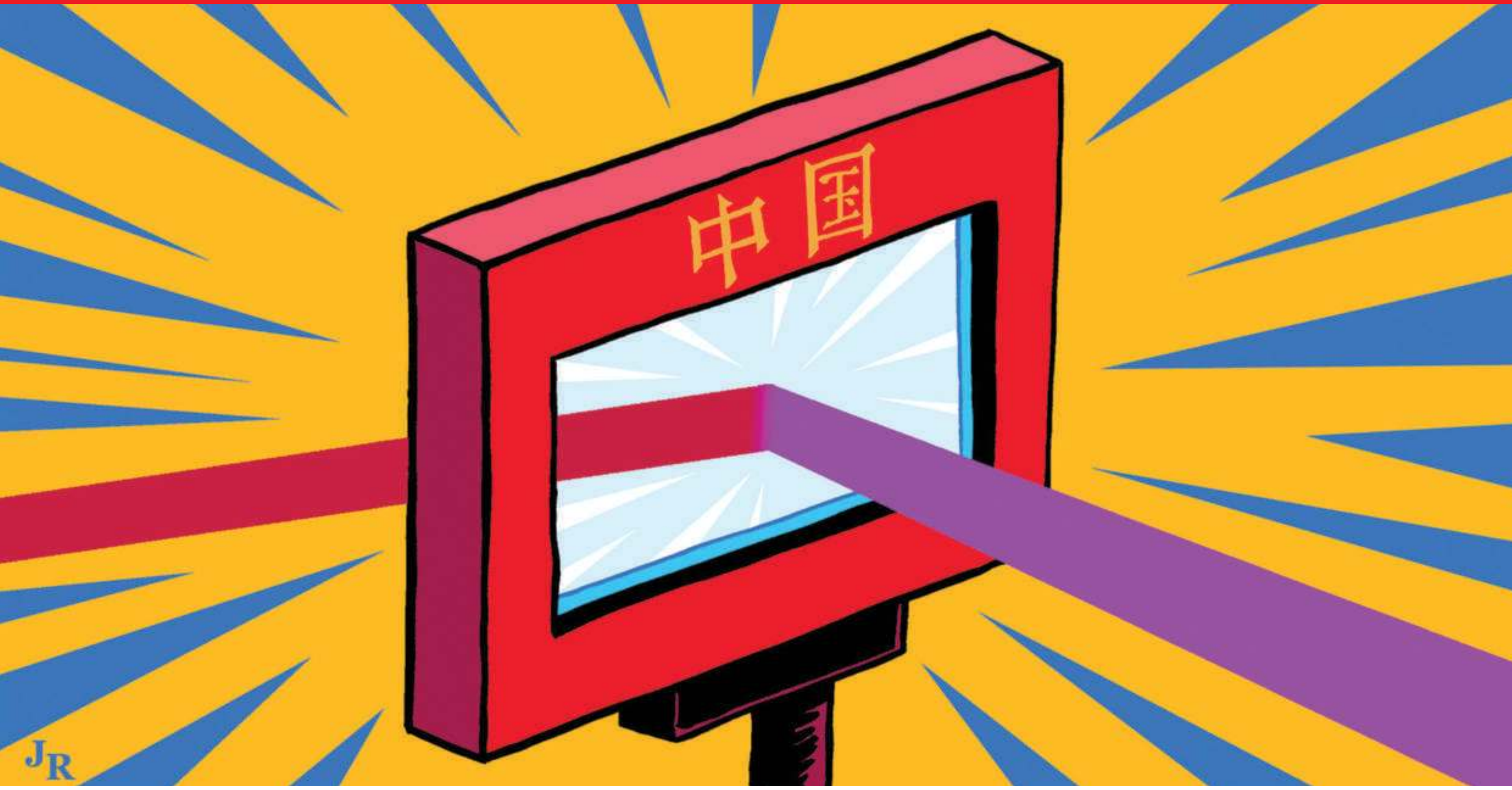


J. RIORDAN

China's crystal cache

A Chinese laboratory is the only source of a valuable crystal. **David Cyranoski** investigates why it won't share its supplies.

One of Daniel Dessau's prized possessions is a small crystal of potassium beryllium fluoroborate (KBBF). Dessau, a solid-state physicist at the University of Colorado at Boulder, uses the crystal to convert the light of a US$100,000 laser into a deep ultraviolet, a good wavelength for studying the surface of superconductors. But because the laser light gradually degrades the crystal, Dessau has to save it for special projects. "It is a beautiful crystal," he says. "It would really move the field forward — if people could get it."

But Dessau can't get any more of it. Nor can Peter Johnson, a condensed-matter physicist at Brookhaven National Laboratory in Upton, New York, who was once promised it by Chuangtian Chen, the Chinese physicist who runs the only laboratory that knows how to make the crystals. And nor can any of a host of other solid-state physicists outside China. "There has been a limited release," says Johnson. "I don't know the politics behind it."

In fact, the politics is simple. The Chinese government is squeezing the crystal for every bit of academic and, eventually, commercial potential it can yield. In October 2008, the finance ministry sidestepped traditional scientific funding channels and started throwing 180 million renminbi (US$26 million) at a three-year national project to find better ways to produce and use KBBF. China has selected a handful of groups to work with Chen's crystal, including teams studying the newest type of superconductor, called pnictides.

China's monopoly of this crystal is no fluke. At a time when materials scientists and solid-state physicists elsewhere are seeing a lack of investment, their counterparts in China are surging ahead in a wide range of materials research for much the same reasons as they did with KBBF. The nation has accumulated a great depth of crystal-growing know-how over the past three decades; it has steadfast government support; and its scientists are willing to subsume themselves in a large team effort and take on the often thankless, sometimes dangerous and always tedious trial-and-error task of synthesizing new materials. "Many great discoveries in this field come from putting things together and getting the temperature and timing just right," says Christos Panagopoulos, a materials researcher at Nanyang Technological University in Singapore. The discovery process "doesn't require genius", he says.

> "You need a lot of equipment and you need to move slowly."
> — Chuangtian Chen

KBBF's ability to shorten the wavelength, and thereby boost the frequency, of laser light is an example of 'nonlinear' optics, a field that first blossomed in the 1960s as lasers became more widespread in laboratories. Under ordinary circumstances, light passing through water, glass or any other material will perturb the atoms only slightly, so that they vibrate in sync with the light wave. As a result, light can be reflected, refracted, scattered and absorbed ad infinitum without its frequency being affected. Nonlinear effects are evident only when the light is so intense that the vibrations it causes compete with the binding forces on the atoms. When highly perturbed, as in the case of high-intensity lasers, the atoms can absorb the energy of the incoming light and re-emit the light with a frequency that is double, triple or even some higher multiple of the original. A variety of materials have been discovered that can boost laser light to frequencies that the lasers alone cannot produce, and each has a set of signature frequencies that it can achieve.

China might easily have fallen behind in this field, as it did in so many others. Just as nonlinear optics started coming into its own, China was caught up in the Cultural Revolution, a particularly dark period starting in the mid-1960s when many academics were criticized as being elitist or impractical and sent to do farm work for 're-education'.

But Chen, now a spritely 71-year-old at the Technical Institute of Physics and Chemistry in Beijing, was lucky. “The government always considered crystals important for industry,” he says. So by agreeing to the government’s request to switch from its theoretical studies to growing crystals, Chen’s lab was able to continue doing materials science throughout this period.

Crystal blueprint

In the 1970s, Chen developed a formula that set out the conditions needed for a material to generate nonlinear effects. In 1984, the formula led Chen and his team at the Fujian Institute of Research on the Structure of Matter to investigate barium borate (BaB_2O_4), which proved to be the first material able to generate an ultraviolet wavelength of close to 200 nanometres. The crystals are now widely used in femtosecond lasers, which use ultrashort bursts of infrared light to slice through materials with extreme precision, making them ideal for some types of surgery.

> “It is a matter of time before the United States becomes alarmed by this rapid reverse of the brain drain.” — Hong Ding

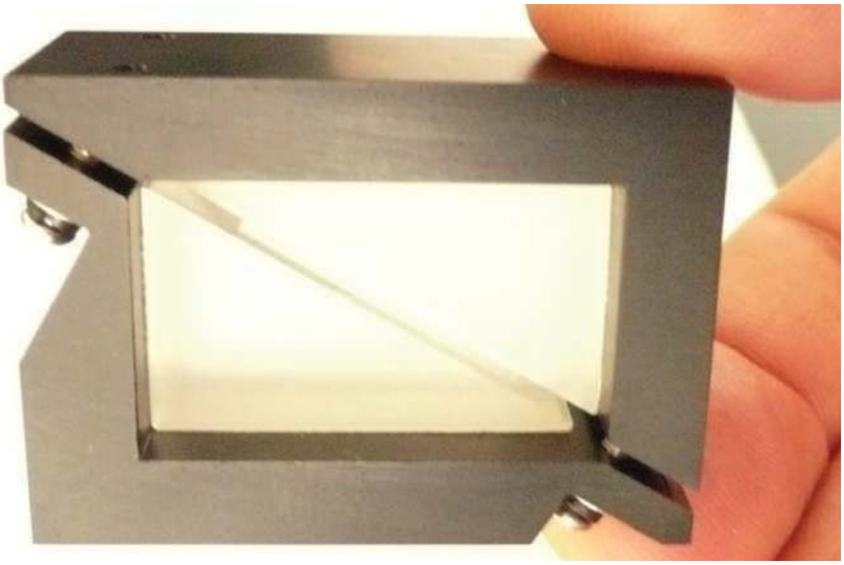
This was before China had any laws covering intellectual property, so Chen received no royalties, but his salary jumped from 87 renminbi a month to 147 renminbi a month. Chen thought he had hit the big time.

Another seminal discovery came in 1987, when Chen’s group demonstrated nonlinear optics in lithium triborate (LiB_3O_5). Engineers now use the compound to create high-powered green and near-ultraviolet lasers. As the crystals are extremely resistant to damage, they are particularly useful in applications such as welding and semiconductor manufacturing. Some 80–90% of all solid-state lasers and laser systems now use lithium triborate crystals for frequency conversion. Castech, a corporate spin-off set up by the Fujian Institute of Research on the Structure of Matter to manufacture and develop crystals for use in lasers, has been making several million US dollars a year from the compound.

But Chen and his PhD student Rukang Li were not done shortening wavelengths. Starting in 1988 on what would be a long journey, Li examined the chemistry of “hundreds, if not thousands of compounds” using Chen’s formula. “KBBF looked good,” remembers Li. Eight years later, they proved that the crystal could produce a laser of an unprecedentedly short, 184.7-nanometre wavelength[1].

However, the crystal was still not ready for practical use. KBBF grows thin and plate-like, making it difficult to cut at the angles needed in lasers. It took another seven years before a collaboration set up in the late 1990s between Chen’s group and Shuntaro Watanabe at the University of Tokyo succeeded in getting KBBF into a laser system[2].

That is when scientists really started to get excited. Exploiting the fact that the ultraviolet light from a KBBF-equipped laser has an extremely narrow frequency range, allowing it to measure the energy level of electrons in solids down to a resolution of just 360 microelectronvolts, Shik Shin from the University of Tokyo and his colleagues were able to show that the fine spacing of energy levels in certain superconductors depends on the direction in which the electrons travel through the lattice[3]. “It was the first time I could really say I was a pioneer, that I was seeing something that nobody else had seen,” says Shin.



D. CYRANOSKI

KBBF sandwich: it took Chen’s team nearly 15 years to grow KBBF and put it into a usable form.

That discovery, the first to be made with a KBBF laser, opened up investigations of many different kinds of superconductors that had been impossible before because there was no laser available that had sufficient energy resolution. Since then, Shin and Chen have co-authored more than 20 papers.

Xingjiang Zhou, of the Institute of Physics in Beijing, was also using KBBF to examine superconductors. He discovered an entirely new type of electron pairing[4] — the fragile coupling that allows the electrons to move though the lattice without resistance. One leading condensed-matter physicist, seeking a collaboration, told Zhou in an e-mail, “These are the highest quality data that I have ever seen.”

Clamp down

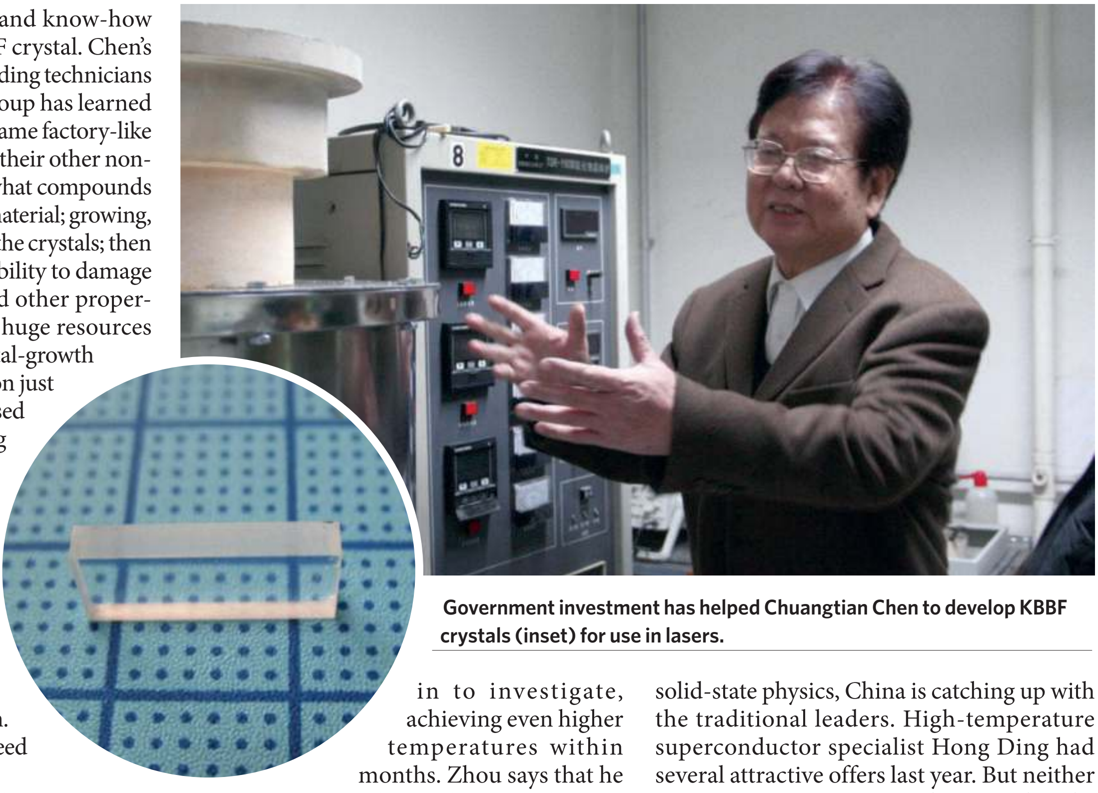
By 2008, thanks to these and other stories, requests for KBBF crystals were rolling in to Chen’s institute. And that, in turn, caught the attention of the institute’s parent organization, the Chinese Academy of Sciences, which told Chen not to distribute the crystal any further without its permission.

Chen is planning to use his share of the government’s 180 million renminbi to install more large ovens in which to grow crystals. This will allow his institute to ramp up from the 15 KBBF-crystal devices it made in 2008 to 50 in 2009, and then 100 in 2010. His team will also be looking for ways to produce better KBBF crystals. Thicker crystals allow for a more powerful laser and make possible hugely profitable applications, such as replacing the bulky exciplex lasers, another type of ultraviolet laser used in surgery and in semiconductor lithography. Chen, who is discussing the possibility of technology transfer with two companies in Beijing, hopes to find some commercial applications within three years.

Seven other projects will be aiming to create advanced versions of photoemission spectrometers, Raman scattering spectrometers and scanning tunnelling microscopy. Zhou will receive 20 million renminbi to head two of the projects. In one, he plans to make a tunable KBBF laser that can analyse a wider variety of materials — at present, these lasers need to be set at one frequency. In the other project, he will develop a KBBF-based laser to look at the spin of electrons in superconductors. Until now, research has focused on momentum and energy.

Chen is reluctant to talk about the terms of the government’s restriction. He says he would like to share the crystals with people in other countries, but first has to meet demand from Chinese KBBF projects. “The government gives me so much money,” he says.

Crystal growers in other countries are unlikely to be able to fill the gap, mainly because of the



C. CHEN

C. CHEN

Government investment has helped Chuangtian Chen to develop KBBF crystals (inset) for use in lasers.

time, people, infrastructure and know-how needed to create a good KBBF crystal. Chen's laboratory has 70 people, including technicians and some 30 students. The group has learned how to make KBBF using the same factory-like process they use to develop all their other non-linear crystals — calculating what compounds might work; synthesizing the material; growing, cutting, polishing and coating the crystals; then testing them for their vulnerability to damage by intense laser radiation and other properties. Chen's group has put in huge resources for infrastructure such as crystal-growth ovens. It has spent US$7 million just on platinum for the crucibles used to grind up the crystals during the production process. Even now, with the KBBF process honed, it takes 3 months and about US$20,000 to produce just one KBBF device. Bruce Chai, president of Crystal Photonics in Sanford, Florida, says that anyone trying to duplicate the work would easily burn through US$10 million. "And they wouldn't be guaranteed success," he adds.

Perhaps the greatest obstacle to making a KBBF crystal is the beryllium it contains, which can cause pneumonia-like symptoms and cancer if inhaled. China has strict policies regarding its use, says Chen, but researchers are allowed to work with the element if they have the right infrastructure. "You need a lot of equipment and you need to move slowly," he says. In other countries, the restrictions are more severe. In the United States, for example, lawsuits over beryllium poisoning led the Department of Energy to hunt down and remove even trace amounts from national laboratories.

"The demand for KBBF is spurring researchers to look for other fluoroborates that present fewer challenges," says Vincent Fratello, vice-president of research and development at Integrated Photonics in Hillsborough, New Jersey. But until that search bears fruit, the benefits of Chen's dogged pursuit will stay in China.

KBBF is a special case, but it illustrates China's growing strength in materials science. Fratello, himself a solid-state physicist, says that he has been impressed by the "sheer volume of work that comes out of China".

Fudan University's Dongyuan Zhao has more citations than anyone in the field of mesoporous materials (and the second highest number of citations per article). Last year, after Japanese researchers discovered high-temperature superconductivity in iron-based arsenic oxides, several Chinese groups jumped in to investigate, achieving even higher temperatures within months. Zhou says that he intends use the KBBF laser to take arsenic oxide studies even further.

Material leads

Some researchers see China as following the lead of Japan, where significant investment in materials sciences in the 1990s has been paying off in discoveries such as the superconductor magnesium diboride[5]. Panagopoulos, who last year moved from the University of Cambridge, UK, to Singapore to continue his research on functional materials, says he tried and failed to get Cambridge to bulk up its materials-synthesis capacities in the late 1990s. "We wait for Japan, and now China, to make it," he says — a sure recipe for mediocrity. "The person who has the greatest knowledge of everything about a material is the one who is distributing it to everyone," says Panagopolous.

> "Many great discoveries in this field come from putting things together and getting the temperature and timing just right."
> — Christos Panagopoulos

There is also concern in the United States. "It is a well-known fact that the support for basic research on crystal growth is literally gone in the United States," says Chai. This spring, the US National Academy of Sciences will release a report on the health of, and future opportunities for, new materials and crystal-growth research.

Even in trendier, related fields such as solid-state physics, China is catching up with the traditional leaders. High-temperature superconductor specialist Hong Ding had several attractive offers last year. But neither Boston University in Massachusetts, where he had been for a decade, nor any other institution could match the deal he was offered at the Institute of Physics in Beijing. "It is a matter of time before the United States becomes alarmed by this rapid reverse of the brain drain," says Ding. Dessau, who tried and failed to recruit Ding, says that "10 years ago it would have been unheard of [for a Chinese person to turn down a position in the United States]. But I wouldn't be surprised if the trend continues."

In fact, many credit the hard-working, selfless laboratory worker for some of China's success, and Japan's before it, in rapidly increasing their capabilities to synthesize materials. Fratello says that Chinese groups "tend to excel at studies that require patience and looking at a lot of different systems". But in materials sciences, labour-intensive work can often be the most productive. "That is, after all, how you discover new materials," Fratello says. ■

David Cyranoski is *Nature*'s Asia-Pacific correspondent.

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