had capacity for 100 furnaces that was all sold at the moment they broke ground. But by the time the building was complete, there was no market. So, I had to go in and start looking at government grants for other applications, and we built that up and the market eventually recovered. It was great because Steve Licht and I got reunited and we worked together for 30 years total. We have very complimentary skill sets.

AACG: What were you using as a substrate?

VF: We're using a substituted gadolinium gallium garnet. It's a larger lattice parameter garnet, but it had a different coefficient of thermal expansion than the film. So, you had the situation where you had to have a lattice match at room temperature, but at high temperature when you were growing, you didn't. As you grew the film, the film/substrate composite would bow downward into the melt, and you were right on the thin, hairy edge of it breaking up into pieces. Then if you cooled it back very slowly to room temperature, it came flat again.

AACG: Didn’t this process introduce lots of dislocations and defects and things?

VF: There's a catastrophe that occurs. If you're bowing too much; you will get massive dislocation from the mismatch. The other factor is that you want to add as much bismuth as possible because it increases the Faraday rotation and lets you grow thinner. But if you add more bismuth you get more coefficient of thermal expansion mismatch and a higher tendency to make misfit dislocations. So you have to balance those things out and that's one of the things that we had to study extensively.

AACG: So, this was the middle third of your career doing LPE of thick film garnets. What was the final third?

For the latter third of my career, I had to think about what my future with Integrated Photonics was. And the reality was because I wasn't one of the founders of the company, there was not going to be a big payoff for me. There was also a personal reason that my wife and I wanted to move to the west coast. So, I hired a replacement, and I left. The last 14 years have been out in the Seattle area. I ended up at a place called Quest Integrated.

AACG: What was Quest’s area of business?

VF: Non-destructive testing.

They were having me make magneto-optic indicator (MOI) films when I was at Integrated Photonics, which is why they first got interested in hiring me. The MOI films were used to look for rivet cracks in aircraft fuselages. They generate an eddy current in the fuselage and when it hits a crack, it pops up as a magnetic vector and that would show up on the MOI film, which was of a

similar composition to the thick film magneto-optic garnets but much thinner. But I never actually did grow those at Quest though.

When I came in, they were taking some gambles. The CEO had just sold a portion of the company for $42 million, and so he made a couple of bets. I was one of those. He said to me, “I want you to invent something that will change the non-destructive testing industry,” which, you know, is a pretty interesting charter.

AACG: A modest request!

VF: What I zeroed in on was the unsolved problem of what are called unpiggable gas pipelines. In oil pipelines, the company had pretty much solved the problem of how to do ultrasonic testing of wall thickness in a pipe with varying internal diameter by having a standoff so that the tool could collapse up to 70% of the original diameter. If you do that in a gas pipeline, the problem is that putting ultrasound into a gas is like trying to put light through a mirror. Everything highly reflects at every surface, and you've got to go through four surfaces. You've got to get the ultrasound out of the transducer, into the pipeline, out of the pipeline and back into the transducer. You've got three orders of magnitude loss right there. Even if you have the capability to detect such a small signal when it comes back, you are also dealing with the strong front wall reflection. If it has a long tail, you'll never see that three orders of magnitude lower reflection from the back wall 2 microseconds later because it gets swallowed up in the tail, so your pulse needs to be really short.

I set off on two paths in solving that and one of those was crystal growth, because of course I'm a crystal grower. One of my first things was reaching out to my old friend Zuo-Guang Ye at Simon Fraser University. He invited me to the piezoelectric crystal conference that goes on every year at Penn State, and he reported that they had grown these small crystals of lead zirconate titanate (PZT), which is one of the best piezoelectric materials, but it's almost impossible to grow in single crystal form. He and his student had grown some good crystals, but they were small. I looked at that, and being naïve, I said “I could do that.” Eventually I did, though it took some years. It was quite an interesting problem because I had to derive the phase diagram first, which nobody had adequately understood previously. Most everybody was growing crystals out of what amounted to a slush. They would say, “I want equal amounts of titanium and zirconium in the crystal, so I'm going to put that in the liquid.” If you put it in the liquid, all the zirconium drops to the bottom as lead zirconate. So your liquid is not what you think it is, and your crystals don't come out the way you think they should. By working out the phase diagram, I was able to solve that.

Now you know they always say to a kid with a hammer, everything looks like a nail. How I viewed it was as an expert in liquid phase epitaxy. I said I've got to be able to find a substrate to do this, and so I looked and looked and there was nothing. I said, okay, I've got to invent something. I started looking at solid solutions because Dave Brandle and I at Bell Labs had done that together. We had seen one solid solution that had been invented elsewhere, but that he was able to perfect called LSAT (Lanthanum Strontium Aluminum Tantalate), which is a perovskite that is a solid solution with a congruently melting minimum. But it's not a line compound, it's just a continuous solid solution. I asked how that works thermodynamically, and he waved his hands and said, “Oh, that's just an azeotrope.” When I started looking at it at Quest, I said, how does this not violate Gibbs’ Phase Rule? That's when I started looking at these solid solutions with indifferent points and coming to an understanding of that, and that's the subject of the article that I submitted to the Newsletter.

AACG: Did you find a promising substrate?

VF: I found a number of perovskite solid solutions with indifferent points but, unfortunately, they weren't a good enough lattice match, so finally I had to succumb to reality. I said okay, if I'm going to make this, I'm going to have to do top seeded solution growth. I had to create a seed and bootstrap my way up to do that. Then, the problem I had to solve was compositional stability because hardly any zirconium dissolves in the melt. You have to figure out what you're going to do about that, because as soon as you start to grow, you start to deplete that zirconia. Then you don't have a constant composition, but the best composition of PZT is a very precise composition. Any crystal that you grow goes off that composition too quickly to grow large and uniform. Finally, I embraced this lack of solubility of zirconia and did something that that's kind of similar to the traveling solvent method. I just put in a whole bunch of the composition that I wanted, and it falls to the bottom of the melt and the resulting liquid is the right composition to be in thermodynamic equilibrium with what's on the bottom. Now, I knew from the phase diagram what the liquid was for the solid that I wanted. So at a certain temperature I could equilibrate that solid and that liquid, and then I put a seed on the top and I would get continuous solid-state transport from the bottom to the top because there was a temperature gradient. I used the temperature gradient in that way and was able to get much larger uniform crystals of better quality than could get by any other means. The problem though was one of throughput, because it's a fairly slow growth process. But I got it a long way, I'd say 95% of the way to commercialization, and then we lost the lease on our building, and we got bought by another company and they said, yeah, we're going to do this a different way.

AACG: Ah, that's, too bad.

VF: Yeah. Now the upside is that when you're an industrial crystal grower, your problem always is that your best work remains a trade secret. There's been tons of stuff that I've done that never will see the light of day in publication. But now because they decided that they were not going to pursue it, they said, well, you should patent it so we can have some benefit from this technology if anyone else decides to use it. Once you patent it, of course, then you can publish it. So I've published these three monster publications on the work of my past 14 years; two are in print and one I've just submitted. So that's kind of nice.

AACG: That's great. And now it's off to retirement?

VF: The decision was a combination of things. I probably thought over the years, oh, I'll work to 75, maybe even 80. And then COVID came along, and I said life is short. I want to spend time with my wife, and she'd retired from the pharmaceutical industry some years before. She was always clear that she'd be very happy

for me to retire, and so I made the decision in the middle of COVID. I was taking my daughter across the country to college, and I stopped off at State College to interview somebody there and hired him in to be my replacement.

We did make a breakthrough on the transducer and he's doing much more of the transducer development. We found a way to make these gas couple transducers that work well and he's pursuing that. But the crystal growth kind of went by the by the wayside.

AACG: What are your plans for retirement? I saw you wrote a book called *Way of the Bow*. How did that come about? Had you always had an interest in writing a novel?

VF: I'll tell you the story, because there's always a story. In our family, we've always made a big deal about decade birthdays, and my brother was coming up on his 70th birthday about eight years ago now. Unfortunately, he also had about a year and a half to live with a cancer diagnosis, and I said to myself, “What do I give the man who's about not to need anything?” He was a teacher of communications, mass media, and screen writing. He'd written a couple of screenplays himself, and I thought I could write a screenplay representing all the lessons that he has taught me in life. So I sat down and started writing. It probably was about ¾ finished when he passed, but he enjoyed it and afterwards I finished it up, shared it with some friends and never thought too much about it until I shared it with a friend who had a cousin, Armand Mastroiani, who has directed and produced 50 movies.

He looked at it and said it was good, but it's got some flaws and it's too long. I turned it around in about 10 days and sent it back to him and he said, “Oh!”, because writers never wanted to edit their work. So, he gave me some more ideas and eventually he said look, if you want somebody to take this more seriously, you should turn it into a novel which I'd never thought about, but I had a good friend from 50 years who's written seven books. So I talked with her and I sat down with it and in two months I had a novel. I could have sent it off to a publisher, but I’m not into rejection, and I didn't want to be bothered with it. So, I just self-published. It's well-reviewed, but marketing is hard. But I found I enjoyed it, so I've written a sequel. It's about to be ready to go on to print. I'm going to see this time if I can find a publisher. I suspect that writing will be an activity I will continue to do in my retirement. I have a number of people that are very eager for the sequel to come out because they're vested in the characters, and it's been very enjoyable. I even got a little TV interview on the Spotlight Television Network, which gets you to YouTube, but that’s about all it gets you.

AACG: That’s great! Since it started as a screenplay, is there still a goal to see it become a film?

VF: Of course! I think the novel is an easier sell than a screenplay. If you've got the got the novel and it does well, or somebody's impressed with it, then you can say well, I already have a screenplay. The other thing I found was that the process of writing a screenplay gives you a big leg up on the novel. You've got your dialogue, your plot, your scene structure, your characters. A screenplay is about 20,000 words and my novels are about 75,000. So obviously there's a lot of extra writing to be done, but you've got so much structure to build around that once I have a screenplay, I can sit down and write a novel in about two months.

AACG: Would you say that's easier or harder than growing PZT?

VF: Much easier. I think that a lot of the things I've gotten assigned to do in my career are things that are kind of almost impossible. One of the advantages I've always had coming out of grad school is my advisor had a real intuition about thermodynamics. That intuition about thermodynamics helped guide me as I've moved through this landscape of what is possible and what isn't. It’s advantageous to say, OK, this is not possible, so I'm not going to work on that, but if I can take this route then that makes it possible. So I've worked in metastable regimes and things like that in order to get to where I'm going.

AACG: Despite the demands of your new literary career, do you have other plans or hobbies you'd like to pursue in retirement?

VF: I walk my dogs two hours every day, and I'm also a certified Iyengar yoga instructor. I enjoy yoga, and one of the things I resolved to do in retirement was to teach more. By happenstance, the last day I physically reported to work, my yoga teacher fell and cracked his femur. So for a week, I was a full-time yoga teacher, I'm on the east side of Seattle, and I had to go into Seattle to teach the 5:30 and 7:00 AM classes, come home and then go back and teach evening classes. That was a little stressful. He figured out how to teach over Zoom into the studio within about a week. Now I'm teaching just two classes a week. My practice and teaching yoga are something that that I'll be doing more of, and I think it always contributed to the patient state of mind necessary to grow crystals. I also plan to stay active in the Association. I think I've got three roles so far in this conference coming up.

AACG: I saw that.

VF: I just published this last paper on crystal growth of PZT. The characterization results on the PZT have been delayed, but there's another paper coming out on that with Penn State as lead authors. So, I still have potential for publications.

AACG: Well, that's great. One last subject I was hoping to touch on was the history of your involvement with the association.

VF: Being at Bell Labs, I was in contact with many seminal figures in the organization. Dave Brandle was my supervisor, Ken Jackson and Bob Laudise were mentors to me, Bill Bonner was a friend. When I went up for my first performance review, Dave Brandle asked me, "Do you visualize yourself going into management?" I said, "Heavens no!" He noted that another way to advance your career is to be active in professional societies. He got me involved going to the local AACG Mid-Atlantic Section meetings. There was the western regional conference and then we established an eastern regional conference. I was involved with that from the very beginning. I worked my way up through being involved with that until eventually that conference went away because of financial issues.

Then in 1992, the AACG hosted the international meeting and Dave Brandle looked at me and he said, "You know, all the senior people in the US are working on this international meeting in 1992 and too busy to work on the next national meeting." He wanted me to pick a bunch of junior people and organize a national meeting in 1993. So I did. We did that in Baltimore, on the Inner Harbor and we had a great time. The big social event was that we did a tall ships cruise. Following that, I was elected as Treasurer and there was at that point kind of a natural flow of people who went from Treasurer to President.

In my role as President, I said this conference every three years isn't working for us because we're just not really feeding our organization. The international conference is all well and good, but if it's not in the US, there's maybe 40 people that can go. So I started doing conferences every year. Eventually it turned out that every year was too much a stress on our volunteer pool, and so we went to every two years as it is now. As a result of doing that, I've now additionally chaired the national meeting twice more and then when we hosted the international meeting in 2019, I was co-chair of that.

AACG: As we conclude, are there any other thoughts you'd like to share?

VF: You know, I just feel so fortunate to be part of this community. I think that's why I've done a lot of volunteer work for it. It really has enhanced my career as well. I think about when I left Bell Labs. I already had this other job lined up, and I had to get rid of my Bell Labs e-mail address, so I sent out a note to people on my mailing list saying I'm leaving Bell Labs, here's my home e-mail. I got emails back from three people who I genuinely consider to be famous people saying "Are you okay? Do you need help finding a job?"
I thought, you know, wow. I didn't put the effort into this community for that reason, but there is real payback in these connections and the friendships you make. These are people that I send Christmas cards to every year and invite to my annual pasta party. I'm really happy just to have been involved with this organization. It's been a real honor.

ACCGE-24
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AACG Awards

As we prepare for ACCGE-24, nominations are open for three awards to be presented at the conference. **AACG award** is presented for outstanding contributions to the field of crystal growth and epitaxy. **AACG Young Scientist Award** is given to an early career scientist working in the fields of crystal growth research, development, practice, theory, modeling, characterization, application or production to recognize his or her outstanding scientific and technical contributions in the field of Crystal Growth. The award shall be made based on published papers, patents, conference presentations, products or teaching coming from the candidate's work. The criteria for selection shall be scientific excellence, clarity of presentation and impact on the field of crystal growth. **The Gentile Service Award** is given for dedicated service to the AACG.

The AACG Award and the Young Author Award prize winners will deliver plenary talks at the conference. These are significant prizes. The AACG Award comes with an honorarium of $1000 and an inscribed plaque with a ruby crystal. The Young Author award also comes with a plaque and $500. The Gentile Service Award for dedicated service to the AACG comes with a clock. The suggested format for nominations will be an overall letter describing the reason for the nomination, three supporting letters from others, and the curriculum vitae of the nominee.

The deadline for submission of award nominations is Monday, June 2, 2025. For more information, please contact Bob Feigelson by email: feigel@stanford.edu.

Save the Date!

June 7-10, 2026

AACG

West Section

The conferences aim to provide an interdisciplinary platform for researchers to discuss the fundamental nanoscale physics and chemistry that are central to the growth of crystals for a wide array of technologies.

The conferences focus on current and emerging challenges in understanding, engineering, and design of crystal growth in nature and technology. We welcome contributions in areas such as crystallization of biological and biomimetic materials, synthesis of crystalline material systems for renewable energy, environment and sustainability, interplay between synthesis and performance of functional materials, and fundamental aspects of nucleation, growth and phase transformations in a wide range of crystalline material systems.. The registration fee always includes all sessions, lodging, recreation and meals.

As a guide, in the past the conference themes have included the following topics:

- **Biological and Biomimetic Materials**
- **Energy and Environmental Material Systems**
- **Functional Crystals and Architectures**
- **Fundamentals of Crystallization**

AACG West Outreach Program

The West Chapter of the American Association for Crystal Growth is committed to introducing youth to the fields of science, technology, engineering, and mathematics (STEM). Our bi-annual conference aims to provide an interdisciplinary platform for researchers to discuss the fundamental nanoscale physics and chemistry that are central to the growth of crystals for a wide array of technologies.

Through fundraising from our very active outreach committee, generous donations from sponsors, and the hosting venue at Stanford Sierra Camp, we were able to have our inaugural class of high school and undergraduate students come to the 28th AACG Western Section Conference on Crystal Growth & Epitaxy, held at Fallen Leaf Lake, CA during June 9th – 12th, 2024.

Students spent their time listening to presentations from researchers from academic institutions, national laboratories and industry on emerging challenges in understanding, engineering, and design of crystal growth in nature and technology. In addition, they engaged in discussions with all participants during the poster presentations and participated on the Career Panel Discussions where every participant is encouraged to ask panel members about their paths and experiences in science and engineering.

This year, we had welcomed a group of high school students and two of their teachers from the Tracy Unified School District in Northern CA, another high school student from the Pringee School in South Hamilton, MA, and several undergraduate students from San Francisco State University, University of California Berkeley, and the University of California Irvine.

Registration, Submission and News can be found on the West website:

https://www.aacgwest.org

Indifferent Points in Perovskite Solid Solutions

Vincent J. Fratello, Song Won Ko, Quest Integrity USA, A Baker-Hughes Company, Auburn, Washington
Lynn A. Boatner Oak Ridge National Laboratory
Hanna A. Dabkowska, Antoni Dabkowski, McMaster University
Theo Siegrist, Kaya Wei, National High Magnetic Field Laboratory and Florida State University
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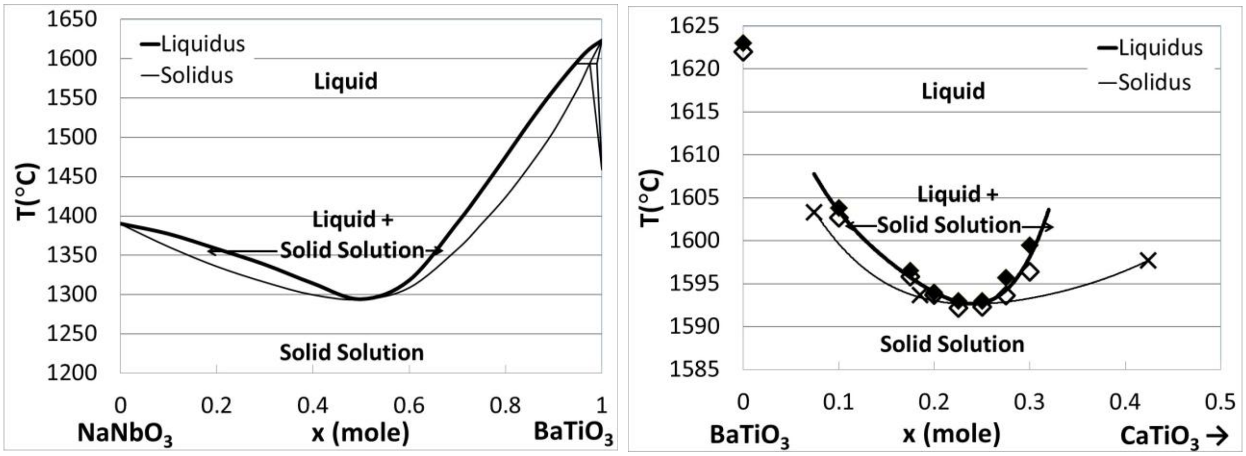
1 Introduction

Archimedes is quoted as saying "Give me a place to stand and I will move the earth." Such is the role of a substrate in epitaxial crystal growth. A high-quality substrate that is a good structure and lattice parameter match to the film is needed to do epitaxial or seeded growth. As the lead author (VJF) has spent the majority of his career working on liquid phase epitaxy (LPE) and top-seeded solution growth (TSSG) of oxide materials, he has also spent substantial time trying to develop new substrate materials in the garnet and perovskite systems of interest.

Minerals with perovskite structure are most abundant inside our planet and constitute most of Earth's lower mantle. The perovskite crystal structure is really a generic structure defined by a network of anions with cube-octahedral (12-sided) and corner-sharing octahedral (8-sided) cation sites. The most common nominal perovskite formula is ABO_3. The cation sites in the anion structure can accommodate over half the metal cations in the periodic table and still retain the perovskite structure, but with properties that Mother Nature never produced. Accessing the full quality of desired perovskites requires single crystals, either in bulk or thin-film form. While many clever methods have been devised to grow perovskite single crystals in bulk form, many perovskites have remained out of reach for large-scale production because the desired perovskites do not melt congruently. Thin film methods have fewer constraints, e.g., many incongruently melting compositions are straightforward to deposit as thin films provided there is an appropriate substrate on which to deposit them. But this brings us back to the same issue of the need for more perovskite single crystals that can be grown at large scale with excellent perfection. Therefore, new materials outside the scope of straightforward combinatorics are required.

Solid solutions readily form between two perovskites, where two end members, e.g., ABO_3 and $A'B'O_3$ may mix with fractions $0<x<1$ to a range of ordered, partially ordered, and disordered materials $A_xA'_{1-x}B_xB'_{1-x}O_3$ that can be viewed in a first approximation as a two-component pseudo-binary solid solution. Because solid solutions are not line compounds with a fixed composition, these commonly have complex melting and crystallization behaviors.

In the late 1980s and early 1990s, Dave Brandle's group at Bell Labs was tasked with developing perovskite substrates for epitaxial growth of high temperature superconductors. In the course of this effort, it was decided to work on a system discovered by Mateika and co-workers, who found congruent or near-congruent compositions by putting paired "guest ions" in $REAlO_3$ perovskites. These are actually solid solutions between $REAlO_3$ and $AEAl_{1/2}B'_{1/2}O_3$ where the alkaline earth AE was Sr or Ca and B' was Ta or Nb.[1] A substrate material of technological importance from this system is the cubic perovskite solid solution between a simple perovskite lanthanum aluminate $LaAlO_3$ and the complex perovskite strontium aluminum tantalate $SrAl_{1/2}Ta_{1/2}O_3$. This compound, known as LSAT, has a previously measured congruently melting minimum temperature of ~1820 °C at $x \approx 0.23$.[2] When VJF asked Brandle about this unusual phase diagram, Brandle noted that it was essentially an azeotrope, a well-known phenomenon in liquid-vapor systems. VJF found that interesting and collected some examples from the ACERS-NIST Phase Diagrams for Ceramists, including $BaTiO_3$—$NaNbO_3$ and $BaTiO_3$—$CaTiO_3$ (Fig. 1). Then he got preoccupied with other projects and set it aside.



(a) (b)

Figure 1: Prior art pseudo-binary phase diagrams of (a) $NaNbO_3$—$BaTiO_3$,[3] and (b) $BaTiO_3$—$CaTiO_3$.[4]

They say that to a kid with a hammer, the whole world looks like a nail. VJF's expertise was in LPE and TSSG from high temperature solutions, which require a substrate or seed. So, when he began to be interested in the growth of single crystal lead zirconate titanate (PZT) in 2011, he started by searching for a possible lattice matching substrate/seed. Since none existed, he looked at a number of possibilities. VJF was intrigued to think whether there might be congruently melting solid solutions that could work and how he could discover them. Then he asked himself the question that he should have asked years before. Why does the condition of two phases in equilibrium at a point not violate Gibbs' phase rule? Two studies that we published in 2024 helped to explain this behavior. [5,6]

2 Gibbs' Phase Rule

Gibbs' phase rule defines the number of phases Π in a materials system at equilibrium as a relation between the rank of the coefficient matrix N (equal to the number of independent components in the system) and the degrees of freedom F of the equilibrium condition. Typically, N is taken to be equal to the number of components in the so-called "condensed" phase rule:

$$\Pi = N - F + 1. \tag{5}$$

In a constrained pseudo-binary phase diagram, it is the common teaching of the phase rule that $N = 2$. Under these circumstances, two phases ($\Pi = 2$) can come together on an equilibrium line ($F = 1$), but an equilibrium point ($F = 0$) requires the meeting of three phases ($\Pi = 3$).

A small number of continuous solid solutions have a unique feature where the liquidus and solidus curves come together at a congruently melting maximum or minimum at some fixed proportion. Some discussion is required to understand how these solid solutions comply with Gibbs' phase rule.

3 Solid Solutions

For this simple illustration, there is assumed to be no dependence of the enthalpies of crystallization/melting on temperature T and the solid and liquid entropies of mixing ΔS_m are assumed equal. The excess free energy of the liquid is given by its entropy of mixing:

$$\Delta G_L = -T\Delta S_m. \tag{1}$$

The free energy of the solid ΔG_S is given by the linear combination of the temperature-dependent free energies of the end members $(1-x)\Delta G_C+x\Delta G_D$ plus the free energy of mixing $\Delta G_m=\Delta H_m-T\Delta S_m$:

$$\Delta G_S = (1-x)\Delta G_C + x\Delta G_D + \Delta H_m - T\Delta S_m. \tag{2}$$

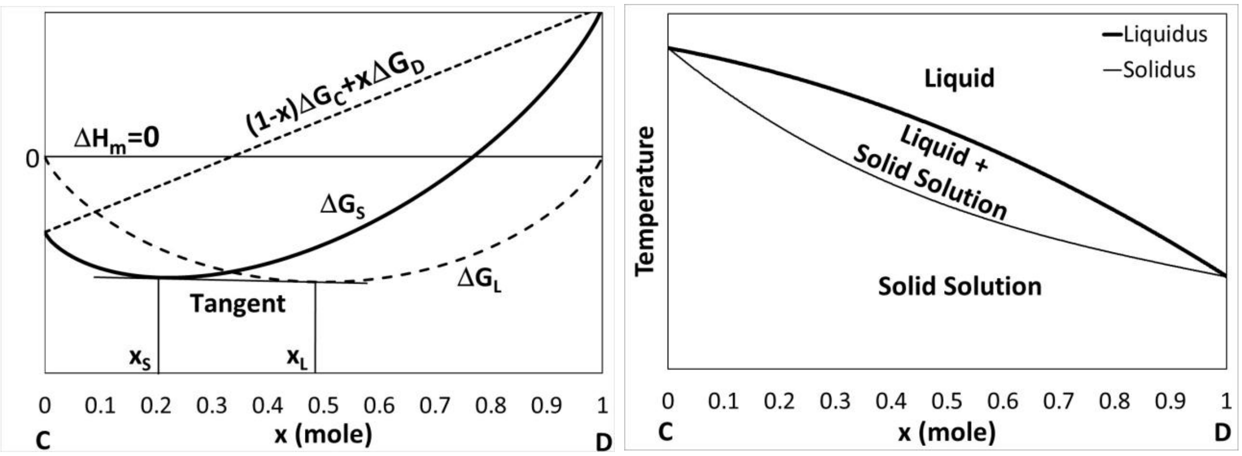
This solid free energy curve shifts up and down as the temperature varies. The simplified form of the entropy of mixing ΔS_m term for a proportion x is assumed to be as shown in Eqn. (3),

$$-T\Delta S_m = RT(x\ln(x) + (1-x)\ln(1-x)), \tag{3}$$

where R is the universal gas constant and ln is the natural logarithm.

3.1 Simple Solid Solution

Figure 2 depicts construction of a simple binary solid solution phase diagram. The free energy diagram is given by the free energy of crystallization of the two end members C and D and the entropy of mixing terms ΔS_m in the liquid and solid. For a simple solid solution it is assumed that there is no enthalpy of mixing in the solid so that C and D can be randomly distributed with no preference for order or disorder but tending toward good mixing because of entropy.



(a) (b)

Figure 2: Construction of a phase diagram of a simple solid solution with no enthalpy of mixing $\Delta H_m = 0$. A large $\Delta G_D - \Delta G_C = 1.25RT$ was used to make the split more obvious. (a) Free energy diagram with mutual tangent. (b) Phase diagram of a continuous solid solution.

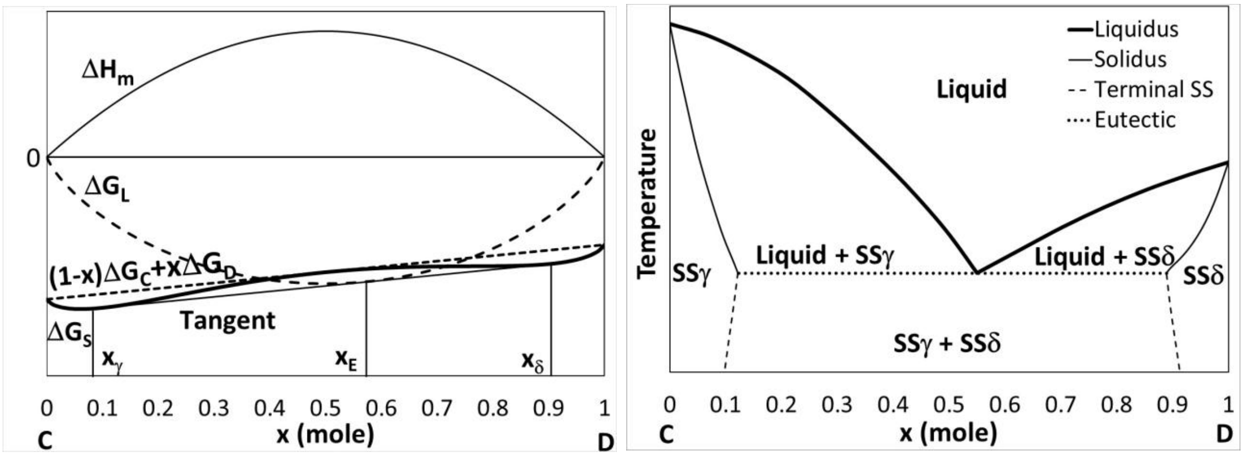
The solid and liquid free energy curves can only be tangent at the same composition at the end members. Therefore, the compound that crystallizes at any composition will be biased toward the higher melting compound. The farther apart the two melting points are, the more the liquidus (temperature where the last solid phase melts on heating or the first solid phase appears on cooling) deviates from the solidus (temperature where the last liquid phase solidifies on cooling or the first liquid phase appears on heating), and therefore more segregation occurs. A crystal grown in this way by cooling along the liquidus curve will have a continuously varying composition, properties, and lattice parameter. Two phases (solid and liquid) are in equilibrium on the solidus and liquidus lines.

3.2 Eutectic

The enthalpy of mixing ΔH_m in a simple C—D mixture can be approximated in terms of the enthalpy of adjacent bonds between two C atoms, H_{CC}, two D atoms, H_{DD} and C and D atoms, H_{CD}:

$$\Delta H_m = x(1-x)[H_{CD} - (H_{CC} + H_{DD})/2]. \qquad (4)$$

If the enthalpy of the C-D bond is <u>higher</u> than the average of the C-C and D-D bonds, which is to say it is unfavorable for C and D to be adjacent, then the enthalpy of mixing is <u>positive</u> (thermodynamically unfavorable), and it counteracts the free-energy contribution of the entropy of mixing. These terms contain the thermodynamic contributions of stress and electromagnetic interactions among the various ions. If there is a significant positive enthalpy of mixing in the crystal, complete unmixing and phase separation occurs in the middle of the phase diagram where the enthalpy of mixing is highest. This is called a eutectic and is depicted in Fig. 3. The different functional forms of the free energy terms of the entropy and enthalpy of mixing result in a complex free energy curve of the solid solution with two local minima that has its lowest free energy for a mixture of the two terminal solid solutions SSγ (a solid solution of D in C) and SSδ (a solid solution of C in D). At the eutectic point, this phase separation results in three phases in equilibrium, the liquid, SSγ, and SSδ consistent with Gibbs' phase rule.

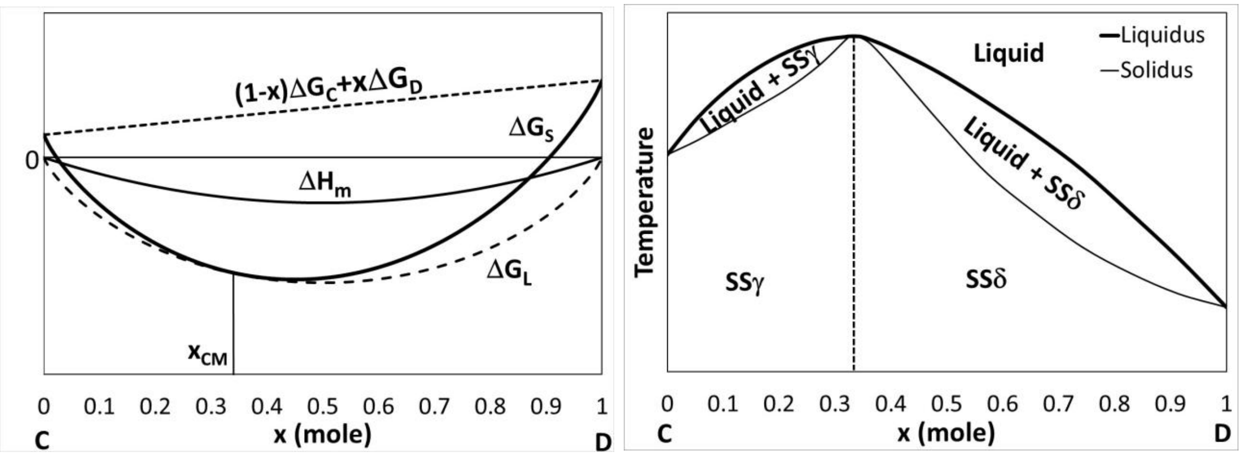


(a) (b)

Figure 3: Construction of a eutectic phase diagram resulting from a positive enthalpy of mixing. (a) Free energy diagram with mutual tangent at two points on the solid free energy curve. The enthalpy of mixing coefficient is $[H_{CD}-(H_{CC}+H_{DD})/2] = 2.77RT$ *and* $\Delta G_D-\Delta G_C = 0.3RT$*. (b) Phase diagram of a eutectic.*

3.3 Congruently Melting Maximum

If, instead of the eutectic example above, the enthalpy of the C-D bond is lower than the average of the C-C and D-D bonds, then the enthalpy of mixing is negative (more thermodynamically favorable), and it is favorable for C and D atoms to be adjacent, reinforcing the free energy contribution of the entropy of mixing. In an imaginary C-D compound this could result in perfect C-D-C-D ordering with a higher order unit cell. Complex $AB_xB'_{1-x}O_3$ perovskites can have different stoichiometries such as 1:1, 2:1 (depicted in Fig. 4), 3:1 and even non-integer mixtures.



(a) (b)

Figure 4: Construction of a phase diagram with a congruently melting 2:1 (33%) maximum resulting from a negative enthalpy of mixing. (a) Free energy diagram with mutual tangent at a point. The enthalpy of mixing coefficient is $[H_{CD}-(H_{CC}+H_{DD})/2] = -RT$ *and* $\Delta G_D-\Delta G_C = 0.3RT$. *(b) Phase diagram of a congruently melting compound.*

Once again, the difference in functional forms of the entropy and enthalpy of mixing allow a different free-energy curve, in this case the solid curve is above the liquid curve at all points with a tangent point in the middle. In this formulation, a negative enthalpy of mixing is a prerequisite for the congruent maximum at x_{CM}. The necessary criterion for a congruently melting maximum is $d(\Delta G_S-\Delta G_L)/dx = 0$ in Fig. 4a, which is satisfied by ΔG_S and ΔG_L having the same slope at the congruent point per the construction in Fig. 4a. This results in the congruent condition $dT/dx = 0$ at x_{CM} in Fig. 4b. Inserting the relevant quantities and solving for the maximum point x_{CM} gives:

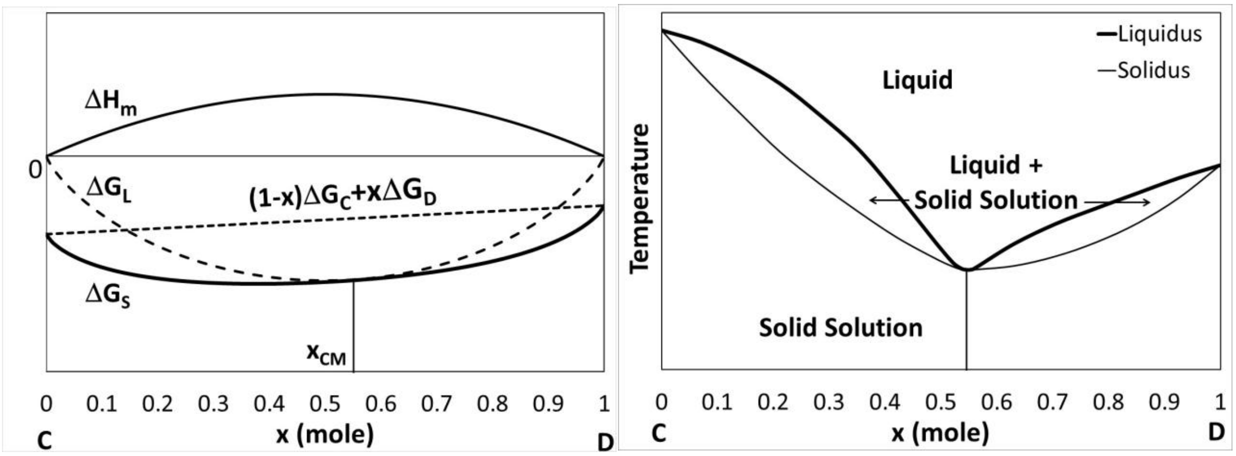
$$x_{CM} = 0.5(\Delta G_D - \Delta G_C)/[H_{CD} - (H_{CC} + H_{DD})/2] + 0.5. \qquad (6)$$

The maximum point comes closer to $x = 0.5$ for a larger negative mixing coefficient $[H_{CD} - (H_{CC} + H_{DD})/2]$ and closer to the higher melting end member for smaller negative $[H_{CD} - (H_{CC} + H_{DD})/2]$ reaching the axis for zero enthalpy of mixing $[H_{CD} - (H_{CC} + H_{DD})/2] = 0$, resulting in a simple solid solution phase diagram as in Figure 2.

It has been argued previously that this ordering transition disambiguates between solid solutions SSγ (a solid solution of D in C) and SSδ (a solid solution of C in D), such that at the congruent point they come together as two solid solutions with the same composition[7], thereby satisfying the conventional form of the condensed phase rule. The argument that SSγ and SSδ remain distinct gives three phases with the liquid at the congruent melting point. A crystallizing composition away from the congruent maximum will move away from the congruent composition as crystallization progresses.

3.4 Congruently Melting Minimum

There is another case to be considered. If the enthalpy of mixing is positive, but small, it may not be sufficient to overcome the entropy of mixing at the melting temperature, and there is only a single flattened minimum. Once again, the difference in functional forms of the entropy and enthalpy of mixing allow a different free-energy curve, in this case the solid curve is below the liquid curve at all points with a tangent point in the middle as in Fig. 5a. This results in a congruent melting minimum as in Fig. 5b. For this condition, a crystallizing composition away from the congruent minimum will move toward the congruent composition as the temperature is lowered and crystallization progresses.



(a) (b)

Figure 5: Construction of a phase diagram with a congruently melting minimum resulting from a small positive enthalpy of mixing. (a) Free energy diagram with mutual tangent at a point. The enthalpy of mixing coefficient is $[H_{CD}-(H_{CC}+H_{DD})/2] = 1.385RT$. *A smaller* $\Delta G_D-\Delta G_C = 0.16RT$ *was needed to keep this near the center of the phase diagram. (b) Phase diagram of a congruently melting minimum at an indifferent point.*

Interestingly, at the congruent temperature there appears to be only a single continuous solid solution phase and only two phases at the congruent point, seeming to violate the phase rule.

While it is possible that there are clustering terms that provide some higher degree of order that could once again disambiguate the two solid solutions, it is not necessary if the full definition of the phase rule is considered.

For liquid-solid systems, this congruent minimum is properly referred to as an indifferent point. There are a substantial number of alkali halides that display this behavior, but few perovskites to date.

3.5 Indifferent Points

The requirements for an indifferent point to occur must be discussed in terms of the full definition of Gibbs' phase rule. This is often oversimplified in the literature, and therefore its application is explained briefly here. As discussed above, N is typically taken to be equal to the number of components, but that oversimplification loses information critical to understanding indifferent points.

The problem arises in the assumption that $N = 2$ for two components. The number of independent components is actually the rank of the coefficient matrix. The rank of the coefficient matrix equals the number of components if the determinant is non-zero. If the state in question strictly minimizes the total internal energy in the sense of Gibbs' minimum energy principle, then the rank of the coefficient matrix equals the number of components and Gibbs' traditional phase rule is valid ($N = 2$ here).[8] Nonetheless, the coefficient matrix for some binary mixtures can mathematically have a zero determinant at some composition, in which case the coefficient matrix rank is 1 (same as the equations not being independent). In this case, the matrix form of the Gibbs-Duhem equation does not require that all differential chemical potentials be zero ($d\mu = 0$) and that the total internal energy be minimized. Federov classified such acnodes in phase diagrams.[9] Tester and Modell suggest that the phase rule must be interpreted to mean that "there are certain sets of intensive properties which, when selected, will completely define the system" but there is not freedom to choose any set.[10] Mathematically, this critical point of the defining polynomial function is referred to as an acnode or singularity where the function must have a local minimum or maximum. This is the condition that permits an indifferent point in a solution/solid solution.

Unfortunately, the mathematical condition of a zero determinant does not usefully predict which chemical systems will have such an indifferent point. Therefore, we studied what conditions empirically yield an indifferent point, specifically with a congruently melting minimum.[5]

4 ABO_3 and $A'B'O_3$ Pairs with Indifferent Points

We studied a wide variety of ABO_3 and $A'B'O_3$ pairs to see which had indifferent points.[5] The following traits were determined to give the best odds of a cubic, congruently-melting, perovskite crystal in the desired lattice parameter range: 1) Near unity tolerance factor, 2) Similar melting temperatures, 3) Stable end member compounds, 4) Common ions, 5) Compatible crystal ionic sizes, 6) Low to moderate vapor pressure of all constituents, 7) Not excessively refractory, 8) Avoiding ions of the same valence on a single site, and 9) Lattice parameter in the desired range.

In particular, the tolerance factor being near unity was critical. The phase stability and crystallographic structure of perovskites depend on the relation between the average ionic sizes on the two sites in the crystal. The ease of formation of an oxide perovskite for any A–B pair depends on the crystal ionic radii or, in the case of more complex structures, averaged site crystal ionic radii, and is given by the dimensionless Goldschmidt perovskite tolerance factor.[11]

$$t = (r_A+r_O)/(r_B+r_O)/\sqrt{2}\ , \qquad (7)$$

where r_A and r_B are the average A- and B-site ionic radii and r_O is the oxygen ionic radius. Goldschmidt[11] observed that stability of the perovskite structure may be found within the limits $t = 0.77$ to 0.99, but cubic symmetry is best found near unity $t = 1.00$. The tolerance factor t can contribute to a thermodynamic energy minimum with an enthalpy contribution:

$$\Delta H_t \propto (t-1)^2/(r_A-r_{A'}) \qquad (8)$$

where r_A and r_A are the ionic radii of the A and A′ atoms.

Table I lists successful solid solution pairs that have been investigated to varying degrees.

ABO_3	$A'B'O_3$	x_m (±0.1)	t	a (nm) (±1%)	T_m (±100)
$BaTiO_3$	$NaNbO_3$	0.32	0.997	0.3958	1285 C
$BaTiO_3$	$NaTaO_3$	0.55	1.019	0.3962	1440 C
$NaNbO_3$	$BaLi_{.25}Nb_{.75}O_3$	0.41	1.004	0.4110	1300 C
$BaTiO_3$	$Na_{.5}La_{.5}TiO_3$	0.35	1.008	0.3920	1625 C
$SrTiO_3$	$NaTaO_3$	0.40	0.981	0.3908	1772 C*
$SrTiO_3$	$Na_{.5}La_{.5}TiO_3$	0.25	0.984	0.3872	1766 C*
$NaNbO_3$	$BaNi_{1/3}Nb_{2/3}O_3$	0.33*	1.000	0.4014	1320 C*

* Estimated

Table I. List the compounds, measured congruent proportion, tolerance factor, lattice parameter and melting temperature for successful solid solution pairs.

Figure 6 shows a measured phase diagram for (1−x)$NaTaO_3$–x$BaTiO_3$.

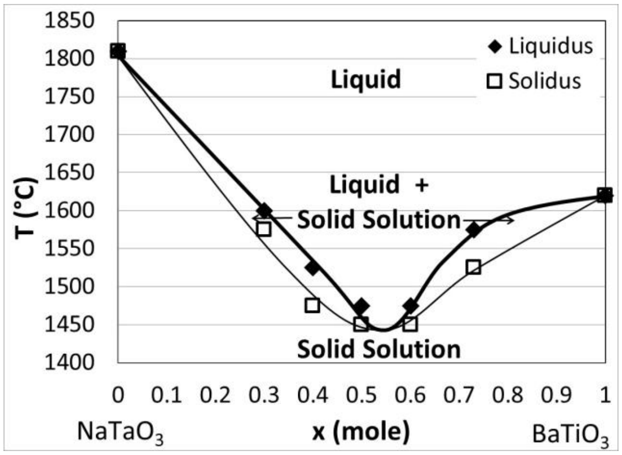


Figure 6: Pseudo-binary phase diagram of the continuous solid solution (1−x)$NaTaO_3$–x$BaTiO_3$ with an observed melting temperature minimum at $x \approx 0.55$ based on current experimental results.

Figure 7 shows a Czochralski-grown crystal from the system x$NaNbO_3$–(1−x)$BaLi_{.25}Nb_{.75}O_3$. Unfortunately growing additional crystals from these systems was not practical with existing equipment because of the hazards associated with sodium oxide vaporization, condensation, and formation of sodium hydroxide when exposed to air

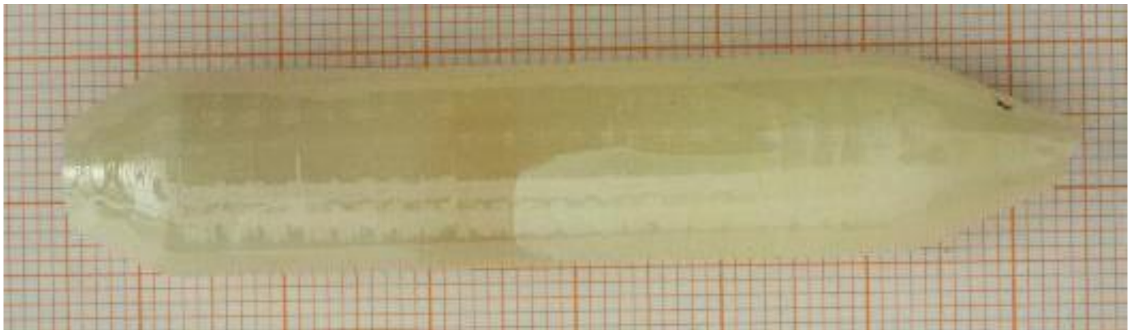
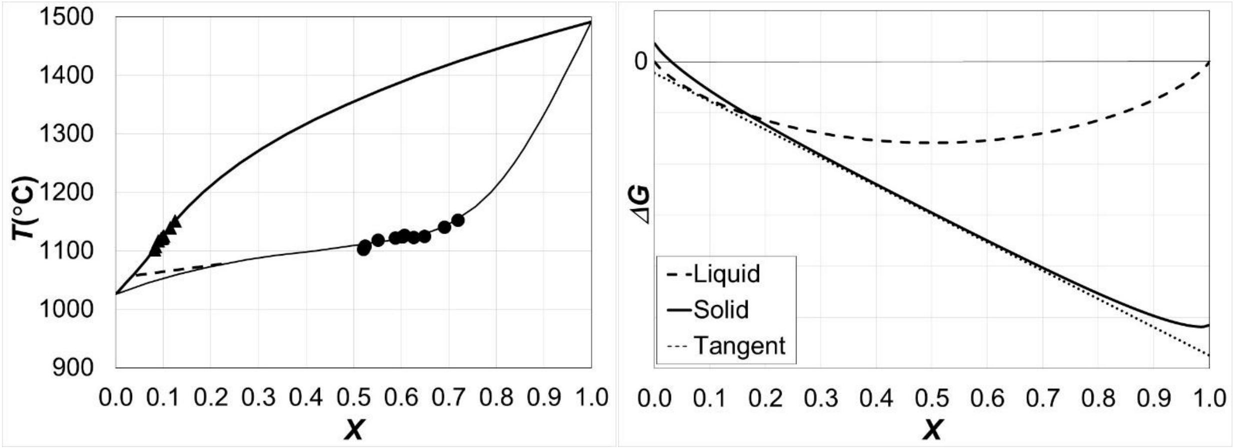


Figure 7: Initial Czochralski boule grown from the $NaNbO_3$*—*$BaLi_{.25}Nb_{.75}O_3$ *system. Three separate crystals can be seen along with clear and cloudy areas likely resulting from a second phase.*

5 Lead Zirconate Titanate (PZT) Phase Diagram

In our study of the lead zirconate titanate phase diagram[6], this system was determined to have an indifferent point very close to the lead titanate end of the phase diagram, though the tolerance factor is far from unity and no crystals from the system were cubic. A set of equations was derived that allowed the fitting of pairs of liquidus-solidus data points in Fig. 8 for a solvent consisting of PbO and $PbLiPO_4$ (PLP) to (a) a full phase diagram at a constant solute ([Zr]+[Ti]) concentration and (b) the corresponding free energy curves. The dashed line in Fig. 8a is a linear extrapolation that is believed to be to a congruent minimum indifferent point based on phase equilibrium observations in this region. There is a long flat region in the solid free energy in Fig. 8b, which is characteristic of an indifferent point and is similar to Fig. 5a. This results in a rapid change in the solidus as it swings across the phase diagram in response to a small change in the liquid composition.



(a) (b)

Figure 8. (a) Fitted solution phase diagram for lead zirconate-lead titanate with octahedral cation concentration C = [Zr]+[Ti] = 5 cation% fit to liquidus-solidus pair data. In a PbO-PLP solvent. (b) Free energy diagram for lead zirconate-lead titanate in a PLP solution with octahedral cation concentration C = [Zr]+[Ti] = 5 cation% at 1121 ℃ resulting in a crystal with $X_S = 0.52$.

6 Conclusion

Indifferent points in solid-liquid systems have been explained herein with respect to the full Gibbs' phase rule. Perovskite solid solutions with congruently melting minimum indifferent points constitute a broad and important class of compounds not previously anticipated. Given the number of successes, a full mapping of all perovskite solid solutions may yield a significant additional number of indifferent congruently melting compositions at melting temperature minima. Some of these could prove to be useful substrates for perovskite film systems.

7 Acknowledgements

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