

# INORGANIC PHOSPHORS

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COMPOSITIONS,  
PREPARATION AND  
OPTICAL PROPERTIES

**The CRC Press**  
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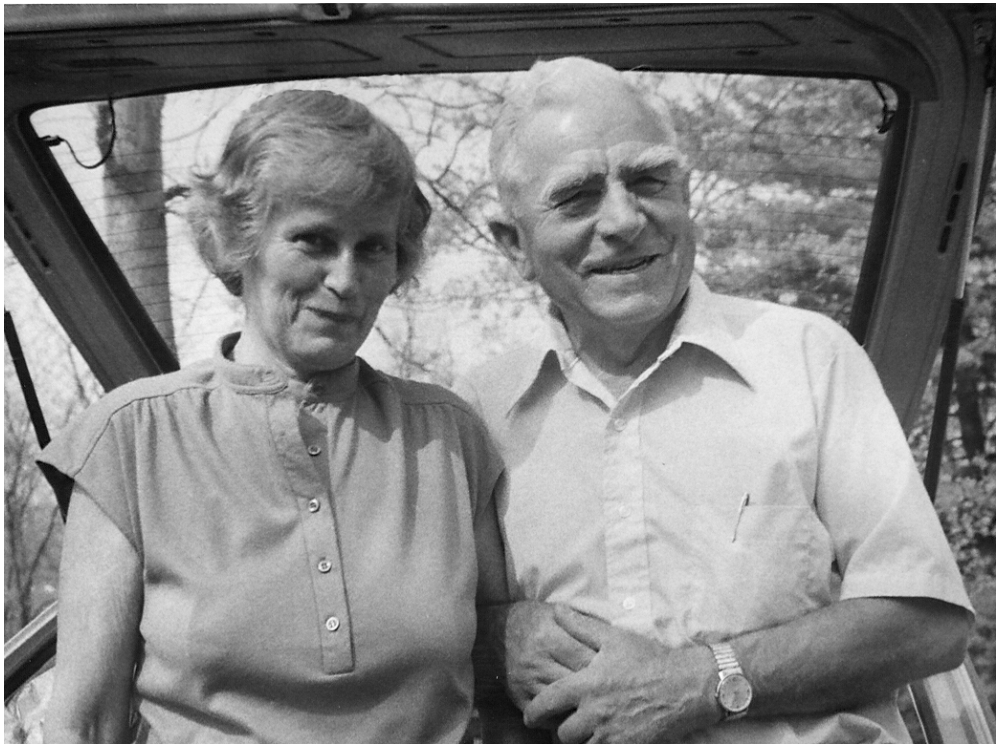
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Willi and Renate Lehmann (circa 1970).

# TABLE OF CONTENTS

FOREWORD

PREFACE

PART 1: LEHMANN'S PHOSPHOR COOKBOOK AND PHOSPHOR TABLES

SECTION 1: INTRODUCTION

SECTION 2: PHOSPHOR PREPARATION

- 2.1 Starting Materials
- 2.2 Amounts
- 2.3 Mixing
- 2.4 Containers
- 2.5 Furnace
- 2.6 Firing Atmospheres
- 2.7 Treatments after Firing

SECTION 3: PURIFICATION OF SOME STARTING MATERIALS

- 3.1 Carbonates
- 3.2 Sulfates
- 3.3 Oxalates
- 3.4 Sulfur

SECTION 4: PHOSPHOR DATA

- 4.1 Description of Data
- 4.2 Simple Oxides
- 4.3 Silicates
- 4.4 Halosilicates
- 4.5 Phosphates
- 4.6 Halophosphates
- 4.7 Borates
- 4.8 Aluminates and Gallates
- 4.9 Molybdates and Tungstates
- 4.10 Miscellaneous Oxides
- 4.11 Halides and Oxyhalides
- 4.12 Sulfates
- 4.13 ZnS-Type Sulfides
- 4.14 CaS-Type Sulfides
- 4.15 Double Sulfides
- 4.16 Miscellaneous Sulfides and Oxsulfides

SECTION 5: PREPARATION OF PHOSPHOR SCREENS

- 5.1 Phosphor Screens by Brushing
- 5.2 Phosphor Screens by Settling in a Kasil Solution

- 5.3 Phosphor Screens by Cathaphoretic Deposition
- 5.4 Filming of Phosphor Screens

## PART 2: ADDITIONAL DEVELOPMENTS

### SECTION 6: PHOSPHOR SYNTHESIS

- 6.1 Alternative Preparation Methods
- 6.2 Combustion Synthesis of Phosphors
- 6.3 Preparation of Phosphors by Sol–Gel Techniques

### SECTION 7: OTHER PHOSPHOR DATA

- 7.1 Oxides
- 7.2 Silicates
- 7.3 Phosphates, Halophosphates, and Borates
- 7.4 Aluminates
- 7.5 Halides and Oxyhalides
- 7.6 CaS and ZnS-Type Sulfides
- 7.7 Other Compounds

### SECTION 8: COMMERCIAL PHOSPHORS AND SCINTILLATORS

### APPENDICES

- Appendix I Historical Note on Phosphor Recipes
- Appendix II Phosphor Materials Arranged in Order  
of Emission Wavelength
- Appendix III Willi Lehmann: A Brief Biography

### MATERIALS INDEX

## Foreword

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### Willi Lehmann

It is a truism that all individuals are unique. However, in the case of the late Willi Lehmann this is true in the strongest sense possible. One often hears of a person with a “one-track” mind. That concept describes Willi perfectly. He was indeed one of a kind. As far as I know, he lived for and only thought about phosphors. He was a very oriented, strong willed and, yes, stubborn individual. It is my pleasure to have known him and have been his manager (in truth, no one “managed” Willi) for several interesting and productive years.

I knew very little about Willi’s life in Germany. Fortunately, I was able to obtain a copy of an autobiography Willi wrote for his family and was able to learn something about his history. Bill Yen and I present a brief summary of Willi’s life and times in Appendix III. I knew that he served in the German army during World War II, first on the Russian front and then on the Western front. It is difficult for me to conceive of him as a member of a military unit. He always had a very un-Germanic disregard for authority. This undoubtedly explains why, after working his way up to grade sergeant, he was “busted” back to private. I believe he objected to officers riding in comfortable first-class carriages while enlisted men rode in overcrowded second-class carriages. Another un-Germanic trait was that he disliked beer; he called it “seifewasser” (soapy water).

Willi was always resourceful (surely a good trait for a scientist). At the end of the war, after being captured by the French, he managed to escape and be recaptured by the Americans because he knew they treated their German captives better. While he was in POW camp a request came asking whether any prisoner could repair typewriters. Willi, who actually had no prior experience in this line, promptly volunteered and became a successful “typewriter mechanic” overnight. Also during his time as a prisoner he spent his spare time recalling and writing down the essentials of his previously studied elementary physics textbook. I suppose he “borrowed” the necessary paper and pencils from the offices where he repaired typewriters.

After the war Willi studied physics (I am not sure at what university) under Prof. Erich Krautz, who had an interest in luminescence. Later, Krautz became Director of Research at a branch of the Osram Lamp Co., located in Augsburg, near Munich. At that time, the Lamp Division of the Westinghouse Electric Corp., located in Bloomfield, New Jersey, had a patent and technical interchange agreement with Osram. On a visit to Augsburg, E.G.F. Arnott, Director of Research in Bloomfield, asked Prof. Krautz to recommend two of his former students who were interested in luminescence and would like to immigrate to the United States. Krautz recommended Willi Lehmann and Claus Haake, and both accepted the offer. This was probably in 1955, as Willi published his first American papers (*Phys. Rev.*, 101, 489; *J. Electrochem. Soc.*, 103, 667 and *Illum. Eng.*, 51, 684) in 1956. Willi remained with Westinghouse, first in Bloomfield and then in Pittsburg for many years, while Claus left after about 2 years to move to Arizona for reasons of his wife’s health.

In 1956 I was Manager of the Phosphor Research Section of the Westinghouse Lamp Division and thus suddenly found myself responsible for two foreigners about whom I knew nothing. The situation was conceivably complicated by the fact that I was Jewish; I didn’t know how they would react to me and vice versa. Fortunately, this never presented a



problem. Both Willi and Claus turned out to be very diligent and skilled workers (Prof. Krautz would not have recommended dummies). Their knowledge of the English language was good, although Willi always spoke with a pronounced Germanic accent, probably because he spoke only German at home. (I must admit that while Willi worked for me I always edited his scientific papers before publication, but endeavored to leave them sounding like Willi.)

During those years in Bloomfield the attention of the Phosphor Section was directed primarily to electroluminescence, then in its infancy. I can truthfully say the best (brightest and longest lived) electroluminescent phosphors made anywhere in that era were made by Willi Lehmann. This activity, and that elsewhere, is summarized in my book, *Electroluminescence and Related Effects* (Academic Press, 1963). I was later made a fellow of the Institute of Electrical and Electronics Engineers (IEEE) and an Honorary Member of the Electrochemical Society for "leadership in the advancement of the science of luminescence." However, the work which resulted in these honors was primarily due to three outstanding members of the section: Willi Lehmann, William A. Thornton, and Anselm Wachtel. My effort was mainly that of support, coordination, and interpretation.

My approach to "management" of scientific activity was essentially minimalist, consisting of four steps: (1) hire the most capable and self-motivated people, (2) provide them with the necessary equipment and facilities, (3) point them in the directions of interest to the company, and (4) don't bother them, except for occasional encouragement and suggestions as to questions for which no one had an answer at the moment. This minimalist approach certainly worked well with Willi, who was never a "team player." I also learned that minor infractions of company rules could be overlooked unless they were officially brought to my attention: sometimes ignorance of events can be good.

Although trained as a physicist, Willi actually performed best as a self-taught chemist; he was more interested in making better phosphors than in explaining how or why they worked. He was always an enthusiastic worker. I remember one day Claus Haake stuck his head in my door and said, "Willi just made a three-gott-damn phosphor!" I said, "What does that mean?" Claus replied, "Well, when Willi has made a new sample and finds that it tests good, he says 'Gott damn!' Today he tested his latest sample and said, 'Gott damn! Gott damn! GOTT DAMN!'"

About 1963 both Willi and I transferred to the central Westinghouse Research Laboratories in Pittsburgh, but to different departments. I joined the Optical Physics Department, which was primarily concerned with lasers, and in 1969 became manager of the department. Willi went to the Solid State Physics Department, where he continued to work on phosphors, mainly for applications to fluorescent lamps and cathode-ray tubes. Nevertheless, we kept in frequent contact and he always put me on the distribution list for his research reports. It was during this period of his career that he organized the material for his *Phosphor Cookbook*.

Willi always maintained his independence and disregard for rules which seemed pointless to him. There were four types of scientific documents at Westinghouse: patent disclosures, papers to be published, summary research reports for internal use, and short research "memos." For some strange (probably historical) reason, memos had to be addressed to a particular individual, although they could have an extended distribution list. Once Willi (in Pittsburgh) apparently had trouble deciding to whom a certain memo should be addressed so in the proper place he wrote, "The Queen of England." Some unwitting secretary typed it up that way and sent it to his department manager for signature. Considerable consternation ensued, but Willi survived unscathed and hardly ruffled. For Willi, rules were usually meant for lesser beings; he had more important things (phosphors) to think about.

Willi retired from Westinghouse in about 1985 (the reason for my vagueness about dates is that Westinghouse is now defunct and I have no way of accessing company files). He went to live in Hendersonville, North Carolina, and apparently did consultation on electroluminescence for the Rogers Corp. in Connecticut. I am sorry to say that I lost contact with him after 1988.

I have learned since that Willi passed away in January 1993 and that he is survived by his wife Renate and four children, Caren, George, Hans, and Mary. All appear to be prospering and the family has given its approval to the belated publication of Willi's *Phosphor Cookbook* and *Phosphor Tables* he so carefully compiled nearly two decades ago.

When Willi Lehmann was alive and active he was one hell of a great phosphor maker. It was his obsession and sole occupation. He left many important published papers. In 1988 he wrote to inform me that he had been invited to contribute to a book entitled *Phosphors*. He enclosed a copy of his contribution, an extended collection of the main properties of about 300 of the best-known inorganic phosphors, with reference to the original publications. However, this book was never published. He said then, "My *Phosphor Tables* are completed and I don't like the idea of them going to waste." The present volume by Bill Yen and Marv Weber, which combines his *Phosphor Cookbook* and his *Phosphor Tables*, finally solves that waste problem. It will serve as a fitting and belated recognition of the valuable work this unusual individual contributed to the science of luminescence.

Henry Ivey  
Coconut Creek, Florida  
April 1, 2003

## Preface

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About a decade ago, one of us (WMY), in response to a federal broad agency announcement, initiated an effort to establish a baseline for the state of knowledge concerning the methodology for synthesis and the optical properties of a variety of phosphors used for display and other technical applications. Though for various reasons this effort ultimately turned futile, several members of the phosphor/luminescence community called my attention to an existing backlog of published and unpublished literature addressed to this subject. This resulted, for example, in our becoming aware of the existence of the *Phosphor Handbook* published in Japanese under the auspices of the Japan Phosphor Society and led to its eventual translation and publication as the *Phosphor Handbook*, a volume in the CRC Lasers and Optical Sciences and Technology Series.

In connection with efforts to establish a phosphor database, Ronald Petersen (of Motorola, at the time) first presented us with a copy of Willi Lehmann's opus (*Phosphor Cookbook*) on methods for synthesis and properties of over 200 phosphors. This report dates from the late 1970's and covered the majority of phosphors then in use. Dr. Lehmann, of course, was a principal in the development of many of the phosphors included in his cookbook. He later updated and extended this work in 1988 in his *Phosphor Tables* in which the phosphor properties of over 300 luminescent materials were summarized in tabular form. A copy of these tables, which was prepared for a publication that never appeared, was preserved and given to us by Dr. Henry Ivey. Henry had a close working relationship with Willi at Westinghouse as the Foreword to this volume attests.

The scholarship contained in the *Phosphor Cookbook* and the *Phosphor Tables* is quite remarkable and comprises a great deal of meticulous and careful work characterizing Willi Lehmann's career as a phosphor synthesizer. The list of materials presented in the compilations is large and the manuscripts preserve and summarize synthesis and optical data on most of the commonly used phosphors (as well as some less common ones). In the absence of any systematic database on phosphors, the two unpublished manuscripts represent a reasonably complete summary of the state of knowledge on phosphors up to the late 1980's.

Though it might be argued that the art of phosphors synthesis and characterization has advanced considerably since Lehmann's time, we believe that these contributions need to be preserved as part of the phosphor art. Thus, it appeared to us that the content of these two unpublished manuscripts fully deserved publication as a record, if nothing else, of past methodologies; these methodologies are often abandoned and forgotten but often need to be rediscovered and revived when circumstances warrant it. Almost all modern phosphors are synthesized by solid-state reactions at high temperatures. Updated versions of these techniques are presented in this volume along with other techniques such as sol-gel and combustion that have been developed in the past few decades.

This volume is divided into two parts. Most of the contents of Lehmann's *Phosphor Cookbook* and *Phosphor Tables* are preserved in the first part with either no or only slight changes in style and format. The phosphor data presented in Section 4 combine the results of both manuscripts. However, no composition or preparation information was included in the *Phosphor Tables*; thus such information is absent for many compounds. In the second part of the volume we have attempted to supplement Lehmann's work with additional

developments including recent synthesis methods and new phosphors. Because of the plethora of phosphor compositions reported in recent decades, the listing is not exhaustive but rather representative of some of the more significant phosphors developed in recent years. We have restricted consideration to materials that are accessible in the open literature and have not included any recipes or description of phosphors that are proprietary. Only a relatively few phosphors have achieved commercial success. Section 8 presents a list of many commercial phosphor and scintillator materials and the peak wavelength of their emission. Finally, three appendices have been added. The first presents an historical perspective on phosphors; in the second a table of phosphors is arranged in order of emission wavelength as a guide in selecting phosphors for particular applications. The third gives a brief summary of Willi Lehmann's life.

It may be noted that the elements belonging to series such as the lanthanides (4f) have chemical behaviors that are nearly identical to each other. It follows that recipes for compounds doped with a certain ion of a series very likely will also be effective for other members of that series. Other considerations (such as ion sizes) will enter, so that the synthesis of any new compounds remains an area of experimentation; a good beginning point, however, would be with the procedures that are presented here. The preparation methods described in this volume generally entail the use of laboratory procedures which are normally encountered in solid-state chemistry and which expose the experimenter to the usual perils. As such, we emphasize that all normal safety precautions (fume hoods, eye protection, etc.) should be observed in the preparation and synthesis of the phosphors described in the volume.

The American Ceramic Society in collaboration with the National Institutes of Standards and Technology (NIST) has continued to publish and revise *Phase Diagrams for Ceramists* (Vols. I–VI) and the sequel *Phase Equilibrium Diagrams* (Vols. VII–XII); these volumes contain a great deal of material which is extremely useful in developing an understanding as to what can and cannot be synthesized. Much additional information on the synthesis and characterization of a phosphor or luminescent material information can be found in the aforementioned *Phosphor Handbook*.

In this effort we have benefitted from numerous comments, suggestions, and contributions from our Editorial Board. We are very appreciative of their help and that of Ron Petersen and Henry Ivey for having preserved the original manuscripts. We are also very thankful to the Lehmann family for giving their permission to use this material. We note with special appreciation the excellent work of Sergei Basun in preparing the many figures and the final manuscript, Sarah Dunning for typing the manuscript, Mike Caplinger and Jeff Deroshia for their computing assistance, and the valuable interactions with CRC Project Editor James McGovern and Development Manager Helena Redshaw.

We are aware that, as noted in the Foreword, Willi Lehmann was anxious to have the material that he had prepared with such care published in some form. We hope that the publication of *Inorganic Phosphors* serves to fulfill his wish. Indeed, this volume should be considered a tribute to this unusual individual and his contributions to the phosphor art.

William M. Yen  
Athens, Georgia

Marvin J. Weber  
Berkeley, California

April 2004

## Further Readings

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## The Editors

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**William M. Yen** obtained his B.S. (Physics) degree from the University of Redlands, Redlands, California in 1956 and his Ph.D. in Physics from Washington University (St. Louis) in 1962. He served a term of 3 years (1962–1965) as a Research Associate at Stanford University under the tutelage of Professor A.L. Schawlow and accepted a faculty position at the University of Wisconsin—Madison in 1965. He was granted tenure at Wisconsin in 1968 and promoted to a full professorship in 1972; he retired from the Wisconsin system in 1990. In 1987 he was appointed to the Graham Perdue Professorship at the University of Georgia—Athens where he has established a research program in the properties of phosphors and other light-emitting materials.

Dr. Yen has been the recipient of a J.S. Guggenheim Foundation Fellowship (1979–1980), of a A. von Humboldt Senior U.S. Scientist Award (1985), and of a Senior Fulbright to Australia (1995). He has been appointed to Visiting Professorships at the University of Tokyo (1972), the University of Paris—South (1976), the Australian National University (1980, 1995), the Federal University of Pernambuco—Recife (1980), and the University of California—Santa Barbara (1982, 1985). He was also named by Washington University (St. Louis) as the first Edwin T. Jaynes Visiting Professor for the Fall of 2004. He has been a member of the technical staff at the AT&T Bell Telephone Laboratories (1966) and of the Laser Fusion Project at Lawrence Livermore Labs (1974–1975). Dr. Yen has been elected to fellowship in the American Physical Society, the Optical Society of America, the American Association for the Advancement of Science, and the Electrochemical Society.

Dr. Yen is the co-editor of the *Phosphor Handbook* published by CRC Press.

**Marvin J. Weber** received the A.B., M.A., and Ph.D. degrees in physics at the University of California, Berkeley. After graduation, Dr. Weber joined the Research Division of the Raytheon Co. where he was a Principal Scientist working in the areas of spectroscopy and quantum electronics. In 1966 to 1967 Dr. Weber was a Visiting Research Associate in the Department of Physics, Stanford University.

In 1973 Dr. Weber joined the Laser Program at the Lawrence Livermore National Laboratory where, as Head of Basic Materials Research and Assistant Program Leader, he was responsible for the physics and characterization of optical materials for high-power laser used in inertial confinement fusion research. From 1983 to 1985 he accepted a transfer assignment with the Office of Basic Energy Sciences of the U.S. Department of Energy in Washington, DC. Dr. Weber returned to the Chemistry and Materials Science Department at LLNL in 1986 and served as Associate Division Leader for condensed matter research and as spokesperson for the University of California/National Laboratories research facilities at the Stanford Synchrotron Radiation Laboratory. He is presently a scientist in the Department of Nuclear Medicine and Functional Imaging of the Life Sciences Division at the Lawrence Berkeley National Laboratory.

Dr. Weber is Editor-in-Chief of the multi-volume *CRC Handbook Series of Laser Science and Technology* and a Fellow of the American Physical Society, the Optical Society of America, and the American Ceramics Society. Among several honors, he is the recipient of the International Conference on Luminescence Prize, George W. Morey Award of the American Ceramics Society, and an Industrial Research IR-100 Award for research and development of fluorophosphate laser glass.

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