（上册）

现代玻璃科学技术

SCIENCE AND TECHNOLOGY
OF
MODERN GLASS

干福熹　主编
上海科学技术出版社

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内 容 简 介

本书分上、下两册。上册着重介绍玻璃的结构和性质；下册介绍新的玻璃系统和品种以及新的工艺。书中有关资料主要选自我国玻璃科技工作者的研究成果，有二十余位玻璃科技专家参加了各专题的撰写。为了反映当代玻璃科学技术的发展趋势，也引用了国外已发表的文献和资料。

本书可供国内外要了解我国玻璃科学技术的进展和国际发展动向的读者以及玻璃科学技术工作者参考，也可作高等院校玻璃教学的辅导材料。

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序　　言

近半个世纪以来，国际上玻璃的科学和技术有了很大的发展．由于吸引了不少物理和化学方面的科学家，应用了各种新的结构分析方法，对玻璃态物质的微观和亚微观结构的了解日趋深入，形成玻璃态物质的系统不断扩大，从这些新的玻璃系统中发现了很多新的物理和化学特性，从而又扩大了玻璃态物质的应用范围．此外，人们还采用了各种新的制备技术和工艺，因此，新的玻璃制品和玻璃工业不断兴起．可以讲，当前玻璃科学是固体物理和固体化学的前沿；玻璃态物质是高技术发展中的重要材料．国际上每年都出版许多有关国际玻璃会议的论文集及各种玻璃专题的书籍和丛书．

新中国成立后，我国玻璃制造工业得到了较快恢复和发展，全国各地扩建和新建了不少玻璃制造企业，玻璃品种也有较大的扩展；同时，在中国科学院、高等学校、工业部门和地方建立了一批从事玻璃研究和发展的机构，并取得了较多的科研成果，促进了我国玻璃工业的发展．中国硅酸盐学会所属的各个玻璃专业委员会召开了许多有关玻璃科学技术的学术会议，在我国的各种学术刊物上发表了不少有关玻璃科学技术的文章．但是，较全面地总结我国玻璃科学技术的研究成果的著作不多，较有影响的专著如《光学玻璃》[干福熹等著，1964年初版，1982～1985年第二版(上、中、下三册)，科学出版社]也是专题性的．1981年和1984年在北京举行了国际玻璃学术讨论会，会后由北荷兰出版社在国际《非晶态固体》杂志出版了英文版论文集[J. Noncrystalline Solids Vol 52, No. 1—3(1982)；Vol. 80, No.1—3(1986)]，也不是系统性的专著．

为了较系统地总结我国玻璃科学技术的研究成果和反映当代玻璃科学技术的发展趋势，我们邀请了国内近二十名玻璃科技专家撰写了各专题，编辑成这本书．本书共分上、下两册．上册着重介绍玻璃的结构和性质；下册介绍了新的玻璃系统和品种以及新的工艺．尽管书中选入上述两方面的专题(章、节)是不够全面的，但这是由于我国在玻璃科学技术的研究和发展上也是不平衡所致．我们选择的这些专题，其中有较多自己的研究成果(观点、数据和结果)．由于编著者的水平有限，对国内外情况的了解不全，有可能遗漏了一些重要的专题和重要的内容．同时书内所提出的数据和观点，错误也在所难免．希望读者，特别是我国玻璃工作者阅后提出宝贵意见，以便今后在再版时修改和补充．

此外，本书主要涉及玻璃态化合物(氧化物和非氧化物)材料，金属玻璃和其他半导体和合金薄膜等较少叙述，此后将由另外的著作介绍．

本书是集体写作，其中有关章节的著者姓名列于目录中．在本书编辑和出版中承上海科学技术出版社钱增英和我的同事顾冬红等同志的大力协助，没有他(她)们的努力，本书很难和读者见面．

中国科学院学部委员　**干福熹**

1987年6月于上海

PREFACE

For nearly half a century, great progress has been made for glass science and technology in the world. Thanks to the involvement of many physists and chemists, and the introduction of various new methods of structure analysis, the understanding to microstructure and even submicrostructure of vitreous substances has gradually been deepened. The glass forming systems have become wider and wider, and novel physical and chemical properties have been found for these new glass systems. Hence, the application of glassy materials has been expanded. New glass sorts and glass industries came into being because of the adoption of innovatory technology and processes. Glassy substances are believed to be the important materials of high-technology. In every sense, it can be said that glass science is the front of the modern solid state physics and chemistry. Every year, a good number of proceedings of international conferences on glass come into public, and other books or series concerning glass subject are also published.

Since the foundation of People's Republic of China in 1949, glass manufacturing industry in this country has been recovered and developed quickly. Glass enterprises have been extended or rebuilt all across China, and the sorts of glass have been increased greatly. In the meantime, a lot of glass research institutes were set up in Chinese Academy of Sciences, colleges and universities, industrial departments, as well as at localities. A wealth of results are obtained. All of that have stimulated the glass industry in this country. The glass commissions attached to the Chinese Silicate Society have sponsored many academic conferences and syposiums on glass science and technology. A plenty of papers appeared in Chinese academic journals and magazines. But few have widely summarized these research achievements, even the influencent treatises such as "Optical Glasses" (edited by Gan Fuxi, the first edition in 1964, second edition, consisting of three volumes, in 1982—1985; Science Press) was also limited to some special subjects. The proceedings of International Conferences on Glass held in Beijing respectively in 1981 and 1984 (J. Noncryst. Sol. , Vol. 52, No. 1—3 (1982); Vol. 80, No. 1—3 (1986)) are not the systemmatic reviews either.

In order to systemmatically summarize the research achievements on glass in this country and to follow the modern developing trends of glass science and technology in the world, inviting more than twenty glass scientists to contribute to each special subject, we edited this treatise which consists of two volumes. In the first volume, we focus our attention mainly on the structure and properties of glass, while the second one is devoted to review new glass systems and sorts, as well as innovatory technological processes of glass. It is not quite enough to select those chapters in the book for discussing the two special subjects mentioned above, this is due to the imbalance of development and research of glass science and technology in this country. We tried our best to choose those subjects that contain authors' own research achievements (ideas, data and results). It might be possible to omit some important subjects or contents due to the limit of editors' knowledge and incomplete access to foreign materials. In the meantime, there might be some errors of data and ideas. We hope that readers, especially glass experts, will give their valuable suggestions in order to be able to make corrections and complements in the next edition.

In addition this treatise is mainly concerned with vitreous materials of compounds (oxides and nonoxides). Little attention is paid to glassy metals and semiconductor or alloy films. We are to discuss these topics in the following works.

This book is collectively written. The contributors of the chapter concerned are listed in Contents. We wish to thank Miss Qian Zengyin (Shanghai Publishing House of Science and Technology) and my colleague Mr. Gu Donghong (Shanghai Institute of Optice and Fine Mechanics) for their cooperation during edition and publishing. Without their help, this treatise would not come into public.

Gan Fuxi
Academic Member of Academia Sinica
Shanghai, June 1987

导　　论

自然界，如在火山岩和矿物中，存在着玻璃态物质，以往常称为"无定形"物质[1]。早在几千年前，人们就掌握了熔制玻璃的技术。开始作为装饰品，发现于西周后期（公元前约一千年）的墓葬中[2]。以后在日用器皿上得到应用，至今瓶罐和器皿玻璃仍是应用最广和品种与产量最多的。本世纪以来，以窗玻璃为代表的平板玻璃和从电灯泡玻璃发展起来的电真空玻璃得到广泛应用，形成了玻璃工业。以上三大类玻璃，加上化学仪器玻璃、医用和计量玻璃以及早期光学玻璃等，都是以石英砂岩为主要原料的硅酸盐玻璃，二氧化硅含量一般在55～85%，采用以熔融态冷却为主的制备工艺。这些玻璃常称为"常用"或"普通"玻璃。近半个世纪以来，新的光学玻璃和技术玻璃中二氧化硅含量在85%以上或55%以下，同时大量使用非硅酸盐氧化物（如硼酸盐、磷酸盐、锗酸盐、碲酸盐和铝酸盐等）。最近，特种玻璃又扩展到非氧化物玻璃（如卤化物、硫系化合物、氮氧化物和卤氧化物等）。用熔体急冷的方法，目前可以制备金属合金玻璃，也得到了新的应用。可以讲，在周期表中的元素，除惰性气体和放射性元素外，都参与了玻璃态物质的合成。由于新的玻璃系统具有很多新的特殊的物理性质，从而获得了新的应用领域，所以玻璃已成为现代高技术发展中不可缺少的重要材料。

本书中比较系统地总结了近十几年来我国玻璃科学技术的研究成果，同时也引用了国外已发表的文献和资料，反映了当代玻璃科学技术的发展趋势。在上、下两册中，从玻璃的结构、性质、系统、品种和工艺等五个方面作了较全面的介绍。

一、玻璃的结构

除了从熔体冷却的途径得到玻璃态物质以外，目前用气相化学和电沉积、液相的分解和沉积、真空蒸发和溅射、离子注入和激光辐照等方法都可以得到远程结构无序的非晶态物质。用这些方法获得的非晶态物质，在其组成、性质和应用上与上述传统的玻璃态物质有所不同，因此在学术界有时分为两个不同的领域。本书中，我们企图从玻璃态物质的特性、生成规律和分类等方面来统一讨论上述两方面（玻璃态和非晶态）物质的结构，介绍了现代不同的光谱和衍射方法对玻璃态（非晶态）物质的近程和中程结构分析取得的新结果；同时对结构上的有序和无序问题作了详细讨论，提出了各种系统玻璃的结构模型（第一章）。玻璃结构上的均匀和不均匀又是一个重要问题，特别是在纳米级的结构（又称亚微观结构）与结晶和分相初始阶段密切有关。电子显微术已成功地应用于玻璃的亚微观结构研究，特别是高分辨率电镜和微区能谱仪的应用，获得了纳米级结构的比较清晰的图象，在第二章中比较着重地介绍了这方面研究结果。在这里也提出了玻璃的纳米结构对宏观性质的影响。

从玻璃态在热力学上的不稳定性，导致玻璃的结晶和分相是必然的趋势（第三、四章）。书中比较系统地介绍了玻璃结晶的动力学过程和从热力学定量计算玻璃的分相成分和范围，成功地应用于各种无机玻璃系统。

从热力学上讲，玻璃是处于亚稳态，因此玻璃的结构有弛豫过程，即随时间、温度和外界

条件而变化。玻璃的结构弛豫反映在玻璃的宏观性质的弛豫，特别在电学和力学性质上，本书第五章作了详细介绍。作者总结了用测量内耗的方法研究玻璃和微晶玻璃的弛豫过程。

近年来，我们较多地用光散射、电子自旋共振、核磁共振和EXAFS等方法，研究玻璃中原子或离子近程的配位状态，和彼此之间的化学键作用。在第六～九章中，开始都介绍了这些方法的物理基础和测试设备。玻璃的光散射中我们较着重地介绍了用拉曼光谱方法对含多种玻璃生成体氧化物玻璃、卤化物玻璃和硫系化合物玻璃的最新研究结果以及玻璃中受激拉曼和受激布利渊散射的光谱。用核磁共振方法研究具有核磁矩的离子的配位状态是十分有效的，书中较系统地总结了硼酸盐、硼硅酸盐和硼磷酸盐等玻璃中硼的配位状态的变化以及硼氧分子集团的结构；也报道了含锂的超离子导体玻璃和氟化物玻璃的结构分析结果。玻璃中的顺磁中心的结构可用电子自旋共振方法测定，书中比较系统地介绍了过渡金属离子和稀土离子的电子自旋共振谱，着重地报道了玻璃基质对若干过渡金属离子的ESR谱的影响的研究结果，和用激光选择激发使ESR谱变窄的手段研究玻璃中过渡金属离子不同格位状态的结果。书中介绍了用EXAFS结构分析方法研究简单硅酸盐玻璃、磷酸盐玻璃和锗酸盐玻璃，后者为作者近年的研究结果。

二、玻璃的性质

叙述硅酸盐玻璃的一般物理性质已有不少著作[3~6]。在我国较有影响的专著《光学玻璃》(上册)中，已对各种性质的测试方法和装置以及玻璃性质随成分变化规律和计算方法作了较系统的介绍[7]。本书中选择了若干较有实验积累的新的专题。在研制激光玻璃的过程中，我们对过渡金属和稀土金属离子在成分变化颇为广泛的无机玻璃中的吸收光谱、发光光谱、激发光谱和弛豫光谱进行了深入研究；近年来又用新的激光光谱技术，如时间分辨谱和激光选择激发等，对激活离子之间的相互作用和激活离子与基质相互作用引起的能量转移过程进行了动力学研究并提出了新的模型。这些研究成果总结于书中；同时也报道了玻璃中半导体微晶的光谱性质(第十章)。关于玻璃的光学性质，第十一章中系统地介绍了非氧化物玻璃，主要是氟化物玻璃和硫系玻璃的光学性质，这类玻璃目前已作为重要的红外材料，它们的光学性质以往较少报道。本书较全面地分析了无机玻璃的光学色散问题，特别注意到部分色散与紫外和红外吸收极限的关系。在强光作用下玻璃中产生一系列非线性光学效应，其中关键的性质为非线性折射率，书中对它的产生机理、测量和计算方法作了较仔细的介绍。

基于断层力学的理论和方法研究了玻璃的力学性质(第十二章)，书中报道了作者近年来提出的玻璃的微强度、微塑性区和断裂预测和寿命估算等新的观点和实验结果。在讨论玻璃的电性质(第十三章)中，我们不把玻璃如传统地那样仅看成是电绝缘体，而考虑到玻璃可以作为半导体和超离子导体。特别注意到玻璃的分相和晶化对电性质的影响。

国外已有好几本著作介绍玻璃的表面性质[8~9]。本书中讨论玻璃的化学稳定性也从玻璃表面的侵蚀机理出发，介绍了在不同介质中(酸、碱、盐、水溶液等)各种无机氧化物玻璃的离子交换和侵蚀过程。着重总结了玻璃成分对化学稳定性的影响，分析了“中和效应”、“压制效应”等机制(第十四章)。

本书上册包括玻璃的结构和性质，如上所介绍的，主要内容取自国内这方面的科研成果，其中有些发表于1981年和1984年两次北京国际玻璃讨论会的论文集上[10~12]。

三、新的玻璃系统

在《光学玻璃》中册书中，我们已较详细地叙述了各种硅酸盐、硼酸盐和磷酸盐等氧化物玻璃系统的玻璃生成和物理性质变化规律，以及玻璃成分和结构对性质的影响[13]．本书中，我们重点选择了非氧化物玻璃系统，包括卤化物玻璃（第十六章）和硫系化合物玻璃（第十五章），以及混合化合物玻璃，即卤氧化物玻璃（第十七章）和氮氧化合物玻璃（第十八章）．众所周知，作为红外透镜、棱镜和窗口材料，特别是最近发展起来的红外光导纤维，主要是用非氧化物玻璃．卤化物玻璃中重点介绍了以 BeF_2—，ZrF_4—和 AlF_3—为基础的三个氟化物玻璃系统，它们的玻璃生成范围、光谱和光学性质以及析晶和分相等行为；也报道了若干个新的氯化物玻璃系统．硫系玻璃中着重介绍了玻璃形成和结构以及电学性质和光电性质．硫系玻璃的光学和光谱性质已在上册玻璃的光学性质一章中作了叙述．与电学和光电性质密切有关的硫系玻璃的缺陷模型和能带结构也作了介绍．

目前，氮氧化物玻璃还是以氧化物为主，提高氮的含量是关键的问题．本书第十八章中重点介绍了氮气在玻璃中的溶解度、气氛的影响以及玻璃氮化的方法，报道了几种氮氧化物系统玻璃及微晶玻璃的性能、结构、应用和实验结果．卤氧化物玻璃系统主要为氟氧化物玻璃，其中氟化物含量为主要的．氟磷酸盐玻璃系统是当前光学玻璃和激光玻璃的主要新品种，其中磷酸盐的含量只有10%左右，但生成玻璃的稳定性比全氟化物玻璃高得多，书中作了详细介绍．

本书还包括了氧化物和水的玻璃系统——含水玻璃（第十九章），水在玻璃中的结构状态、水化过程动力学、水对玻璃性质的影响等都是研究含水玻璃的重要内容，书中都给出了我们的实验结果，同时也介绍了含水玻璃的制备方法和应用范围．逆性玻璃是指玻璃中含有大量的碱金属氧化物，它具有高的离子导电性能，结构上也与一般玻璃相异（第二十二章）．

四、新的玻璃品种

各种类型的玻璃品种已有千万种，本文开始时已介绍了几大类型玻璃工业的发展过程，至今每种玻璃工业还在不断发展各种玻璃新品种．本书中不准备叙述这些常用玻璃的品种发展，而是重点介绍对当前高技术发展中起重要作用的新的玻璃品种．

熔石英玻璃已形成大量生产的玻璃工业，高纯熔石英玻璃在电子、空间和光学技术中起重要作用．本书第二十三章中介绍了高纯石英玻璃的性能，特别是羟基的影响以及几种制备高纯石英玻璃的工艺．我国在微晶玻璃的研制方面进行了大量的工作，书中总结了这方面的研究成果（第二十章），包括系统、品种、性能和制造方法．

玻璃在光电子技术上的应用是今后发展新品种玻璃的重要方向．书中介绍了激光玻璃（第二十一章），光导玻璃纤维（第二十五章）和红外玻璃纤维（第二十六章）．近二十年来，我国在激光玻璃方面开展了比较全面和深入的研究工作，形成了我国的激光玻璃品种系列，玻璃的性能和质量达到国际先进水平，发展了我国有特色的制备工艺，本书作了较仔细的说明．

近十年来，我们逐步建立起光通信玻璃纤维的研究，开发和生产．发展了多模光纤和单模光纤以及单偏振光纤等，目前正在开展色散位移光纤和红外光导纤维的研究工作．这些工作对开拓我国光纤通信技术是十分重要的，本书作了重点介绍．

另一种颇有发展前景的新品种玻璃为生物玻璃（第二十四章），它在医学和生物工程中起重要作用．我国在有生物活性和无活性的生物玻璃的研制上作了有成效的研究．书中对

生物玻璃的组成、结构、制备和作用机理等方面作了介绍。

五、新的玻璃工艺

各类玻璃都有自己的工艺发展过程，有些已在新品种玻璃中作了介绍。书中还着重介绍了几种有重大开发意义的玻璃新工艺。浮法制造平板玻璃是本世纪板玻璃生产工艺的一个重大改革，国外大都应用专利建立生产线，我国从六十年代开始自行研究和试验用浮法(floating)生产平板玻璃的工艺，七十年代建立了试验性的生产线，八十年代初扩建的生产线已经国家鉴定，目前已推广新建了一批生产线，书中对这项制造工艺从原理、设备和生产中问题作了介绍(第三十章)。

化学气相沉积(OVD)是制备高纯玻璃的重要方法，也是今后制备新品种玻璃的重要途经。书中从化学气相反应热力学、动力学原理、计算和控制到改进的各种气相沉积法都有较详细的说明(第三十一章)。另一种脱离从熔体冷却制备玻璃的方法是从溶胶凝胶低温合成法(第二十八章)，用这方法可以制备高纯度和高熔点玻璃，也可以制备大面积的玻璃薄膜和纤维。在溶液中，将无机分子链和有机高分子聚合可以得崭新的功能玻璃，这也是一种正在发展中的新工艺。书中叙述了聚合、成胶、脱水和烧结等工艺过程的原理和方法，展望了应用前景。

改变目前玻璃熔炼的外热方式，用玻璃原料的介电损耗和涡流加热的内热法——高频介质熔炼法，也是制备高纯度和高温玻璃的新工艺（第二十九章)。书中对电场加热和磁场加热的原理、参数的确定、高频设备和实验结果作了报道。从熔体冷却制备玻璃的传统方法的另一重大改革为急速冷却法(spalt cooling)，使冷却速度达到 10^6°C/s，可以制备金属合金玻璃和极易析晶的氧化物和非氧化物玻璃等带，这类玻璃组成特殊的材料具有特殊电、磁和机械性能，书中对这一方法制备的玻璃的性质作了介绍。

最后，本书介绍了作为玻璃表面改性的离子扩散和离子注入新工艺。在玻璃表面用离子扩散和离子交换产生玻璃增强、着色和光波导等效应已有较多应用，书中讨论了离子自扩散和互扩散等过程，用来控制和设计离子扩散。用离子注入的方法使玻璃表面改性是较新的发展，书中作者提供了在此领域中的新的实验数据。

通过本书，我们希望向读者展示我国玻璃研究和发展取得的进展和国际玻璃科学技术发展的趋向。也提出了我们在玻璃科研工作中的一些薄弱方面、玻璃科学技术发展中的一些问题以及待进一步研究的课题。我们要加强国内外学术和技术交流，努力提高玻璃的科学技术水平，为实现我国四个现代化服务。

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Introduction

There exist glassy substances, which used to be called "amorphous substances", in nature, e.g. in volcanic rocks and minerals.[1] Artificial glasses have been produced for a long time. As far as thousands of years ago people mastered the technique of melting glass. In the tombs of late western Zhou Dynasty (about 1000 B. C.) glasses were found to have been used as ornaments.[2] Later glasses got use in house utensils. Up to now, bottle and utensil manufacturing has been developed to be a glass industry with the widest application, the most sorts and the largest output. Since the begining of this century, plate glasses represented by window glasses, and electric vacuum tube glasses developed from electric lamp glasses have come into wide use, and the glass industry was established. All the three kinds of glass, plus the glasses used in chemistry, medicine and metrology, as well as primitive optical glasses are silicate glasses made mainly from quartz sand. They contain in general 55—85% silicon dioxide and are obtained principally by cooling from melts. They are often referred as "common-used" or "common" glasses. For nearly half a century, new sorts of optical or technical glasses have been developed which contain more than 85% or less than 55% silicon dioxide, meanwhile other oxide (such as borate, phosphate, germanate, tellurite, aluminate, et al.) glasses have been widely used. Recently, special glasses are extended to nonoxides (e.g. halides, chalcogenides, oxynitrides, oxyhalides, et al.) By the method of spalt cooling, it is now able to produce metal-alloy glasses which also come into use. It could be said that all elements in the periodic table except inert gases, and radiative elements are able to take part in the composition of vitreous substances. Thanks to their novel physical properties, new glass systems have got some new application areas and are believed to be the necessary materials for high technology.

In this two-volume treatise, we are to systematically summarize the research achievements of glass science and technology during the part decade in this country, at the same time, the papers and data published in other countries are alse consulted in order to follow the modern trends of glass science and technology. Glass structure, properties, systems, sorts, as well as technological processes are reviewed here in detail.

1. Structure of Glass

Up to date, we can obtain noncrystalline, i.e. long-range disorder, substances not only by cooling from melts, but also by other methods such as chemical or electrical vapor deposition, liquid decomposition and deposition, vacuum evaporation and sputtering, ion imptantation as well as laser radiation et al.. The composition, properties and application of the non-crystalline substances obtained by the later methods are a little different from those of traditional glassy substances, therefore, in academic circle, they are sometimes distinquished to be two research areas. We will try to generally discuss the structure of two kinds (glassy and noncrystalline) substances in view of characteristics, forming laws and classification of vitreous substances. We introduce the new results of short and middle range structure analysis for vitreous (noncrystalline) by different modern spectroscopic and diffraction methods. We also discuss the structural order and disorder of glass in detail, and put forward the structural models for various glass systems (chapter 1). Homogenous or inhomogenous of glass structure is another important aspect of glass science. Specially, nano-structure (also known as sub-microstructure) has much to do with the primary steps of crystallization and phase separation. Electron microscopy has been successfully applied to study the sub-microstructure of glass. We have obtained clear images of nano-structure using high resolution electron microscope and micro-probe analysis. In chapter 2 we pay more attention to the achievements in this field, and the effects of glass nano-structure on their macro-properties are also discussed.

Thermodynamic instability of glass intends to result in crystallization and phase separation in it. In chapter 3 and 4, We systemmatically discuss the dynamic processes of crystallization in glass. And the quantitative calculation of composition and range of phase separation by thermodynamics which have successfully been applied to various inorganic glass systems.

Thermodynamically, glass is in metastable state. Therefore, there are relaxations for glass structure, namely, there are structural changes according to time, temperature and other evironmental conditions. The structural relaxation of glass is able to be reflected by the relaxation of macro-properties, especially electric or mechanical properties, These are discussed in chapter 5. It is also reviewed to study relaxation processes in glass or glass cermics by the method of measuring interfriction.

In recent years, we paid much attention to examining short-range coordination of the atom or ion and the chemical bonding in glass by optical scattering, ESR, NMR and EXAFS et al.. The physical fundamentals and measuring apparatuses of these methods are introduced from chapter 6 through chapter 9. With discussing the light scattering, we are more concerned with latest research achievements of Raman spectrum for containing several glass-forming oxides glasses, halide and chalcogenide glasses. The stimulated Raman scattering and stimulated Brillouin scattering in glass are also touched upon. NMR is an effective tool for determining the coordinations of nuclear magnetic ions. In this book we systematically discuss the coordinations of boron and the structure of boron–oxy groups in borate, borosilicate, borophosphate glasses. The structural analysis results of Li–containing super ionic conductor and fluoride glasses are also reported. The structure of paramagnetic centers in glass can be determined by ESR. Here we review the ESR spectra of transition or rare–earth ions in glass, main attention are paid to both the effects of glass hosts on the ESR spectra of some transition metal ions and the research results for site structure of transition metal ions in glass by laser–induced narrowing of ESR spectra. We also present the structural analysis results for single silicate, phosphate and germanate glasses by EXAFS, which were obtained by the authors during the past few years.

2. Glass Properties

General physical properties of silicate glass have been reviewed in a lot of monographs. [3-6] The influent one, "Optical Glasses" (1 st volume) was devoted to describe the measuring methods or apparatuses for different properties and the changing rules of glass properties according to the composition, as well as the calculation of glass properties.[7] Those subjects for which there have been much latest achivements are selected here. Inventing laser glasses, we have intensively studied the absorption, emission, excitation and relaxation spectra of transition and rare–earth metal ions in inorganic glasses whose composition was changed in a large scale. Recently, by new technique of laser spectroscopy such as time–resolved spectrum and laser–selected excitation we investigated the dynamics of energy transfer processes and put forward new models for the processes. All the results are summarized in the book. Meanwhile, the spectroscopic properties of semiconductor crystallites in glass are also reported (chapter 10). In chapter 11, we give a systemmatic review of optical properties of nonoxide, mainly halide and chalcorgenide glasses. They are now widely used as infrared glasses, but their optical properties have not been reported much more before. The optical dispersion of inorganic glasses are discussed in detail, and special attention is paid to the relationship between the partial dispersion coefficients and the infrared or ultra-violet absorption edge. The critical parameter of nonlinear effect in glass which is caused by intense light radiation is nonlinear refractive index. The mechanism of nonlinear effect, and the methods of measuring or calculating nonlinear refractive index are all discussed in detail here.

The mechanical properties of glass have been studied with the theory and method of fracture mechanics. New ideas and the latest experimental results about microstrength, micro–plastic–area, fracture forecasting, life estimation which were put forward by the authors in recent years. While discussing their electric properties, we not only refer to glass as insulator as before, but also consider them to be able to become semiconductor or super-ionic conductor. Special attention is paid to the effect of phase separation and crystallization in glass on their electric properties.

A few of monographs concerning the surface properties of glass have been published in other countries. [8,9] Here in view of mechanism of surface errosion in glass, we discuss the chemical durability of glass, and the ion exchange, ion errosion of glass in different media (acid, base, solt, as well as water). More attention was focused on the effect of glass composition on its chemical durability, and the mechanism of "neutralization" or "constraint" effect are also analysed.

The first volume of the treatise is concerned with glass structure and properties. As mentioned above, main contents come from the research achievements in this country, some of which have been published in the proceedings of International conferences on Glass held in Beijing repectively in 1981 and 1984. [10-12]

3. New Glass Systems

In the second volume of "Optical Glasses" we have thoroughly described the forming laws and the changes of physical properties for oxide such as silicate, borate, phosphate glasses, as well as the effects of glass composition and structure on the properties. [13] Here we focus our attention on those of nonoxide glass systems including halide(chapter 16). chalcogenide(chapter 15). oxynitride(chapter 18) as well as oxyhalide (chapter 17) glasses. As well known, it is nonoxide glasses that are widely used as infrared lens, prism, window materials, particularly as infrared optical fibers which are developed recently. As for halide glasses, we are mainly concerned with BeF_2, ZrF_4 and AlF_3 based glass systems and their spectroscopic or optical properties, devitrification, phase separation. Some new halide glass systems are also touched upon. The formation, structure, as well as electric or opto-electronic properties of chalcogenide glasses receive much attention. The spectrosocpic and optical properties have been discussed in the first volume. We give an introduction to the defect model and energy band theory of chalcogenide glasses which have much to do with their electric or opto-electronic properties.

Up to date, oxynitride glass is mainly composed of oxides. The crucial problem is how to increase the content of nitrogen. In chapter 18 we pay much attention to the solubility of nitrogen in glass, the effect of atmospher, and the methods of glass nitrogenization. The characteristics, structure, application, as well as experimental results of some oxynitride glass systems and glass ceramics are reported. Oxyhalide glass is mainly referred to as oxyfluoride glass in which fluoride is dominant. Fluorophosphate glass has now run the first as optical and laser glass. Although the content of phosphate in it is only 10%, fluorophosphate glass is much more stable and durable than all-fluoride glass. All of these are discussed in detail in the book.

In chapter 19 we introduce oxide–H_2O glass system—H_2O-containing glass. The structure of water in glass, the dynamics of hydrolysis, and the effect of water on glass properties are important aspects for studying water-containing glass. The experimental results concerning these fields are presented in the book, the preparation methods and application areas of water-containing glass are introduced too. Inverted glasses mean those glasses containing high content of alkai oxides, they possess high ionic conductivity and different structure with ovdinary one(chapter 22).

4. New Sorts of Glass

There have now been thousands of sorts of glass. At the begining of this introduction, we have outlined the development history of some main glass industries. Up to now, the number of glass sorts continues to be increased. Here we are not going to describe the development of common-used glass sorts, while focus our attention on those new sorts of glass which play an important role in high technology.

There has been a large manufacturing industry for fused silica glasses. But super-pure fused silica is of great significance in electronics, space and optical technology. In chapter 23 we review the characteristics of super-pure fused silica and the technological processes for producing them, with special attention to the effect of hydroxyl group. Much work about glass ceramics have been done in China, The research achievements are summarized in chapter 20, including systems, sorts, characteristics as well as production methods.

The important direction to develop new sorts of glass lies in the application of glass in opto-electronic technology. Here we give an introduction to laser glass (chapter 21), optical waveguide fibers (chapter 25), and infrared glass fibers (chapter 26). For nearly twenty years, the extensive and intensive research on laser glasses has been carried out in this country. Developing the specific technological processes of our own, we have produced a series of sorts of glass, their characteristics and qualities are able to compete with the best in other countries. All of those are reviewed in detail.

In the past ten years, we gradually carried out the research, exploration and production of glass fibers for optical communication. Multi-mode, single-mode as well as single polarized optical fibers have been developed. Now the interest is turned to dispersion-shift optical fibers and infrared optical fibers. All of the works are crucially important for developing the optical communication in this country, and receive much attention in this book.

Another prospective sort of glass is bioglass (chapter 24) which are important for medicine and biological engineering. Much fruitful work has been done for bioactive or non-bioactive bioglasses. Their composition, structure, production and acting mechanism are introduced in the book.

5. Innovatory Technological Processes of Glass

Different technological processes have been developed for different sorts of glass, some of which were reviewed in the last section. Special attention is paid to those innovatory processes which are of great significance for glass industry. Production of plate glasses by floating method was a process revolution for glass manufacturing in this century. A good number of patent production lines have set up abroad. In this country, research and experiment on floating method have been carried out since 1960's. During 70's trial-production lines were built, and by the beginning of 80's the extended production lines had been appraised at national level. Up to now, a lot of production lines have been rebuilt. Here we give an introdution to the principle, equipment and remaining problems for this technological process(chapter 30).

Chemical vapor deposition(CVD)method is an important one to make super-pure glasses, and also a useful way to develop new sorts of glass in the future. In chapter 31, we discuss the principles, calculation and control of CVD method in view of chemical gas reaction, thermodynamics, kinetics. Different improved CVD methods are also introduced. Another method to make glass, different from the method of cooling from melts, is low temperature proparation by sol-gel, by which we can produce super-pure or high melting point glasses, as well as large-area glass films and fibers.

Polymerizing inorganic molecular chains with organic polymers in solution to obtain novel functional glasses is also a new technological process for glass manufacturing in progress. We here describe the principles and methods of polymerization, gelation, dehydration, sintering. Application prospect of this method is glorious.

It is also an innovatory technological process for super-pure and high melting point glasses to change the external heating in to the internal heating method which takes advantage of the dielectric loss or vortex in raw glass materials, e.g. high-frequency melting method. In chapter 29, we describe the heating principles in electric or electro-magnetic field, the determination of parameters, high frequency heating equipment, and experimental results for this method. Spalt cooling is another invention of tranditional processes for glass manufac-