Crystal growth in China

By M.H. Jiang

Crystal growth in ancient China

Crystal growth in China has a long history, going back more than one thousand years. A book written by Cheng Daichang in the Song Dynasty explains that: "Salt becomes brine, exposing under the hot sun; square seals formed, white and lovely; first small then larger; some tens of seals train together." This is exactly the method of growing salt crystals from supersaturated solution by evaporation process. In fact, this kind of crystal growth method had appeared much earlier than it was recorded. The Chinese character of brine means salts in early time, and its pictograph symbolizes a birdseye view of brine evaporating: The square seals of salt crystals crystallized from regularly arranged salt pan (Fig. 1).

The refining process of vermilion (or cinnabar, *i.e.*, mercury sulfide, or synthetic vermilion) is another practical example of crystal growth in ancient China. In a book written by Hu Yan in the Tang Dynasty, the refining process has been described in detail. The Chinese character of pellet has a somewhat mysterious meaning in ancient China. For a long time, pellets had been refined and used as a kind of medicine for longevity. It can also be seen from the pictograph of pellet that the minerals were placed in the furnace for refining into pellet (Fig. 2).

FIGURE 3

Fig. 3 shows the operation of cinnabar refining. The operator in this figure (he could be called an ancient Chinese crystal grower) was rubbing the cover of the furnace with a water-dipped brush to cool it down, which was beneficial to the formation of large crystal grains. This is the earliest CVD technique. In China, such a technique was matured at least in the Tang Dynasty of 1,300 years ago.

The development of modern crystal growth

Chinese modern crystal growth started rather late but is developing quickly. It can be summarized in four stages over the past 30 years. By the end of the 1950s, Chinese crystal growth had undergone a general spreading status in some institutions. For example, the Verneuil's for the growth of gem ruby, hydrothermal growth of quartz, Kyropoulos growth of alkaline halide, CZ growth of semiconductor germanium single crystals, aqueous solution growth of Rochelle salt, flux growth of YIG and other ferrites — all of these crystals were developed during that period. The characteristic of this stage is the overspreading of various kinds of growth techniques, laying the foundation for the further development of modern crystal growth.

The 1960s was a period of verification and improvement. The emerging of laser techniques during this time brought forth in our country the growth of laser ruby and studies to perfect it. The research developed quickly. Significantly, piezoelectric crystals such as ADP,

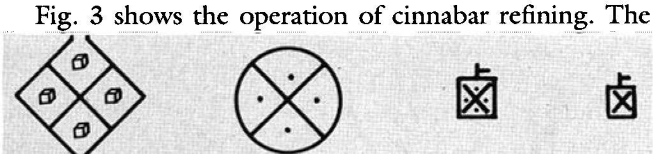


FIGURE 1: Development of Chinese character "鹵" (brine).

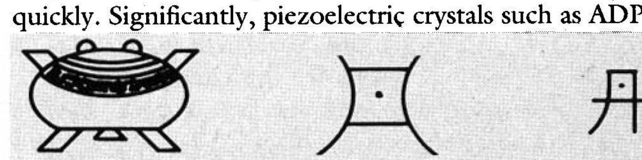


FIGURE 2: Development of Chinese character "丹" (pellet).

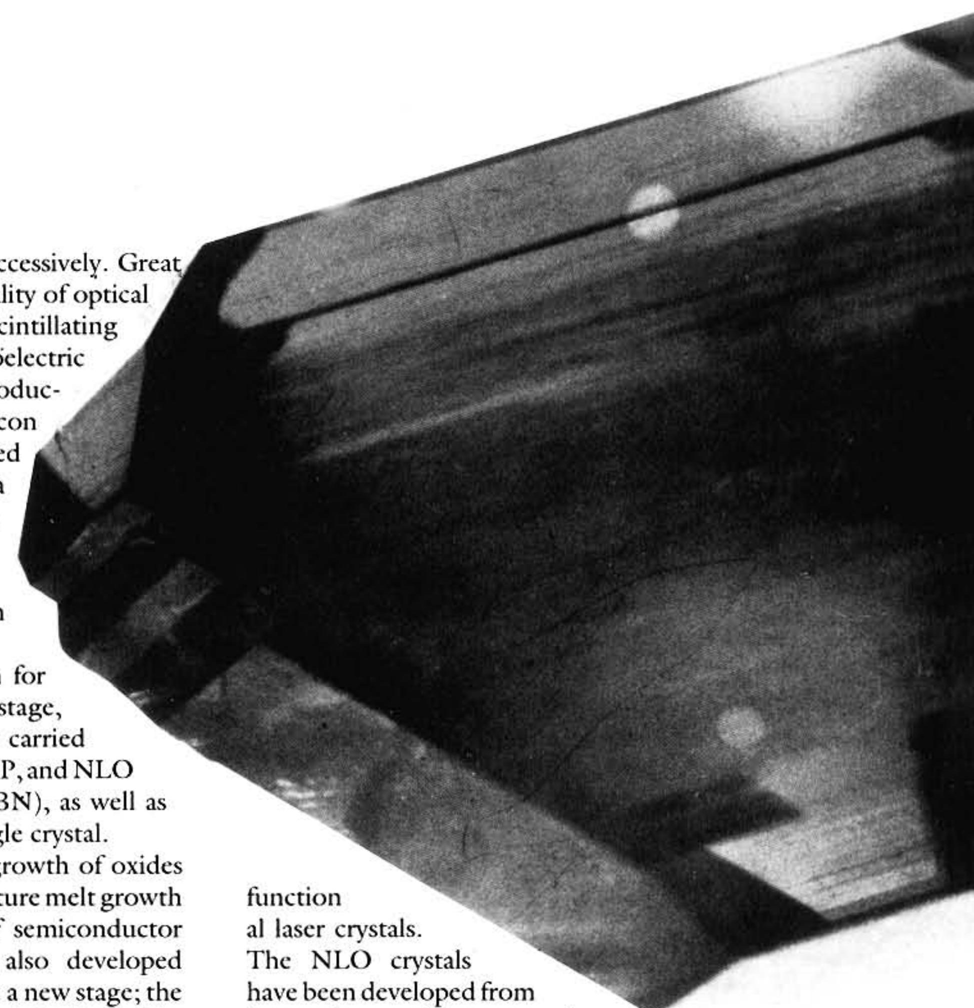
KDP, and LSH have been developed successively. Great efforts have gone into improving the quality of optical crystals like NaCl, CaF_2, LiF, and scintillating crystals such as NaI (Tl), etc. The piezoelectric quartz was put into small batches of production. Semiconductor materials (*e.g.*, silicon and III-V compounds) were developed initially. In addition, the synthesis of mica and diamond have achieved great success. Some universities and colleges set up the specialties related to crystal growth during this period and began to train people in crystal growth.

The 1970s saw the further expansion for crystal growth in China. During this stage, concentrated and extensive studies were carried out on some laser crystals such as YAG, YAP, and NLO crystals (*e.g.*, $LiNbO_3$, $LiTa0_3$, BNN, SBN), as well as the magnetic bubble substrate GGG single crystal.

Investigations into the single crystal growth of oxides have laid the foundation for high temperature melt growth in China. The single crystal growth of semiconductor materials silicon and gallium arsenic also developed rapidly. The solution growth also entered a new stage; the representative crystals in this respect are DKDP, $-LiI0_3$, TGS family. Besides, CVD and LPE techniques were established continuously. At this stage, people began to pay attention to the exploration of new crystal materials and the studies on crystal growth theories. The anion group theory was proposed at this time.

Chinese crystal growth achieved great progress in the 1980s. Crystal materials research has been carried out independently and has gone beyond the simple point of imitation. As a result, a group of new NLO crystals such as BBO, LAP and BGO have been developed and have attracted foreign attention.

As crystal growth research continues and the quality and growth techniques of crystals improves, some useful crystals with wide ranges of applications have entered the international markets. Among them, BBO, BGO, and KTP have won high prestige. In addition, crystal varieties have increased. For example, the laser crystals have been extended to tunable, color center, self-activated, and multi-functional laser crystals. The NLO crystals have been developed from inorganic materials to organic materials, and even to inorganic-organic complex materials. And the inorganic NLO crystal materials have entered the international advanced list.



Research institutes and academic organizations

According to incomplete statistics, there are about 70 institutions and a team of 1,000 people engaged in crystal growth research in China. They are at universities (colleges), institutes affiliated with the Chinese Academy of Sciences (CAS), and different industrial departments. About 80% of them are along the eastern coast area. The best known include:

Universities

Shandong University—Institute of Crystal Materials, Jinan.

Nanjing University—Institute of Solid State Physics, Nanjing.

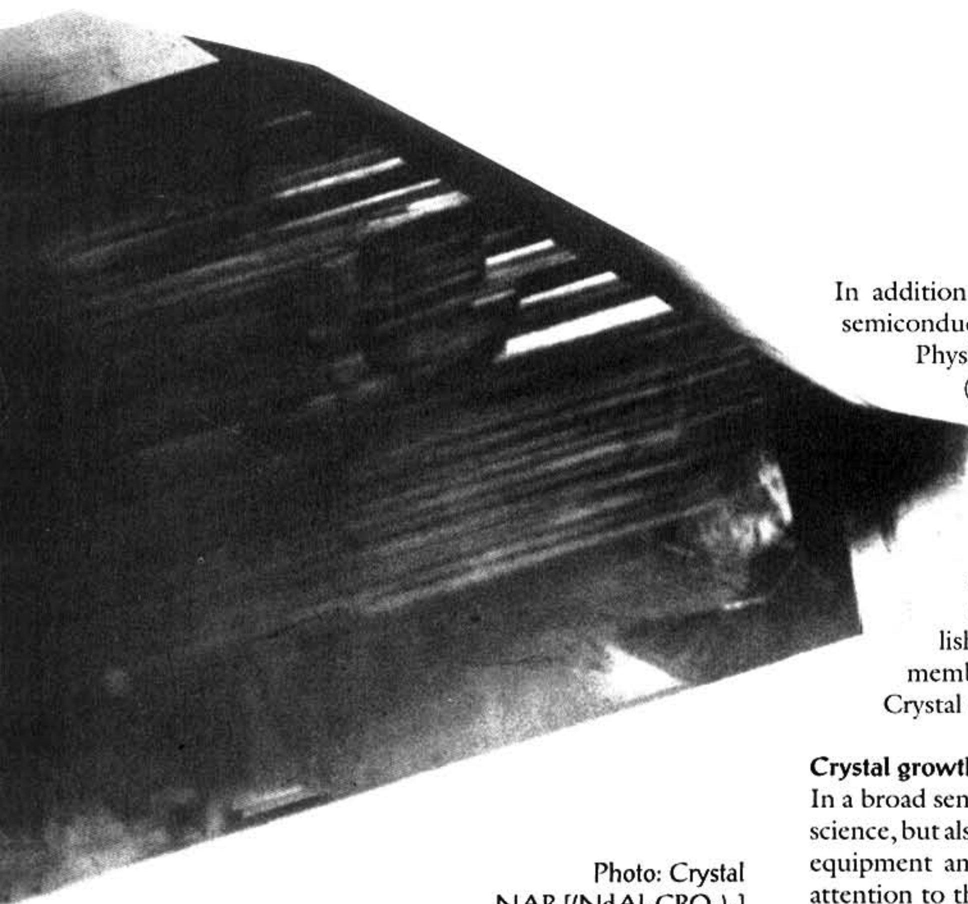


Photo: Crystal NAB [$(NdAl_3CBO_3)_4$]

Institutes (CAS)

Institute of Physics, Beijing.
Fujian Institute of Research on the Structure of Matter, Fuzhou.
Shanghai Institute of Ceramics, Shanghai.
Shanghai Institute of Optical and Fine Mechanics, Shanghai. B.

Industrial departments

Research Institute of Synthetic Crystals, Beijing.
North China Research Institute of Opto-Electronics, Beijing.
Southwest Institute of Technological Physics, Chengdu.

At present, the academic organization of crystal growth in China is mainly the Special Committee of Crystal Growth and Crystal Materials affiliated with the Chinese Ceramics Society (CCS). The Chinese Conference on Crystal Growth (CCCG) sponsored by CCS meets every three years. Eight sessions have been held since 1962.

In addition, there are several special committees on semiconductors affiliated with the Chinese Society of Physics (CSP), Chinese Society of Metals (CSM), and Chinese Society of Electronics (CSE) that have sponsored numerous academic conferences.

Academic exchanges related to crystal and semiconductor materials are strengthening gradually. To extend these interactions internationally, the Chinese Organization of Crystal Growth (COCG) will be established in the near future and will become a member of the International Organization of Crystal Growth (IOCG).

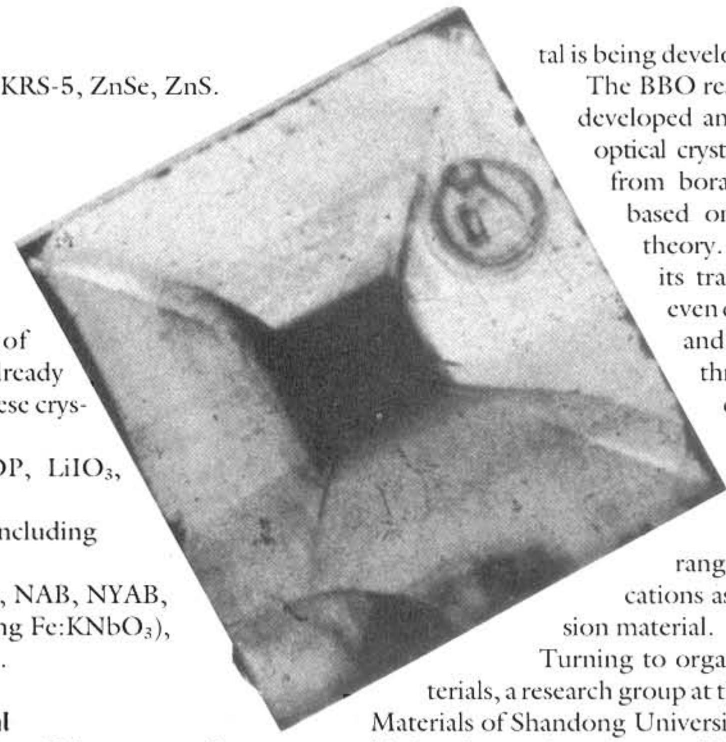
Crystal growth techniques

In a broad sense, crystal growth is not only a discipline of science, but also a matter of art that relies both on advanced equipment and skilled personnel. China has paid great attention to the growth of useful crystals for science and technology, and now has a large group of first-rate, skillful, and devoted crystal growth experts who have mastered various growth techniques. By using different kinds of growth apparatus (most of which they make themselves), they have grown and are growing many good quality and useful crystal materials. They also study crystal growth conditions and fundamental theories to further the growth technologies. Through their efforts, almost all the important crystal materials have been synthesized and grown out successfully (see Table 1).

Table 1. Some synthetic crystals

Laser crystals
Nd:YAG, Nd:YAP, $LiYF_4$, $Ti:Al_2O_3$, $Cr:BeAl_2O_3$, NdPP, NAB, NYAB, $KMgF_3$, and color-center crystals
Nonlinear optical crystals
DKP family, BBO, KTP, LBO, BNN, $KNbO_3$, $LiNbO_3$, SBN, KNSBN, BSO, LAP, $BaTiO_3$, Tl_3AsSe_3, organic crystals
Semiconductor crystals
Ge, Si, III-V and II-VI compounds
Piezo-electro, acousto-optic crystals
quartz, $LiTaO_3$, $Li_2B_4O_7$, TeO_2, $PbMoO_4$

Optical crystals
  $NaC1$, $KC1$, CaF_2, BaF_2, MgF_2, KRS-5, ZnSe, ZnS.
Scintillating crystals
  BGO, NaI(T1), $ZnWO_4$, CsI
Gems
  Color gems, $CZZrO_2$), GGG.
Superhard crystals
  Diamond, CBN



The sizes and qualities of some of the crystals listed in Table 1 have already reached the international level. These crystals are:

- Solution growth: DKDP, KDP, $LiIO_3$, Urea;
- Melt growth: BGO, $LiNbO_3$ (including MgO: $LiNbO_3$);
- Flux growth: BBO, LBO, KTP, NAB, NYAB, $BaTiO_3$, $KNbO_3$ (including Fe:$KNbO_3$), SBN (including KNSBN).

Exploration of new crystal material

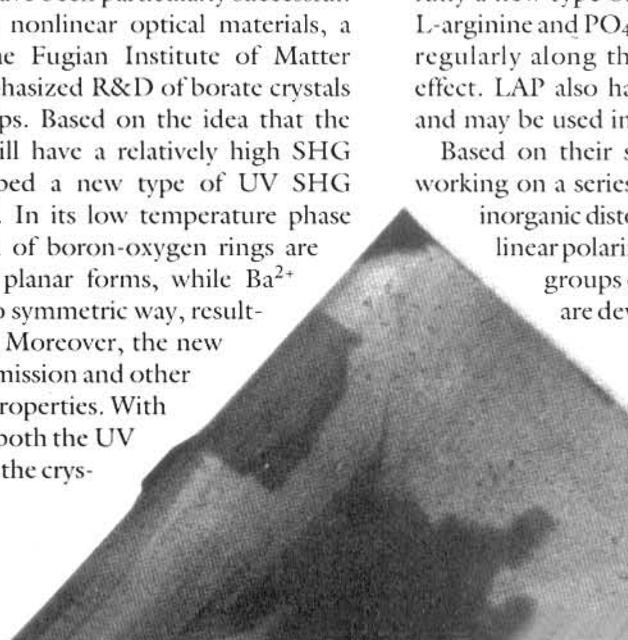
By combining theory with practice, Chinese researchers have been exploring useful new crystal materials systematically over the past decade. Their work involves theoretical modeling, chemical synthesis, crystal growth, and experimental physics. Efforts in the area of nonlinear optical (NLO) materials have been particularly successful.

In exploring inorganic nonlinear optical materials, a group of scientists at the Fugian Institute of Matter Structures (CAS) has emphasized R&D of borate crystals possessing $(B_3O_6)^{-3}$ groups. Based on the idea that the planar conjugate orbit will have a relatively high SHG effect, they have developed a new type of UV SHG crystal—BaB_2O_4 (BBO). In its low temperature phase structure, the orientation of boron-oxygen rings are identical and arrange in planar forms, while Ba^{2+} distributes in a non-centro symmetric way, resulting in a high SHG effect. Moreover, the new crystal has good UV transmission and other useful physical-chemical properties. With promising applications in both the UV and near-infrared regions, the crystal is being developed for practical use.

The BBO research group has also developed another new nonlinear optical crystal—LiB_3O_5 (LBO)—from borate oxide compound based on their anion group theory. Compared to BBO, its transmission penetrates even deeper into the region and its high damage threshold can make up certain disadvantages of BBO. Thus, LBO is a promising new NLO crystal material with a wide range of anticipated applications as a frequency conversion material.

Turning to organic NLO crystal materials, a research group at the Institute of Crystal Materials of Shandong University focused on studies combining inorganic groups with organic groups to synthesize new organic NLO crystals. After overcoming many difficulties due to the mutual constraint caused by the nonlinear effect of the conjugate groups and the UV transmission properties, this group has grown successfully a new type of UV SHG crystal material—LAP. The L-arginine and PO_4 in its structure oriented and arrayed regularly along the b axis, thus giving LAP a high SHG effect. LAP also has a high damage threshold (15 GW) and may be used in laser fusion.

Based on their success with LAP, this group is now working on a series of compounds that will combine the inorganic distorted polyhedron possessing strong nonlinear polarizability with the assymmetric conjugate groups of organic materials (that is to say, they are developing a series of new crystal materials that possess the characteristics both of organic and inorganic NLO crystals). This work has opened a new NLO crystal material field never before ex-



plored: organometallic complexes. These complexes mainly have the ions of transition metals as the center of the ligand and the assymmetric organic conjugate molecules (or with the other groups together) as the ligands.

At this point, the research group has found more than 10 new crystal materials such as allythiourea cadmium chloride (ATCC) and thiosemicarbazide cadmium chloride monohydrate (TSCCC) with SHG effect as high as that of urea or even corresponding to that of KTP. Based on the data from the related measurements, it has been shown that all of these crystals are potential NLO crystal materials with useful properties.

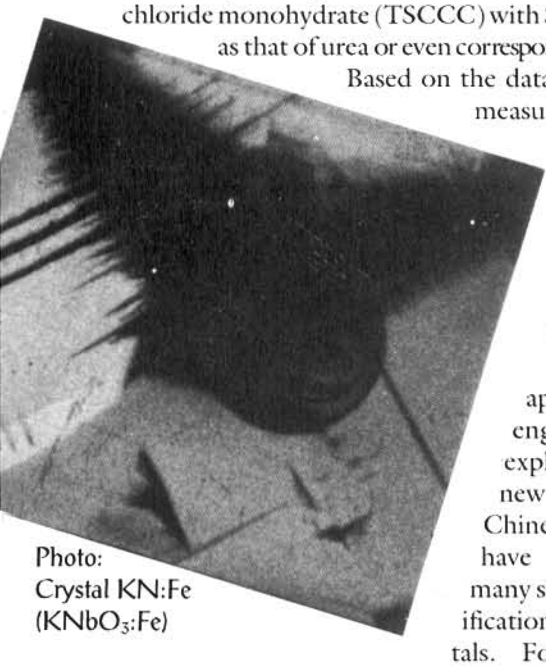
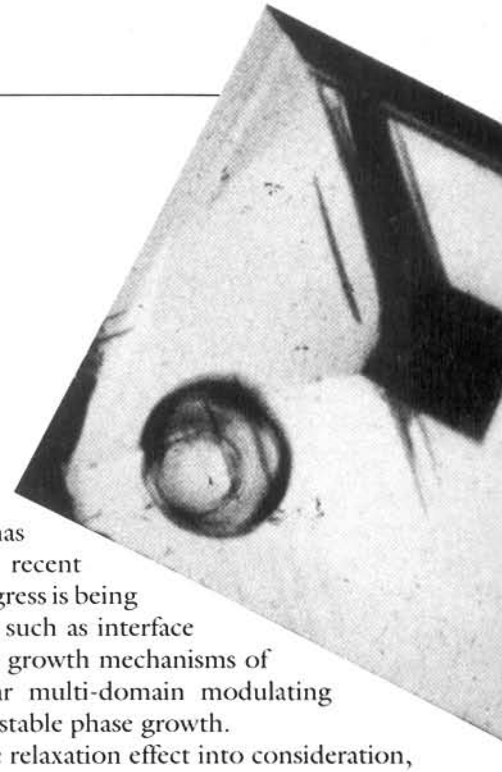


Photo:
Crystal KN:Fe
($KNbO_3$:Fe)

In addition to applying molecular engineering to the exploration of useful new materials, the Chinese crystal growers have also carried out many studies in the modification of existing crystals. For example, the highly doped $LiNbO_3$ (MgO:$LiNbO_3$) has been developed by the Southwest Institute of Technological Physics. This doping has raised the damage threshold of $LiNbO_3$ two orders of magnitude higher, thus expanding potential applications of this crystal. Their achievement has attracted the attention of foreign colleagues. Other important modifications are: TGS and its doped series (*e.g.*, ATGSAs, ATGSP); the promising photorefractive materials—modified SBN series (*e.g.*, KNSBN); the multifunctional laser crystal materials—self-SHG, self-Q-switching, and self-mode-locking laser crystals (*e.g.*, NYAB).

Fundamental research

Fundamental research in crystal growth began later than the studies of crystal growth techniques, but the development in this respect has quite rapid during recent years. Some real progress is being made in many areas such as interface kinetics, defects and growth mechanisms of real crystals, laminar multi-domain modulating structures, and metastable phase growth.



Taking the surface relaxation effect into consideration, researchers at the Institute of Solid State Physics of Nanjing University have suggested a new argument that the

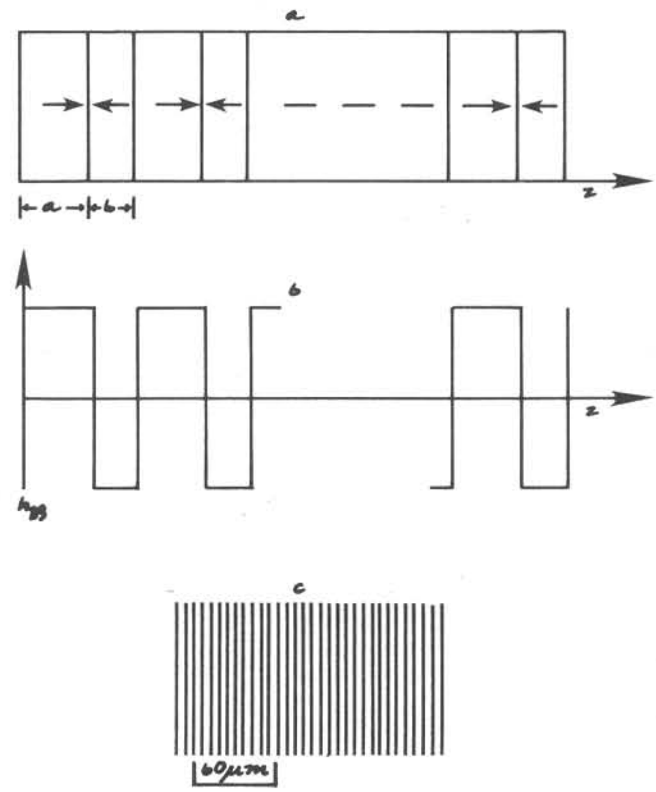


FIGURE 4: Acoustic superlattice of $LiNbO_3$—a single crystal with periodic laminar ferroelectric domain structure (PLFEDS). (a) Schematic diagram of PLFEDS (the arrows indicate the directions of the spontaneous polarization), (b) Corresponding piezoelectric coefficient as a periodic function of Z, (c) Optical photomicrograph of PLFEDS in $LiNbO_3$ revealed by etching, lamellae perpendicular to Z-axis.

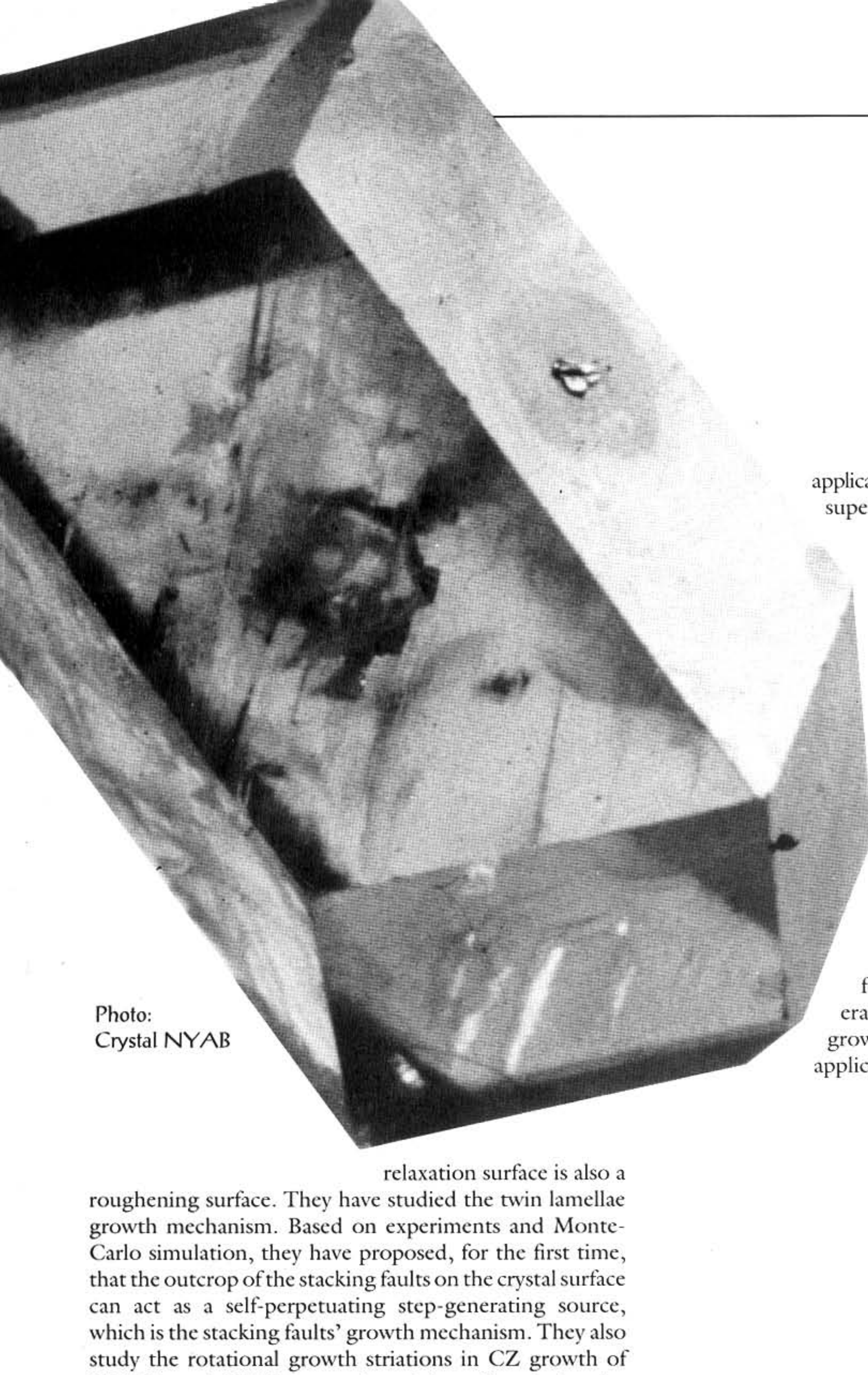


Photo:
Crystal NYAB

relaxation surface is also a roughening surface. They have studied the twin lamellae growth mechanism. Based on experiments and Monte-Carlo simulation, they have proposed, for the first time, that the outcrop of the stacking faults on the crystal surface can act as a self-perpetuating step-generating source, which is the stacking faults' growth mechanism. They also study the rotational growth striations in CZ growth of $LiNbO_3$ and $LiTaO_3$ crystals and have found that the solute concentration gradient that caused the formation of the striations can also induce the ferroelectric domain in the crystals. On the basis of this discovery, they have grown successfully the laminar multi-domain crystals with periodical modulating structures, observed their enhanced SHG effect, and realized primarily the quasi-phase matching. Recently, they have suggested the acoustic superlattice concepts (Fig.4) for the first time and they have developed applications for such modulating structures in supersonic and acousto-optic techniques.

Toward the future

Crystal growth in China has a long history. Modern crystal growth has been developing rapidly and Chinese researchers are recognized among the international crystal growth community.

China has a large team of crystal growers. Chinese crystal growth techniques have reached a high level, with exploration into new crystal materials yielding significant results. Fundamental research is developing extensively. The Chinese crystal growth community now hopes to augment efforts at academic exchanges and cooperation with the international crystal growth community, as well as expanding applications to industry.

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