# PHOSPHOR HANDBOOK

*Edited under the Auspices of*
**Phosphor Research Society**

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# Preface

This volume is the English version of a revised edition of the *Phosphor Handbook* (*Keikotai Handobukku*) which was first published in Japanese in December, 1987. The original Handbook was organized and edited under the auspices of the Phosphor Research Society (in Japan) and issued to celebrate the 200th Scientific Meeting of the Society which occurred in April, 1984.

The Phosphor Research Society is an organization of scientists and engineers engaged in the research and development of phosphors in Japan which was established in 1941. For more than half a century, the Society has promoted interaction between those interested in phosphor research and has served as a forum for discussion of the most recent developments. The Society sponsors five annual meetings; in each meeting four or five papers are presented reflecting new cutting edge developments in phosphor research in Japan and elsewhere. A technical digest with extended abstracts of the presentations is distributed during these meetings and serve as a record of the proceedings of these meetings.

This Handbook is designed to serve as a general reference for all those who might have an interest in the properties and/or applications of phosphors. This volume begins with a concise summary of the fundamentals of luminescence and then summarizes the principal classes of phosphors and their light emitting properties. Detailed descriptions of the procedures for synthesis and manufacture of practical phosphors appear in later chapters and in the manner in which these materials are used in technical applications. The majority of the authors of the various chapters are important members of the Phosphor Research Society and they have all made significant contributions to the advancement of the phosphor field. Many of the contributors have played central roles in the evolution and remarkable development of lighting and display industries of Japan. The contributors to the original Japanese version of the Handbook have provided English translations of their articles; in addition, they have all updated their contributions by including the newest developments in their respective fields. A number of new sections have been added in this volume to reflect the most recent advances in phosphor technology.

As we approach the new millennium and the dawning of a radical new era of display and information exchange, we believe that the need for more efficient and targeted phosphors will continue to increase and that these materials will continue to play a central role in technological developments. We, the co-editors, are pleased to have engaged in this effort. It is our earnest hope that this Handbook becomes a useful tool to all scientists and engineers engaged in research in phosphors and related fields and that the community will use this volume as a daily and routine reference, so that the aims of the Phosphor Research Society in promoting progress and development in phosphors is fully attained.

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*chapter one*

# *Introduction to the handbook*

***Shigeo Shionoya***

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This Handbook is a comprehensive description of phosphors with an emphasis on practical phosphors and their uses in various kinds of technological applications. Following this introduction, Part II deals with the fundamentals of phosphors: namely, the basic principles of luminescence and the principal phosphor materials and their optical properties. Part III describes practical phosphors: phosphors used in lamps, cathode-ray tubes, X-ray and ionizing radiation detection, etc. Part IV describes the common measurement methodology used to characterize phosphor properties, while Part V discusses a number of related important items. Finally, Part VI details some of the history of phosphor technology and industry.

## *1.1 Terminology*

The origin and meaning of the terminology related to phosphors must first be explained. The word *phosphor* was invented in the early 17th century and its meaning remains unchanged. It is said that an alchemist, Vincentinus Casciarolo of Bologna, Italy, found a heavy crystalline stone with a gloss at the foot of a volcano, and fired it in a charcoal oven intending to convert it to a noble metal. Casciarolo obtained no metals but found that the sintered stone emitted red light in the dark after exposure to sunlight. This stone was called the "Bolognian stone." From the knowledge now known, the stone found appears to have been barite ($BaSO_4$), with the fired product being BaS, which is now known to be a host for phosphor materials.

After this discovery, similar findings were reported from many places in Europe, and these light-emitting stones were named *phosphors*. This word means "light bearer" in Greek, and appears in Greek myths as the personification of the morning star Venus. The word *phosphorescence*, which means persisting light emission from a substance after the exciting radiation has ceased, was derived from the word *phosphor*.

Prior to the discovery of Bolognian stone, the Japanese were reported to have prepared phosphorescent paint from seashells. This fact is described in a 10th century Chinese document (Song dynasty) (see 18.7 for details). It is very interesting to learn that the credit for preparing phosphors for the first time should fall to the Japanese.

The word *fluorescence* was introduced to denote the imperceptible short after-glow of the mineral fluorite ($CaF_2$) following excitation. This is to distinguish the emission from *phosphorescence*, which is used to denote a long after-glow of a few hours.

The word *luminescence*, which includes both fluorescence and phosphorescence, was first used by Eilhardt Wiedemann, a German physicist, in 1888. This word originates from the Latin word *lumen*, which means light.

Presently, the word *luminescence* is defined as a phenomenon in which the electronic state of a substance is excited by some kind of external energy and the excitation energy is given off as light. Here, the word *light* includes not only electromagnetic waves in the visible region of 400 to 700 nm, but also those in the neighboring regions on both ends, i.e., the near-ultraviolet and the near-infrared regions.

During the first half of this century, the difference between fluorescence and phosphorescence was a subject actively discussed. Controversy centered on the duration of the after-glow after excitation ceased and on the temperature dependence of the after-glow. However, according to present knowledge, these discussions are now meaningless.

In modern usage, light emission from a substance during the time when it is exposed to exciting radiation is called *fluorescence*, while the after-glow if detectable by the human eye after the cessation of excitation is called *phosphorescence*. However, it should be noted that these definitions are applied only to inorganic materials; for organic molecules, different terminology is used. For organics, light emission from a singlet excited state is called *fluorescence*, while that from a triplet excited state is defined as *phosphorescence* (see 2.5 for details).

The definition of the word *phosphor* itself is not clearly defined and is dependent on the user. In a narrow sense, the word is used to mean inorganic phosphors, usually those in powder form and synthesized for the purpose of practical applications. Single crystals, thin films, and organic molecules that exhibit luminescence are rarely called phosphors. In a broader sense, the word phosphor is equivalent to "solid luminescent material."

## 1.2 *Past and present phosphor research*

The scientific research on phosphors has a long history going back more than 100 years. A prototype of the ZnS-type phosphors, an important class of phosphors for television tubes, was first prepared by Théodore Sidot, a young French chemist, in 1866 rather accidentally (see 3.7.1 for details). It seems that this marked the beginning of scientific research and synthesis of phosphors.

From the late 19th century to the early 20th century, Philip E.A. Lenard and co-workers in Germany performed active and extensive research on phosphors, and achieved impressive results. They prepared various kinds of phosphors based on alkaline earth chalcogenides (sulfides and selenides) and zinc sulfide, and investigated the luminescence properties.

They established the principle that phosphors of these compounds are synthesized by introducing metallic impurities into the materials by firing. The metallic impurities, called luminescence activators, form luminescence centers in the host. Lenard and co-workers tested not only heavy metal ions but various rare-earth ions as potential activators. Alkaline chalcogenide phosphors developed by this research group are called Lenard phosphors, and their achievements are summarized in their book.[1]