无机材料研究

RESEARCH IN INORGANIC MATERIALS

1979

中国科学院上海硅酸盐研究所

前　言

中国科学院上海硅酸盐研究所是从事无机非金属材料科学研究的专业研究单位，它的前身是中国科学院工学实验馆窑业组，后为上海冶金陶瓷研究所窑业室，一九六〇年初正式成立了中国科学院上海硅酸盐研究所。

研究所目前有人工单晶、特种玻璃、电子陶瓷、结构陶瓷、无机涂层等六个研究室；电子、机械设计和化学分析、结构分析等三个技术室，还有试验、机修二个附属工厂。

研究所的主要研究方向和任务是：以新型无机非金属材料为对象，开展材料的物理、化学、工艺的研究，发展新材料及其在新技术中的应用，丰富和发展材料科学。

这里我们从一九六〇年建所以来开展的研究工作中，选择部分研究论文报告摘要汇编成这本册子，以满足我国社会主义现代化建设中日益增多的科学交流的需要。

PREFACE

The Shanghai Institute of Ceramics is a research unit under the direction of Academia Sinica dealing with the investigation of materials science for inorganic nonmetallic materials. Formerly, it began as a small ceramic group in the Experimental Laboratory of Technology, Academia Sinica, and then became Department of Ceramics of the Shanghai Institute of Metallurgy and Ceramics. At the beginning of 1960, the present institute was formally established.

In this institute, there are now six research laboratories working on synthetic single crystals, special glasses, electronic ceramics, structural ceramics, and inorganic coating materials as well as three technical laboratories on electronics, mechanical design, chemical-instrumental analysis and structural (including microstructural) analysis. There are a pilot plant and a machine shop in addition.

This institute devotes mainly on the study of the physics, chemistry and technology of inorganic nonmetallic materials with the aim to develop new materials exploiting their usage as new devices in modern technology as well as to make contributions in the realm of materials science.

This booklet with selected short notes of some of the works done since the establishment of the Institute may serve partly the purpose of increased scientific exchange that is flourishing during the socialist construction of our country for modernization.

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A Brief Account of Some of the Works Carried Out at the Shanghai Institute of Ceramics, Academia Sinica

Director Yan Dongseng (Yen Tung-sheng)

The Shanghai Institute of Ceramics is a research unit under the direction of the Chinese Academy of Sciences. It had an early start since the foundation of the People's Republic of China. A small unit named as the Experimental Laboratory of Technology was reinstated shortly after liberation in which there were a handful of people working on problems relating to glasses and ceramics in close connection with the restoration of our national economy. A few years later, in 1954, this Laboratory changed her name and began to be called as the Shanghai Institute of Metallurgy and Ceramics, and our group of ceramic research personal had increased and founded the Department of Ceramics with more than forty persons. The works we did at that period were concerned with such problems as on high voltage electrical porcelains, alumina ceramics, fine chinese porcelain, industrial glasses, refractory materials and inorganic coating materials etc. At the beginning of 1960, the Academy decided to split the Institute of Metallurgy and Ceramics into two separate Institutes with ours named as The Institute of Ceramic Chemistry and Technology, which may be translated in short as "The Shanghai Institute of Ceramics, Academia Sinica".

Gradually, six research laboratories have been successively organized. They are the laboratories on single crystal growth, special glasses, electronic ceramics, structural ceramics and inorganic coating materials and are facilitated by three technical laboratories, mechanical design, chemical-instrumental analysis and structural (including

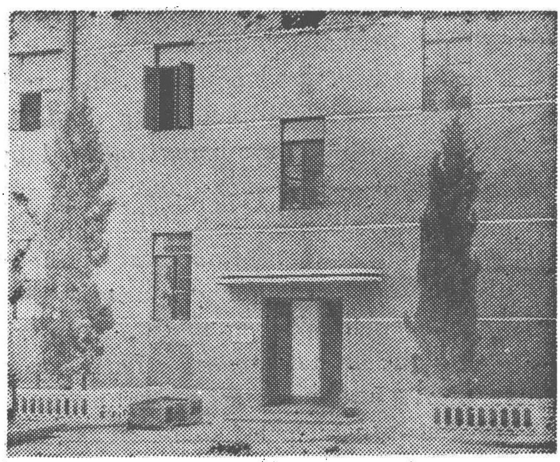

Fig. 1. The side entrance of main research building (Built in 1934)

microstructural) analysis. There are a pilot plant and a machine shop in addition. At present, more than 400 scientific and technical staffs are working in the institute. (Fig 1 and Fig 2)

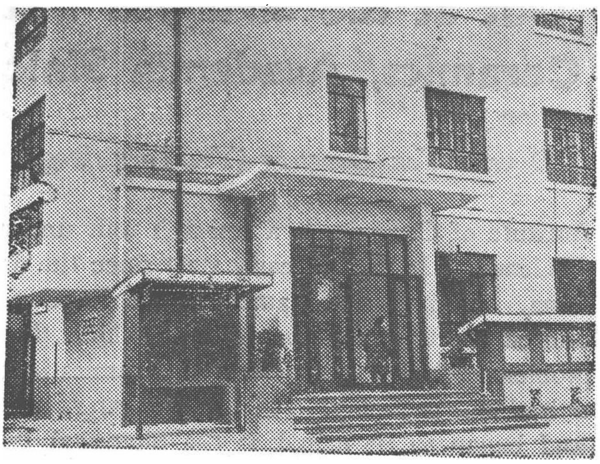

Fig. 2. The main entrance of new building (Built in 1962)

This institute devotes mainly on the study of the science and technology of inorganic nonmetallic materials with the aim to develop new materials. Considerable attention had also been paid in the realm of materials science. But these type of work was interrupted due to the interference of the "gang of four". After clearly up the fallacies spread by them, we have already paid effort to direct our work on more fundamental basis with the hope that its weight will be increased in the near future so as to serve the needs of the "four modernization" of our country on a more sound basis. In the following a brief account of some of the works that have been done or are still going on in our Institute will be given.

We have two laboratories working on single crystal growth. In one of them, we have studied for some years on the growth of synthetic mica, the synthesis of large diamond crystals under high temperature and high pressure conditions, and the growth of quartz crystals under hydrothermal conditions.

As you know, mica is a layer-structured mineral with a rather complex composition. The type of mica studied is fluorophlogopite $KMg_3(AlSi_3O_{10})F_2$ with the OH-ion commonly occurring in natural mica being replaced by fluoride ion. The problem that we have tried to attack is to grow large single crystals with high yield and low defect concentrations. We decided to use the Stockbarger technique by introducing well aligned seed crystals at the bottom part of the crucible, while on top of them were charged with powdery mica of high purity. The difficulty lies in the fact that the melt is easily supercooled, owing to the complexity of its components, which leads to imperfections in the crystals grown. These are overcome by lowering the temperature extremely slowly and now large mica crystals of 60–100 × 100 mm in size can be grown in booklet form, which can be cleaved into very thin sheets of almost perfect appearance. (Fig. 3, Fig. 4) These synthetic mica have been tested to have better transparency, be able to stand much higher temperature without decomposition and with similar electrical properties as compared with natural mica materials.

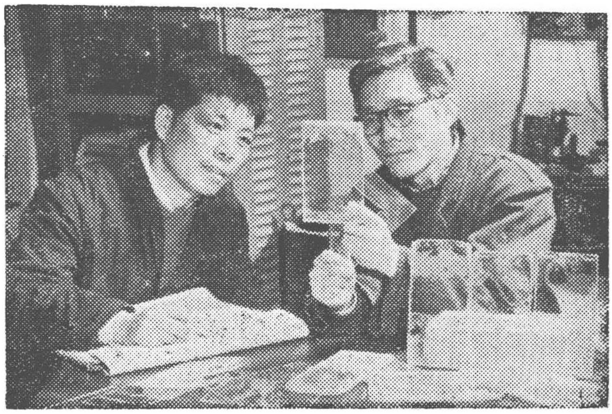

Fig. 3. Synthetic fluorophlogopite in booklet form which can be cleaved

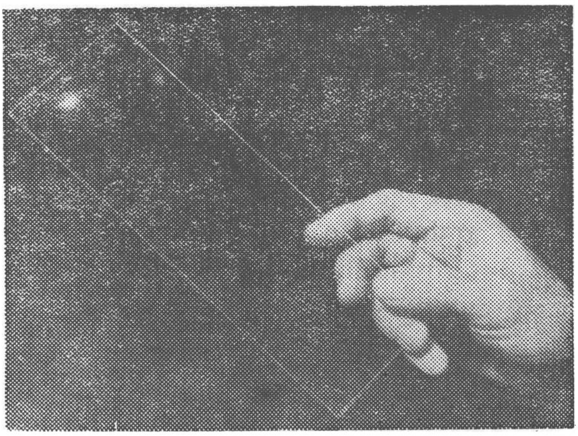

Fig. 4. Cleaved thin sheet synthetic mica with almost perfect appearance

The research on artificial diamond has attracted us not only from the practical point of view and also in the study of crystal growth under high temperature and very high pressure conditions. We have designed and built in 1962 our own high pressure apparatus with six anvils driven simultaneously by one power source. Experiments carried out in this setup through these years have proved that it had a better synchronization in performance and was rather steady in pressure maintenance. Both of which are essential for the growth of large diamond crystals. With the experience gained in these years, we have built a much larger press of 5000 ton capacity with similar design about two years ago. (Fig 5) Using these equipments, some works have been done including such topics as:

(1) The effect of temperature and pressure gradients on the growth of large grained diamonds;

(2) The nucleation and growth of artificial diamond in the graphite-diamond system;

(3) On the mechanism of graphite to diamond transformation in the presence of molten metal;

(4) The effect of metal catalysts used on the growth of diamond, etc.

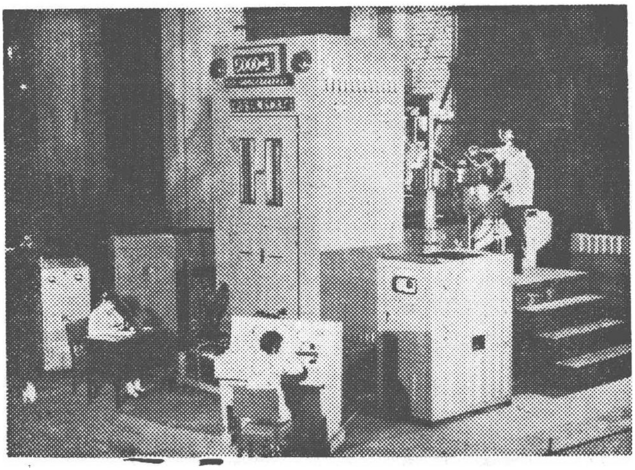

Fig. 5. A general view of the 5000 ton capacity press with its control panels

From these investigations it can be concluded that the optimization of temperature and pressure gradient and time holding factor, as well as the selection of metal catalyst etc are important either for the growth of large single crystals or for a high yield of diamond with medium grains. (Fig 6)

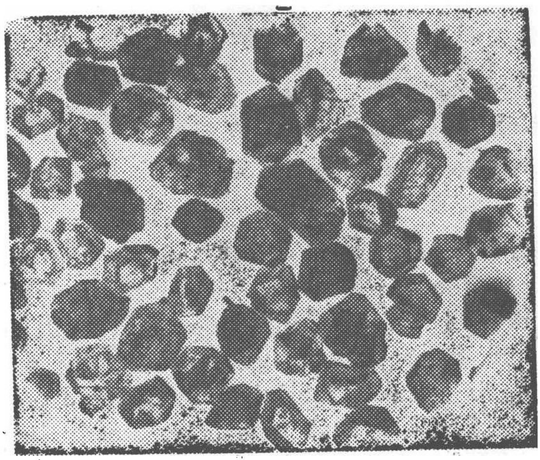

Fig. 6. Diamond single crystals synthesized with rather perfect octahedral growth morphology

In this laboratory, the hydrothermal growth of synthetic quartz has also been studied with some depth. The establishment of a syntheitc quartz industry in China has been duly accomplished to meet our needs in various fields. (Fig 7)

Fig. 7. Arrays of synthetic quartz just out of the autoclave

In the second crystal growth laboratory, a variety of electro-optic and nonlinear optic crystals for laser technology such as lithium niobate, lithium tantalate, sodium barium niobate etc and acousto-optic crystals such as lead molybdate and tellurium oxide etc have been grown from the melt by the pulling method. (Fig. 8) The growth mechanisms and the parameters suitable for the growth of crystals having high optical uniformity have been studied. (Fig 9) The crystal defects and their influence on the modulation or SHG as well as acousto-optic effects are being investigated. (Fig 10, 11) Some crystal chemistry study in relation with ferroelectric materials, for instance, the correlation between certain bord parameters with their ferroelectric properties (Ps and Tc etc) are being pursuited. The practical purpose of this branch of research is essentially for the needs of the development of laser technique.

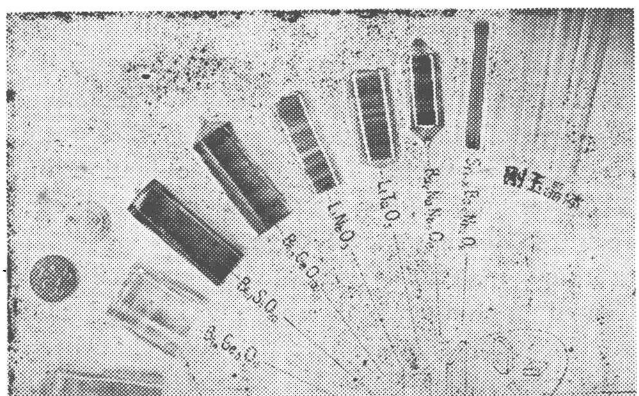

Fig. 8. Some of the electro-optic and acousto-optic crystals grown

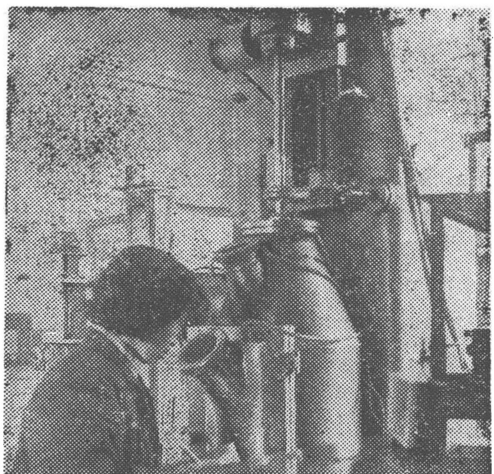

Fig. 9. Czochralski furnace for crystal growth

Fig. 10. A setup for studying the electro-optic properties (e.g. dynamic extinction ratio, half-wave voltage, impulse characteristics, etc) of electro-optic crystals and devices

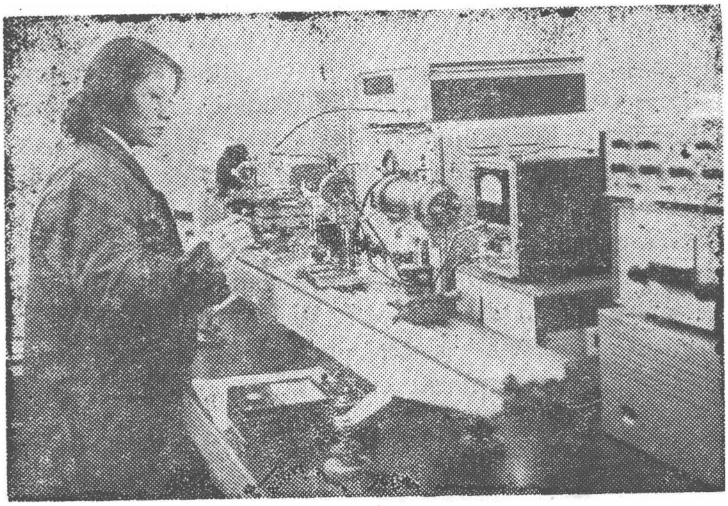

Fig. 11. Setup for measuring the acousto-optic characteristics (such as diffraction efficiencies at different input powers, frequency respond, etc) of PM acousto-optic devices (deflectors and modulators)

In the glass research laboratory, a number of projects have been carried out. They include the study on glass ceramic materials; the phase separation phenomena in Na_2O-B_2O_3-SiO_2 and other related systems and the preparation of useful materials therefrom; the study of semiconducting glasses of the chalcogenide series; the study on filtering glasses and the origin of coloring effects; and the recent investigation on extra-pure silica including doped silica glasses for optical waveguide purposes etc. I shall proceed to elaborate a few more words about some of them.

We started our research on glass ceramic materials from late fifties, since then many oxide systems have been investigated, including both optically induced and thermally induced nucleation systems. (Fig 12) Considerable attention has been paid on the nucleation and crystallization phenomena. Much work has been done on the interrelationship between microstructure and properties and the influence of processing parameters on them. As a result of these investigations, useful materials with high mechanical strength, low thermal expansion coefficient, good electrical properties or high optical transmittance have been developed, some of them have been enlarged into production scale in the factories. Some fundamental research has also been initiated in relation with glass ceramic systems. For instance, we have carried out an internal friction study on the Li_2O-K_2O-Al_2O_3-SiO_2 system before and after crystallization, some intersting phenomena were proposed to be explained by the mixed-alkali ion effect.

With chalcogenide series of amorphous semiconducting materials, we have studied both their electrical switching and optical memory effects. (Fig 13, 14) Materials with good stability and devices with long operating lives have been developed. The recent advance made by Drs. Mott and Anderson and others on the theory of amorphous semiconductors would certainly be a great impulse to promote the rapid development of this branch of materials science.

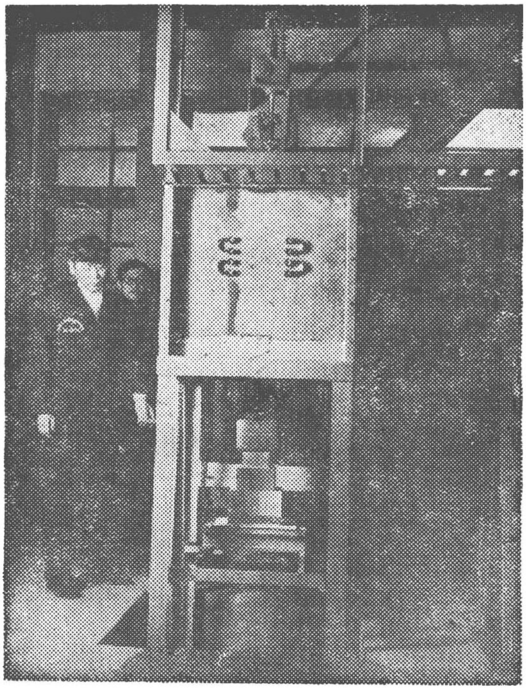

Fig. 12. A laboratory electric glass melting furnace with a top stirring device

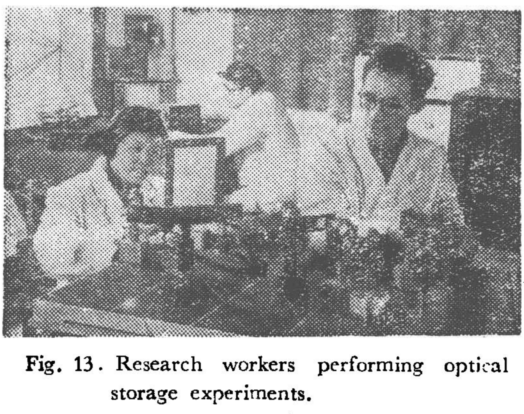

Fig. 13. Research workers performing optical storage experiments.

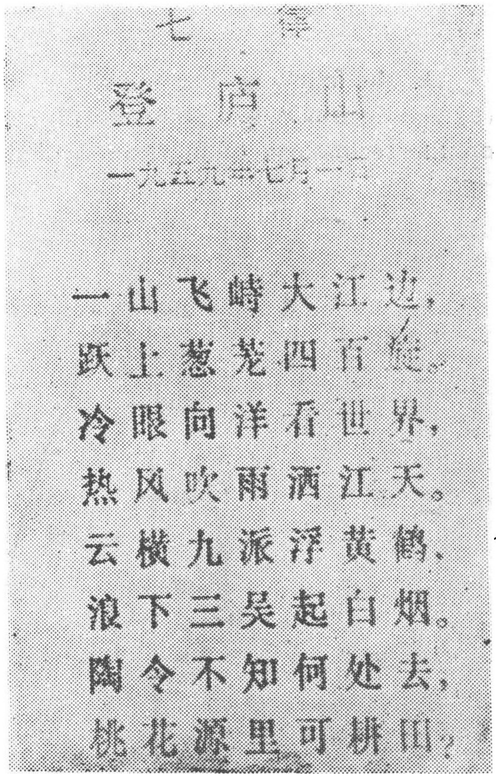

Fig. 14. A poem by Chairman Mao optically stored in a chalcogenide glass medium and displayeed by He-Ne laser

Fiber glass optical waveguide materials with graded indices have been studied by the CVD method. The processing parameters to obtain low loss and high transmission capacity waveguide fibers have been pursuited (Fig 15). Production units in Shanghai have already been established on this basis.