

# **BORATE PHOSPHORS**

## Processing to Applications



Edited by  
**S. K. OMANWAR**  
**R. P. SONEKAR**  
**N. S. BAJAJ**

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# Preface

Borates also play important roles in the family of material science due to its simple structural and chemical properties. The borate-based phosphors have attracted much attention, due to their high optical stability, can be synthesized by using low-cost synthesis through conventional and non-conventional methods. The technology based on these materials are also environmentally friendly. Moreover, it allows to select the number of borates compounds with different structures. Hence, depending on their selection, they can be used in a variety of applications based on phosphor technology that can start from your daily utilities and end up at medical and radiological applications. However, the synthesis of borate phosphors with desired structures is at best tricky and hence the selection of proper technique is plays a vital role.

In this book, we have discussed the structural and chemical parameters of borates as phosphors, the suitable synthesis methods and way of proper characterization of materials. Also, we have made a tremendous literature survey on borate materials based on their applications. This book covers the entire electromagnetic spectra utilized for fetching luminescence from the prepared borate material through the globe. On the basis of that, the chapters were distributed and formulated; likewise the book starts with an introduction to borates, their properties and synthesis technique and ends on their modification in properties of borate functional groups when mixed up or substituted with other metallic functional groups.





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# Editors' Biographies

**Dr. S. K. Omanwar recently retired as a Sr. Professor (HAG) and Former Head**, Department of Physics, on June 30, 2019, and since July 1, 2019, he has been working as a distinguished UGC-BSR Faculty Fellow at Sant Gadge Baba Amravati University, Amravati – 444602 (M.S.), India.

Dr. Omanwar has more than 32 years of teaching and administrative experience and a distinctive research career in developing inorganic luminescent materials for various applications such as mercury free lamps, SSL, display devices, LED-based photo-therapy devices, spectral matching phosphors for solar PV panels, PL-LCD panels, PDP panels, CFL bulbs and TLD and OSL materials for personnel radiation monitoring, as well as biomaterials. He has developed the commercially viable competitive products such as TLD, OSL and SSL devices. He has also developed a cost-effective method such as simple combustion method with little modification for the easy synthesis of these materials. Besides having sponsored research projects, he has received good citations with SCOPUS (163) and Thomson & Reuters (122). He has delivered several invited talks at many international events and is a life member of 11 national organizations. He has been a mentor for many Ph.D. scholars and PG students from 1986 till date. He has been the recipient of 26 awards and 178 recognitions.

**Dr. R. P. Sonekar, Ph.D., Professor**, Department of Physics, G. S. College Khamgaon (MH), India

Dr. R. P. Sonekar was awarded a master's degree from the RTM Nagpur University, Nagpur, in 1989 and his Ph.D. (physics) on borates from SGB Amravati University in 2008. Looking at his excellence soon after his master's degree, he was appointed as assistant professor at G.S. Arts, Commerce and Science College, Khamgaon, affiliated with the SGB Amravati University, Amravati. During his career, he has achieved many milestones in the field of research. He has completed two minor and one major project on borates. He also obtained a FIP fellowship from UGC to complete his Ph.D. work in borates. Dr. Sonekar has expertise in borate phosphors till date and he has guided 5+ students strictly on synthesis and application of borates. He has excellent publications in indexed journals.

**Dr. N. S. Bajaj, Ph.D., UGC- Fellow, Assistant Professor**, Department of Physics, Toshniwal Arts, Commerce and Science College, Sengaon, Dist: Hingoli (MH), India.

Dr. N. S. Bajaj obtained his master's degree from the Vidhyabharti College, Amravati, affiliated with the SGB Amravati University, Amravati, in 2008 and his Ph.D. (physics) from the same university in 2014. He served from 2010–2015 as a UGC-Project Fellow at SGB Nagpur University, in a project sanctioned under the supervision of Dr. S. K. Omanwar. He also served various colleges under the same university as a visiting lecturer. In 2015, he became an assistant professor at the Toshniwal Arts, Commerce and Science College, Sengaon affiliated to SRTM University, Nanded. During his short career, he has achieved many milestones in the field of research and received a couple of international awards and recognitions. Recently, he was awarded the most precious award: Marathwad Bhushan Award. Dr. Bajaj has expertise in the synthesis of phosphors and phosphor application radiation dosimeter. He has excellent publications in indexed journals.



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# Contributors

**A. B. Chauhan**

Department of Physics  
Vidyabharti Mahavidyalay  
Maharashtra, India

**Devayani Chikte (Awade)**

Department of Physics  
G. N. Khalsa College  
Maharashtra, India

**A. B. Gawande**

Department of Physics  
MVPS G.M.D. Arts  
B.W. Commerce & Science College  
Maharashtra, India

**K. A. Koparkar**

M. S. P. Art & Science and K. P. T. Commerce  
College Manora  
Maharashtra, India

**Rupali Korpe**

Department of Physics  
Shri Shivaji Science College  
Maharashtra, India

**Yogesh K. More**

Department of Physics  
Bhiwapur Mahavidyalaya  
Maharashtra, India

**P. A. Nagpure**

Department of Physics  
Shri Shivaji Science College,  
Maharashtra, India

**C. B. Palan**

Department of Physics  
B S Patel ACS College Pimpalgaon  
Maharashtra, India

**Vaishali Raikwar**

Ramniranjan Jhunjhunwala College  
Maharashtra, India

**N. S. Sawala**

Government Polytechnic  
Maharashtra, India

**Pritee K. Tawalare**

Department of Physics  
Jagadamba Mahavidyalaya  
Maharashtra, India



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# 1 Introduction to Borate Phosphors

*P. K. Tawalare and A. B. Gawande*

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## 1.1 INTRODUCTION

The varied aspects of luminescence and the complex processes involved in the origin of light emission, offer interesting challenges for researchers in this field. This is one of the research fields, wherein diverse application area exists, which range from radiation monitoring for health and safety, phosphors for lamps and display purposes to X-ray imaging and other means of medical diagnostics.

Luminescence is a well-established field of scientific research. In 1652, Zechi made an important contribution to the understanding of photoluminescence. It is the emission of light, which persists after the excitation agency, is removed (luminescence). Moreover; he proved experimentally that the color of the phosphorescence light in a material is independent of the color of the exciting light and also clearly distinguished the phenomenon from scattering. About 200 years later, Stoke showed that the incident and emitted light differed in color and enunciated his well-known Stoke's law regarding the increase in wavelength, which accompanies photoluminescence. In 1867, E. Becquerel distinguished two types of phosphorescence or after-glow, which were attributed respectively to monomolecular and to bimolecular decay mechanism.

The last few decades have witnessed dramatic changes in research on luminescence. There has been a phenomenal growth in the subject, and a significant progress has been made in the field of luminescence research. Recent research is characterized by strong interaction among other branches of solid-state physics and between different areas of luminescence using inorganic and organic materials. Both experimental as well as theoretical approaches have been made.

Luminescent materials are called phosphors. The first systematic study of luminescent crystals was made by Lenard [1] and his school, at the beginning of the 20th century. The phosphors they studied are called 'Lenard Phosphors'. The practical interest in luminescent materials for use in efficient cathode ray screens, and eventually for luminescent lamps, which were then developed in 1930s, stimulated the study of crystal luminescence in a very substantial way.

## 1.2 PHOSPHORS

Phosphors are solid, luminescent materials that emit photons when excited by an external energy source, such as an electron beam (cathodoluminescence) or ultraviolet light (photoluminescence). Phosphors are composed of an inert host lattice, which is transparent to the excitation radiation and an activator, typically a 3d or 4f electron metal, which is excited under energy bombardment. The process of luminescence occurs by adsorption of energy at the activator site, relaxation, and subsequent emission of a photon and a return to the ground state. The efficiency of a phosphor depends on the amount of relaxation that occurs during the activation and emission. Relaxation is the process in which energy is lost to the lattice as heat; it needs to be minimized in order to extract the highest luminous efficiency. The luminous efficiency is defined as the ratio of the energy emitted to the energy absorbed.

## 1.3 APPLICATIONS OF PHOSPHORS

The substantial advances in understanding luminescent phenomena and the discoveries of unusual luminescent processes, for example, up-conversion and quantum splitting, present unusual opportunities for the applications of luminescence. In some instances, these possible applications depend on improvements in efficiencies and stabilities of inorganic luminescent materials; in other instances, on the problems of adapting the available scientific understanding of luminescent phenomena to established techniques. Luminescent materials find applications ranging from as commonplace as lighting to very sophisticated such as lasers. Some of the applications of luminescence are given in Table 1.1.

### 1.3.1 LUMINESCENCE PHENOMENON

#### 1.3.1.1 Principle

Luminescence is defined as the emission of light by bodies, which is in excess of that attributable to black body radiation, and persists considerably longer than the periods of electromagnetic radiations in the visible range after the excitation stops.

Important characteristics which distinguish luminescence from other light emitting phenomena are time lag between the excitation and emission, spectral distribution of emission and its temperature dependence. Thus, for black body radiation, the emission maximum shifts to shorter wavelengths with increasing temperature, while the reverse is true for photoluminescence (PL). Again, intensity of emission increases with temperature for black body radiation, while the photoluminescence intensity decreases with temperature due to thermal quenching.

The luminescent system generally consists of a host lattice and a luminescent centre, often called an 'activator'. In general, the host needs to be transparent to the radiation source used for the excitation process. The activator absorbs the exciting radiation and is raised to an excited state. The excited state returns to the ground state by emission of radiation or by non-radiative decay. It is necessary to suppress this non-radiative process. In some materials, the excitation radiation is not absorbed by the activator but the other ion may absorb the exciting radiation and subsequently transfer it to the activator. In this case, the absorbing ion is called a 'sensitizer'. In many cases, the host lattice transfers its excitation energy to the activator so that the host lattice acts as the sensitizer. High-energy excitation always excites the host lattice. Direct excitation of an activator is only possible with ultraviolet and visible radiation [2].

**TABLE 1.1**  
**Classification of luminescence with excitation source and applications**

Luminescence type	Excitation source	Applications
Photoluminescence	Photons	Fluorescent lamps, PL-LCD, plasma display, LASERS, LSCs, paints, inks, upconversion material
Cathodoluminescence	Electrons	TV set, FED, oscilloscope, monitors, storage tubes, flying spot scanners, radars
Electroluminescence	Electric field	LEDs, EL displays, diode lasers
Radioluminescence	Ionizing radiations such as X-rays or gamma rays	X-ray imaging, scintillators, dosimetry
Optically stimulated luminescence	Visible Photons	X-ray radiography, dosimetry
Lyoluminescence	Chemical reaction	Detectors, analytical devices, lyoluminescence dosimetry
Chemiluminescence	Chemical reaction	Analytical chemistry
Bioluminescence	Biochemical reaction	Analytical chemistry
Thermoluminescence	Ionizing radiations	Radiation dosimetry, archeological and geological dating, forensic science
Triboluminescence	Mechanical energy	Mechanical engineering, energy, biological monitoring, and sensors as well as lighting, imaging, and displaying
Sonoluminescence	Ultrasound	Estimating the extreme temperatures generated in the bubbles during implosion

### 1.3.1.2 Excitation

In general, luminescence may be excited by a number of agents such as light, cathode rays or positive ion bombardment or X-rays, by contact with flame, or by friction. The region of wavelengths for which a given material can be excited by optical means with high efficiency usually consists of one or more broadbands, which are characteristic of both the host material and the activator. The position of the bands evidently is of much importance for practical purposes. For example, it is important that the given material possess a prominent excitation band at 253.7 nm, if it is to be excited by radiation from a low-pressure mercury discharge. It should be emphasized that not all crystals possessing a high efficiency for optical excitation, also possess a high efficiency for excitation by cathode rays. It has generally been observed that the efficiency of excitation of luminescence decreases, reversibly, as the temperature is raised sufficiently.

### 1.3.1.3 Emission

The emission spectra of luminescent material usually consists of one or more bands whose position is related to the activator. In general, peaks become narrower and narrower in the crystalline materials as the temperature of the specimen is lowered, and they approximate sharp lines near the absolute zero of the temperature. It is clear that if the electrons, which absorb energy and radiate light, are in the well-shielded inner shells of the atom (for example, rare earth ions), excitation may have relatively little effect upon the chemical binding, in which case the degradation of energy will be smaller than it would be if the electrons that are to be excited are in the outermost shell.

### 1.3.1.4 Decay Characteristics

An examination of the decay properties of the luminescent materials indicate that they fall in to two broad classifications [3]:



In the first type, the decay equation is given by:

$$I(t) = I_0 \exp(-\alpha t)$$

where  $I_0$  is the initial intensity,  $I(t)$  is the intensity at time  $t$  and  $\alpha$  is a constant.

This resembles closely the process governing the progress of monomolecular reaction. This behavior suggests that in these cases the luminescence takes place by simple excitation with subsequent optical emission in the active centre, the excitation energy remaining closely localized in the centre between excitation and emission. The decay constant is independent of temperature and is small.

Most of the luminescent materials, which are valued for their long decay characteristics, obey a decay equation of second type:

$$I(t) = I_0/(\beta t + 1)^n$$

where  $I_0$  is the initial intensity,  $I(t)$  is the intensity at time  $t$  and  $\beta$  and  $n$  are constants.

This equation is similar to the rate equation for the bimolecular reaction. The constant  $\beta$  is dependent on temperature. The atoms or clusters of atoms become ionized during the excitation and the luminescent radiation is emitted during recombination of the free electrons and the ionized centres. Johnson [4,5] has suggested that essentially all centres become ionized during excitation and that a majority of free electrons are recaptured into a state, which has a very long lifetime (of the order of milliseconds), because the optical transition to the ground state is forbidden. These electrons contribute an exponential component to the decay curve. The remaining electrons are captured at the trapping centres and are released over a period of time that is long compared to the lifetimes of the excited state of the fluorescing centre. The second class of electrons is responsible for the bimolecular component of the decay curve.

### 1.3.1.5 Mechanism

The configurational coordinate model describes the electronic transitions of absorption and emission [6]. It shows the potential energy curves of the absorbing centre as a function of configurational coordinates. In optical absorption, the centre is promoted from its ground state to the high vibrational level of the excited state. The centre returns first to the lowest vibrational level of the excited state, giving up excess energy to the surroundings. This is schematically shown in Figure 1.1.

The activator ions possess energy levels that can be populated by direct activation or indirectly by energy transfer, and are responsible for the luminescence. Generally, two types of activator ions can be distinguished. In the first type the energy levels of the activator ions involved in the emission process show only weak interactions with the host lattice (e.g. many of the lanthanide ions  $\text{Ln}^{3+}$ ). The characteristic line emission spectra can be observed in this case. The second types of activator ions strongly interact with the

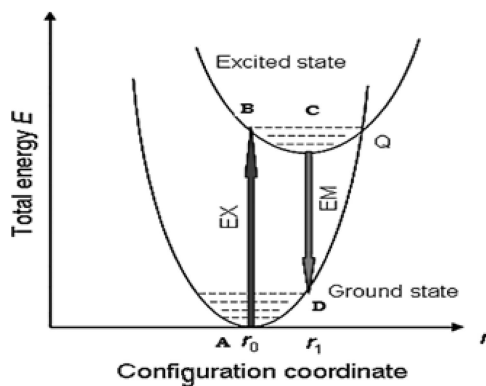


FIGURE 1.1 A schematic illustration of a configurational coordinate model.

host lattice (e.g.  $\text{Mn}^{2+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pb}^{2+}$ , etc.). The strong couplings of the electronic states with vibrational modes of the lattice mainly lead to more or less broadbands in the spectrum. The half width (FWHM) is related to the Stokes shift  $S$ , which is the energy difference between absorption and emission maximum.

$$\text{FWHM} = \sqrt{8 \ln 2} \sqrt{2kT} \sqrt{S[\text{eV}]}$$

$$S = S_e h\omega_e + S_g h\omega_g$$

$S_e$  and  $S_g$  are Huang-Rhys parameters for the excited and ground state, respectively.

Phosphors that show an emission with a large Stokes shift usually exhibit a low quenching temperature, which is disadvantageous for many applications.

In general, the luminescent process can be divided into the steps of energy absorption, energy transfer and emission. Energy absorption need not take place at the activator ion itself but can occur at random places in the lattice. This implies that energy transfer of the absorbed energy to the luminescent centre takes place before emission can occur. The migration of energy absorbed by the lattice can take place through one of the following processes:

- Migration of electric charge (electrons, holes),
- Migration of excitons,
- Resonance between atoms with sufficient overlap integrals,
- Re-absorption of photons emitted by another activator ion or sensitizer.

The occurrence of energy transfer within a luminescent material has far-reaching consequences for its properties as a phosphor. On the other hand, the absorbed energy can migrate to the crystal surface or to the lattice defects, where it is lost by radiation-less deactivation. As a consequence, the quantum efficiency of the phosphor declines.

Besides the quantum yield, the quality of a phosphor material is further characterized by its colour points, the lumen equivalent, the reflection spectrum and the emission lifetime under given excitation conditions. The colour point is derived from the spectral energy distribution of the emission and is defined according to the convention of the *Commission Internationale d'Eclairage* (CIE) in a normalized two-dimensional coordinate system shown in Figure 1.2.

For lighting applications, the colour saturation of the phosphors is of less importance. In contrast, the luminescent materials should emit a spectrum with a high lumen equivalent. This value is calculated by multiplication of the spectral power distribution  $P(\lambda)$  of the phosphor

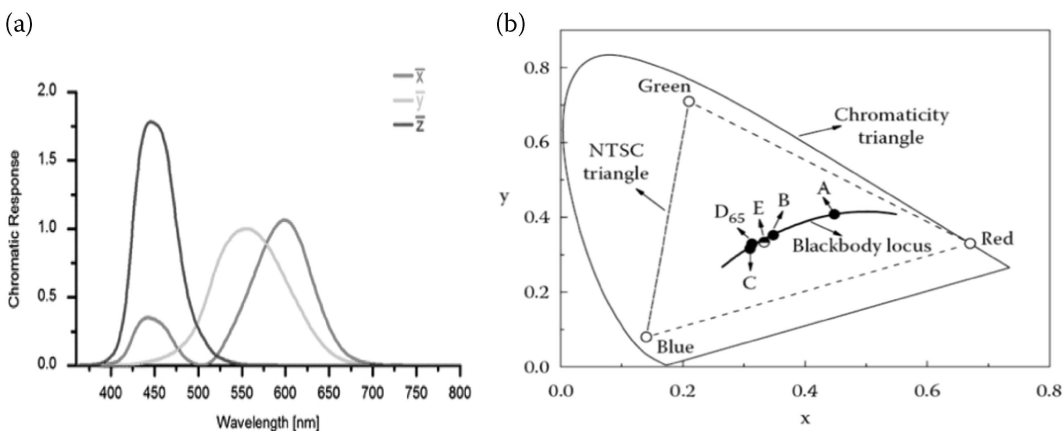


FIGURE 1.2 (a) 1931 CIE XYZ colour-matching. (b) 1931 CIE chromaticity diagram.

emission, which integral has been normalized with the spectral luminous efficiency (LE) for the human eye  $V(\lambda)$ :

$$LE = \int_{380}^{780} V(\lambda) P(\lambda) d\lambda \quad [\text{lm/W}]$$

To obtain white light with a high lumen equivalent, it is important that the phosphors applied in a mixture display very sharp emission spectra or even better emission lines, rather than broad emission spectra; otherwise a light is generated in spectral areas where the eye sensitivity is too low. Naturally, also the emission maximum of line emitting phosphors should not be too far off the eye sensitivity curve maximum.

To determine just how efficient a phosphor is, the term ‘quantum efficiency’ (QE) is defined. It is the ratio between the number of photons emitted and the number of photons absorbed by the phosphor. Generally, the phosphors that have QEs of 80% or greater are considered to be efficient phosphors.

Besides the quantity, there is also a quality performance of light sources with one factor usually being traded off against the other. Light quality is mainly determined by the colour rendering of the light source, which is the ability to display the colours of an irradiated object in a natural way. A qualitative measure is the colour-rendering index (CRI), which by definition can adopt values between 0 and 100. This value is calculated by comparing the reflection spectra of selected test colours obtained by irradiation with the light source under investigation with the reflection spectra when irradiated in the same way with a black body radiator. By definition, a black body radiator has a colour-rendering index of 100. In contrast, a line emitter with a single emission line at any part of the visible spectral region has a CRI of zero, because colours cannot be displayed under such an irradiation source. While a combination of line emitters yields high light output but moderate CRI, broadband emitters enable higher CRI values to be obtained. In addition, colour rendering is dependant on the spectral position of the emission maximum and thus on the spectral power distribution of the phosphor. A compromise has to be found between colour rendering and high light output.

The luminescence efficiency of a phosphor falls at higher temperatures. This is called ‘temperature quenching’. The activator concentration in excess may also cause reduction in the intensity of the phosphor, which is termed ‘concentration quenching’. There are some impurities whose presence, even in very small amount, will reduce the intensity of the phosphor. Such impurities are called as ‘killer impurities’.

### *Classification of Luminescence*

‘Luminescence’ is the general term that covers both fluorescence and phosphorescence. The concept of fluorescence originated from the mineral fluorite because the phenomenon of light emission under ultraviolet radiation was first recognized in that mineral. Phosphorescence is named after the well-known optical property of the element phosphorous. In Greek, the term ‘phosphor’ means ‘light bearer’. But the chemical element phosphorous is not phosphor. The difference between fluorescence and phosphorescence is to some extent arbitrary. Historically, the temperature independent decay is known as fluorescence while the temperature-dependent decay is phosphorescence. According to modern conventions, fluorescence refers to the emission, which persists for  $10^{-3}$  s to  $10^{-8}$  s while the phosphorescence persists for a considerably longer duration from  $10^{-3}$  s to several seconds. The various types of luminescence are distinguished by a prefix, which denotes the mode of excitation, e.g. photoluminescence is caused by the absorption of photons of visible or near-visible radiation, electroluminescence is caused due to electric field etc. Thermoluminescence is rather a misnomer. Thermoluminescence is the thermally stimulated luminescence excited by other means and the thermal energy is not the source of excitation.

There are a variety of luminescence phenomena observed in nature or in man-made materials. The nomenclature given to these is invariably related to the exciting agent, which produce the luminescence. Following description summarizes the main types of the luminescence emission phenomena.

### *Photoluminescence*

This is the emission produced by excitation with the light photons. The fluorescent lamp used in household and general lighting is the principal example of this. A 254 nm UV radiation from the mercury vapor discharge is absorbed by one of activator impurities in the phosphor coated on the inner side of the glass tube. Some of this energy is transferred by resonance to a second impurity. By adjusting the relative concentrations of these activator impurities, one can produce desired modification in the colour of the light. There are a large variety of organic and inorganic phosphors, which are used in the consumer items like in road and traffic signals, displays, laundry whiteners, etc. in addition to those used in industrial and scientific applications. An example of high technology is called LASER, a kind of photoluminescence in which emission is coherent.

### *Cathodoluminescence*

When electron beams generated at the electrical cathodes do excite, the emission produced is called cathodoluminescent. The screens of cathode ray tubes and television tubes glow by this kind of emission. In cathode ray tubes, zinc and cadmium sulfide phosphors are used.

### *Radioluminescence*

When X-rays or nuclear radiations provide the excitation energy, the resulting luminescence is called radioluminescence.

### *Scintillation*

This phenomenon is the same as radio-luminescence. It is given this name because it is used as a technique to detect individual light pulses generated by the incidence of each X-ray, or gamma ray photon or a nuclear particle. Such light pulses are called scintillations, since like a spark they are very short lived. Thallium-activated sodium iodide is a well-known scintillation detector used for gamma ray spectrometry. The intensity of the scintillation (light pulse) is directly proportional to the energy of the incident gamma ray photon (when it is totally absorbed). The measurement of this pulse intensity, therefore, provided the means for knowing the gamma ray energy.

### *Electroluminescence*

Application of electric fields can produce luminescence in many phosphors. There is another type of electroluminescence, known as injection luminescence. In this, electrons are injected from an external supply across a semiconductor p-n junction. On applying a DC voltage across the junction, such that the electrons flow to the p-region, luminescence is produced by the electron-hole recombination in that region. The light emitting diodes (LEDs), which are now commonly used as display devices in many scientific instruments, are based on this principle.

### *Chemiluminescence*

Some chemical reactions are the source of luminescence. The oxidation of white phosphorous in air is the best-known example of this. All chemical molecules are not capable of luminescence. Lyo-luminescence, which is caused during the dissolution of certain compounds, which have been bombarded by X-rays beforehand, is a kind of chemiluminescence. A well-known example is the case of X-irradiated NaCl, which emits a flash of light when quickly dissolved in water.

### *Bioluminescence*

Biochemical reactions inside the cell of living organisms can produce electronic excited states of the biomolecules. Fire flies, glowworms, some bacteria and fungi and many sea creatures, both near the surface and at great depths, are the striking examples of luminescence in living beings.

### *Triboluminescence*

A large number of inorganic and organic materials subjected to mechanical stress emit light, which is called triboluminescence. It has also been named mechanoluminescence by some authors. The spectra of triboluminescence light are similar to those of photoluminescence in many substances.

### *Thermoluminescence*

Unlike the various types of luminescence phenomena listed above, the prefix ‘thermo’ here does not mean the form of excitation energy, but to stimulation of luminescence, which was excited in a different way. The primary agent for the induction of TL in a material is the ionizing radiation (X-rays or gamma radiation) or sometimes even UV rays to which the material is exposed. The light produced by subsequent heating of material is called TL.

The most broadly investigated and utilized of all thermally stimulated phenomena is the emission of light during the heating of a solid sample, previously excited. The initial excitation (typically by irradiation) is the source of energy, whereas the heating serves only as a trigger, which helps in releasing this accumulated energy. The term thermally stimulated luminescence (TSL) is more descriptive; however, ‘thermoluminescence’ is traditionally more often utilized and popularly accepted.

As noted except for very unusual cases, the occurrence of the TL curve following a given irradiation is a ‘one-shot’ effect. Cooling the sample and re-heating it normally does not result in a second TL emission.

### *Luminescent Materials*

The general materials used as phosphors may be classified according to their use in the application or according to the chemical forms. Considering the synthesis viewpoint they are classified here on the basis of their chemical forms. The main categories are as follows:

- a. Inorganic materials: These are mainly solid-state compounds that consist of crystals 1–10  $\mu\text{m}$  in size. The inorganic phosphor usually consists of a host lattice with activator ions doped into it in small concentrations, typically a few mole percent or less. The activator ions possess energy levels that can be populated by direct excitation or indirectly by energy transfer, and are responsible for the luminescence. Generally, two types of activator ions can be distinguished. In the first type, the energy levels of the activator ion involved in the emission process show only weak interaction with the host lattice. Typical examples are many of the lanthanide ions  $\text{Ln}^{3+}$ , where the optical transitions take place solely between 4f terms that are well shielded from their chemical environment by outer electrons. As a consequence, characteristic line emission spectra can be observed. The second type of activator ions strongly interact with the host lattice. This is the case when d electrons are involved. For example, in  $\text{Mn}^{2+}$ ,  $\text{Eu}^{2+}$ , and  $\text{Ce}^{3+}$ , as well as for s2 ions like  $\text{Pb}^{2+}$  or  $\text{Sb}^{3+}$ , or for complex anions such as  $\text{MoO}_4^{2-}$  or  $\text{NbO}_4^{2-}$ . The strong coupling of the electronic states with vibrational modes of lattice mainly lead to more or less broadbands in the spectrum.

Some of the host materials used for inorganic phosphors are aluminates, arsenates, borates, bromides, carbonates, chlorides, chromates, cuprates, fluorides, ferrites, germanates, gallates, indates, iodides, manganates, nitrides, oxides, phosphates, selenides, silicates, sulphides, sulphates, tantalates, titanates, tungstates, uranates, vanadates, zirconates, halophosphates and apatite structures.

- b. Organic materials: These are either polymers or low molecular weight materials applied as thin films or solid solutions. The most recent class of materials comprises main chain polymers with isolated chromophores and side chain polymers with linked chromophores. They are mainly used in organic light emitting diodes (OLEDs) [7].
- c. Hybrid compounds: This class generally includes the organically modified silicates (ORMOSIL) [8] and hybrid organic-inorganic complexes such as  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , or their complexes with  $\beta$ -diketones, aromatic carboxylic acids and heterocyclic ligands such as 2,2'-bipyridine and 1,10-phenanthroline, into various matrices [9].

## 1.4 BORATE-BASED PHOSPHORS

Borates are naturally occurring minerals containing boron, the fifth element on the periodic table. The element boron does not exist by itself in nature. Rather, boron combines with oxygen and other elements to form inorganic salts called borates. Boron has an ionic radius 0.11 Å and hence can occur in both triangular ( $\text{BO}_3$ ) and tetrahedral ( $\text{BO}_4$ ) coordination where bonded to oxygen [10].  $\text{BO}_3$  groups have an average B-O bond-valance approximately equal to 1 valence unit and  $\text{BO}_4$  groups have an average B-O bond-valance approximately equal to 3/4 valence unit. Hence, both ( $\text{BO}_3$ ) and ( $\text{BO}_4$ ) groups can polymerize by sharing corners without violating the valance sum rule. Such polymerization is very common in both minerals and synthetic inorganic compounds. In general, a borate structure contains clusters of corner sharing ( $\text{BO}_3$ ) and ( $\text{BO}_4$ ) polyhedra, which occur as discrete polyanions to form larger clusters, chains, sheets or frameworks [11]. Since the boron atom is capable of coordination in either trigonal or tetragonal mode [12–14], borate anions exist in numerous structural types. There are hundreds of different structures with various borate anionic groups as basic structural units in the known borate crystals [15]. However, there are only a few types of basic structural units of borates of practical interest [12,16]:

- i.  $(\text{BO}_3)^{3-}$
- ii.  $(\text{BO}_4)^{5-}$
- iii.  $(\text{B}_2\text{O}_5)^{4-}$
- iv. (iv)  $(\text{B}_2\text{O}_7)^{8-}$
- v.  $(\text{B}_3\text{O}_6)^{3-}$
- vi.  $(\text{B}_3\text{O}_7)^{5-}$
- vii.  $(\text{B}_3\text{O}_8)^{7-}$
- viii.  $(\text{B}_3\text{O}_9)^{9-}$
- ix.  $(\text{B}_5\text{O}_{10})^{5-}$
- x.  $(\text{B}_4\text{O}_9)^{6-}$

A variety of pre-decided inorganic borate host materials attempted for successful synthesis and verifying the potential photoluminescence characteristics are listed in Table 1.2. In addition to the pre-decided list, a few new materials (hosts) are successfully synthesized.

### 1.4.1 CLASSIFICATION OF BORATES

Inorganic borate host compounds are classified into various groups on the basis of chemical composition and crystal structure.

#### 1.4.1.1 Classification of Borates Based on Chemical Formula

#### 1.4.1.2 Classification of Borates Based on Crystal Structure

Borate host inorganic compounds exist in numerous crystal structures. On the basis of crystal structure, borate compounds were classified as follows:

##### *i. Aragonite-Type Borate*

The aragonite-type borates crystallize in the structure of the mineral aragonite  $\text{ACo}_3$ , A = Ca, Ba, Pb, Sr. The structure of the aragonite borate is composed of the triangular borate ion group ( $\text{BO}_3$ ), with a boron at the centre of the triangle and three oxygens at each corner. It has an orthorhombic symmetry.

Examples:  $\text{LaBO}_3$  [10],  $\text{NdBO}_3$  [11],  $\text{CeBO}_3$  [12].

##### *ii. Calcite-Type Borate*

The calcite-type borates are the polymorphs of aragonite with trigonal symmetry.

Figure 1.3 represents the  $\text{InBO}_3$  unit cell with (110) orientation.

Examples:  $\text{InBO}_3$ ,  $\text{LuBO}_3$ ,  $\text{ScBO}_3$  [13].

TABLE 1.2

Inorganic borates are classified on the basis of a chemical formula

Sr no.	Borate type	Metal oxide	Examples
1	Metaborate	1 B <sub>2</sub> O <sub>3</sub>	NaBO <sub>2</sub> (Na <sub>2</sub> O:B <sub>2</sub> O <sub>3</sub> ), LiBO <sub>2</sub> (Li <sub>2</sub> O: B <sub>2</sub> O <sub>3</sub> ), CaB <sub>2</sub> O <sub>4</sub> (CaO: B <sub>2</sub> O <sub>3</sub> ), BaB <sub>2</sub> O <sub>4</sub> (BaO: B <sub>2</sub> O <sub>3</sub> ), SrB <sub>2</sub> O <sub>4</sub> (SrO: B <sub>2</sub> O <sub>3</sub> ), CsBO <sub>2</sub> (Cs <sub>2</sub> O: B <sub>2</sub> O <sub>3</sub> )
2	Diborate	2 B <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (Li <sub>2</sub> O: 2 B <sub>2</sub> O <sub>3</sub> ), Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (Na <sub>2</sub> O: 2 B <sub>2</sub> O <sub>3</sub> ), ZnB <sub>4</sub> O <sub>7</sub> (ZnO: 2 B <sub>2</sub> O <sub>3</sub> )
3	Triborate	3 B <sub>2</sub> O <sub>3</sub>	LiB <sub>3</sub> O <sub>5</sub> (Li <sub>2</sub> O: 3 B <sub>2</sub> O <sub>3</sub> ), EuB <sub>3</sub> O <sub>6</sub> (Eu <sub>2</sub> O <sub>3</sub> : 3 B <sub>2</sub> O <sub>3</sub> ), CeB <sub>3</sub> O <sub>6</sub> (Ce <sub>2</sub> O <sub>3</sub> :3 B <sub>2</sub> O <sub>3</sub> ), BiB <sub>3</sub> O <sub>6</sub> (Bi <sub>2</sub> O <sub>3</sub> : 3 B <sub>2</sub> O <sub>3</sub> )
4	Tetraborate	4 B <sub>2</sub> O <sub>3</sub>	AgB <sub>4</sub> O <sub>7</sub> (Ag <sub>2</sub> O: 4 B <sub>2</sub> O <sub>3</sub> ), Na <sub>2</sub> B <sub>8</sub> O <sub>13</sub> (Na <sub>2</sub> O: 4 B <sub>2</sub> O <sub>3</sub> )
5	Pentaborate	5 B <sub>2</sub> O <sub>3</sub>	CsB <sub>5</sub> O <sub>8</sub> (Cs <sub>2</sub> O: 5 B <sub>2</sub> O <sub>3</sub> ), Na <sub>2</sub> B <sub>10</sub> O <sub>16</sub> (Na <sub>2</sub> O: 5 B <sub>2</sub> O <sub>3</sub> )
6	Hexaborate	6 B <sub>2</sub> O <sub>3</sub>	SrB <sub>6</sub> O <sub>10</sub> (2 SrO: 6 B <sub>2</sub> O <sub>3</sub> )
7	Heptaborate	7 B <sub>2</sub> O <sub>3</sub>	Li <sub>3</sub> B <sub>7</sub> O <sub>12</sub> (3 Li <sub>2</sub> O: B <sub>2</sub> O <sub>3</sub> )
8	Octaborate	8 B <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> B <sub>8</sub> O <sub>15</sub> (2 Bi <sub>2</sub> O <sub>3</sub> : 8 B <sub>2</sub> O <sub>3</sub> ), BaB <sub>8</sub> O <sub>13</sub> (2 BaO: 8 B <sub>2</sub> O <sub>3</sub> )
9	Nonaborate	9 B <sub>2</sub> O <sub>3</sub>	NaBaB <sub>9</sub> O <sub>15</sub> (Na <sub>2</sub> O:2BaO:9B <sub>2</sub> O <sub>3</sub> ), LiBaB <sub>9</sub> O <sub>15</sub> (Li <sub>2</sub> O:2BaO:9B <sub>2</sub> O <sub>3</sub> ), LiSrB <sub>9</sub> O <sub>15</sub> (Li <sub>2</sub> O:2SrO:9B <sub>2</sub> O <sub>3</sub> ), GdBaB <sub>9</sub> O <sub>16</sub> (Gd <sub>2</sub> O <sub>3</sub> :2BaO:9B <sub>2</sub> O <sub>3</sub> )
10	Deaborate	10 B <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> B <sub>10</sub> O <sub>16</sub> (K <sub>2</sub> O: 10 B <sub>2</sub> O <sub>3</sub> )

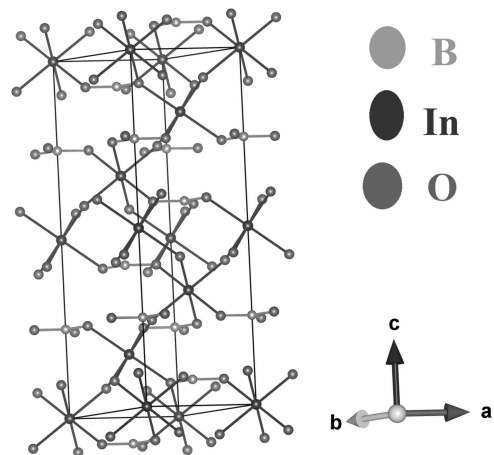


FIGURE 1.3 Ball-and-stick representation of InBO<sub>3</sub> unit cell with (110) orientation.

### iii. Vaterite-Type Borate

The vaterite-type borates are the polymorphs of aragonite with hexagonal symmetry.

Examples: SmBO<sub>3</sub>, EuBO<sub>3</sub> [14–16].

#### iv. *Stillwellite-Type Borate*

Mineral stillwellite is a family of trigonal borates with the general formula  $X [BO(SiO_4)]$  with  $X = Ce, La, Pr, Nd, Th$ . Stillwellite contains helical chains of  $(BO_4)$  tetrahedra polymerized by sharing corners [17]. These chains are decorated by  $SiO_4$  tetrahedra that share two corners with adjacent  $(BO_4)$  tetrahedra. Boron is coordinated by four oxygen atoms in a tetrahedral arrangement. The  $(BO_4)$  tetrahedra polymerize by sharing corners to form a helical chain extending along the z-axis. The periphery of the chain is decorated by  $(SiO_4)$  tetrahedra that share two corners with an adjacent  $(BO_4)$  tetrahedra. The resultant  $[BSiO_5]$  chain is the fundamental building block of the structure that is repeated by the lattice translations to form a hexagonal columnar array.

The lanthanide borate-silicate materials  $LnBSiO_5$  [18,19] ( $Ln = La, Gd, Y, Pr, Nd$ ) exhibits stillwellite structure of  $LaBSiO_5$ , shown in Figure 1.4.

#### v. *Melitite-Type Borates*

Melitite represents a family of natural and synthetic compounds  $A_2XZ_2O_7$ , where  $A = Na, Ca, Sr, Ba, Cd, Pb, Y, Ln$ ;  $X = Be, Mg, Co, Fe, Mn, Cu, Zn, Cd, Al, Ga$ ;  $Z = Be, B, Al, Si, Ge$ .  $Bi_2ZnB_2O_7$ ,  $CaBiGaB_2O_7$  and  $CdBiGaB_2O_7$  are the only examples of synthetic diborate members of the melitite family [20].

#### vi. *Leucite-Type Borates*

The leucite-type structure ( $AlSi_2O_6$ ) exists over a wide range of alkali cations from Na to Cs [21]. Al atoms can be replaced by B [22–25]. The boron-substituted leucite is known as boro leucite [26]. The examples of boroleucite are  $KBSiO_6$  [27] and  $RbBSiO_6$  [28]. The structure of leucite [29] represents a continuous three-dimensional skeleton, formed by  $(Si,Al)O_4$  tetrahedra, each of which shares all its oxygen with its neighbours [30,31].

#### vii. *Warwickite-Type Borate*

The warwickite is an orthorhombic oxyborate minerals [31] with the general formula  $M_2OBO_3$  ( $M = Mg^{2+}, Mn^{2+}, Fe^{3+}, Ti^{4+}, Al^{3+}$ ). Most transition metal oxyborates with the general formula  $M^{2+}M^{3+}BO_4$  crystallizes in an orthorhombic structure of warwickite ( $Mg_{1.5}Ti_{0.5}BO_4$ ), representing a system of linear, weakly interacting ribbons comprising two internal and external chains in which octahedrally coordinated divalent and trivalent transition metal atoms are randomly distributed over nonequivalent crystallographic positions of two types [32].  $MgGaBO_4$  is isostructural to the mineral warwickite  $(Fe,Mg)Ti(BO_4)_2$  [33]. The structure of  $MgGaBO_4$  along [001] contains ribbons of four edge-sharing octahedral formed from two pseudo-packed layers of oxygen atoms between which magnesium atoms occupy the octahedral interstices shown in Figure 1.5.

#### viii. *Mineral Huntite Borate*

These borate compounds crystallizes in the structure of the mineral huntite. These materials generally adopt a noncentrosymmetric structure, trigonal space group R32. The general formula of huntite borates is  $LnM_3(BO_3)_4$  where  $Ln = Lanthanide$  and  $M = Al, Sc, Cr, Fe, Ga$ .

Examples:  $CeSc_3(BO_3)_4$  [34],  $TbAl_3(BO_3)_4$  [35].

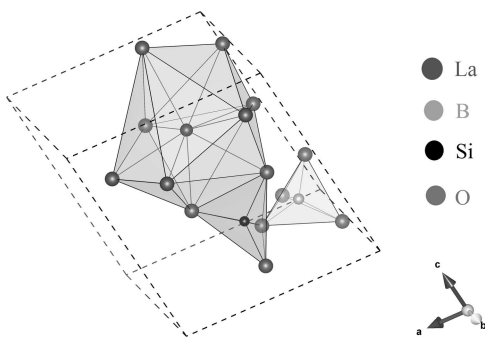


FIGURE 1.4  $LaBSiO_5$  with stillwellite structure.



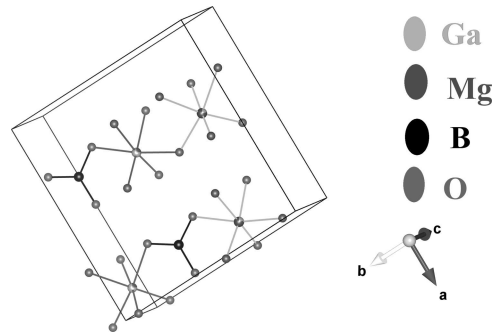


FIGURE 1.5 The structure of  $\text{MgGaBO}_4$  along  $[001]$ .

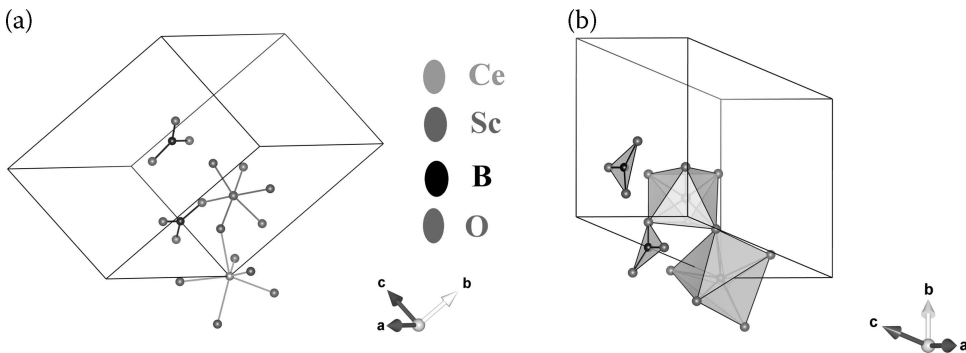


FIGURE 1.6 (a) Unit-cell contents of  $\text{CeSc}_3(\text{BO}_3)_4$ . (b)  $\text{Sc}_6\text{O}$  polyhedral connections in  $\text{CeSc}_3(\text{BO}_3)_4$ .

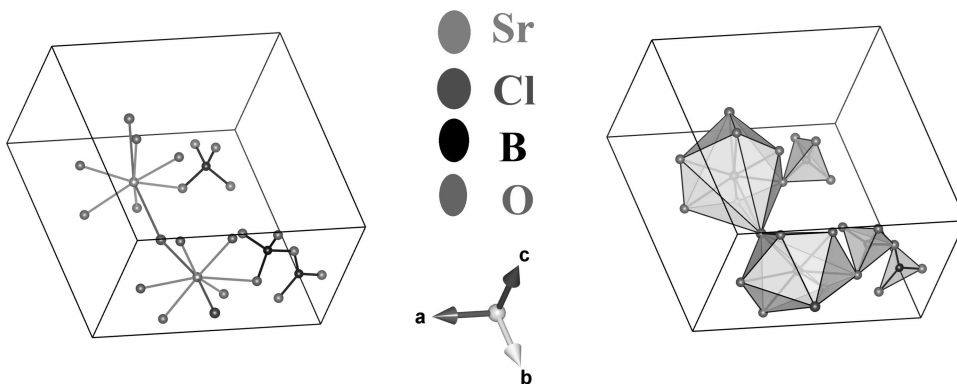
The compound  $\text{CeSc}_3(\text{BO}_3)_4$  adopts the normal trigonal huntite structure shown by Figure 1.6 with Ce-centred distorted trigonal prisms and Sc-centred distorted octahedra dispersed between planes of  $\text{BO}_3$  triangles that extend parallel to  $(001)$ . Dissimilar polyhedra share only vertices, resulting in isolation of the  $\text{CeO}_6$  prisms and  $\text{BO}_3$  triangles; the  $\text{ScO}_6$  octahedra share edges to form helices extending along  $(001)$ .

#### ix. Mineral Boracite

The boracite represents a family of compounds having the general formula  $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$  where  $\text{M} = \text{Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd}$  and  $\text{X} = \text{Cl, Br, I}$ . The term ‘boracite’ is due to the mineral  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$  [36]. At present, more than 25 isomorphous boracite compounds exist. A complete structural investigation of high and low boracite  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$  was reported by Ito et al. [37,38]. High boracite was described as cubic and low boracite as orthorhombic. Complete structural analysis was given for  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  is given in Figure 1.7.

### 1.4.2 CRYSTAL CHEMISTRY OF BORATES

In recent years, more and more research has been concentrated on borate crystals. Most of the obtained crystals contain independent orthoborate  $\text{BO}_3$  groups in their structures. The structural chemistry of anhydrous borates is characterized by a variety of discrete and condensed  $\text{BO}_3$  and  $\text{BO}_4$  anions [39]. Predominant among these structures, especially binary and more complex borates are isolated  $\text{BO}_3$  triangles (65%). Of the rest, almost one-half is represented by framework structures containing three-dimensional  $\text{B}_n\text{O}_m$  polyanions. In this case,  $\text{BO}_3$  and  $\text{BO}_4$  groups join by sharing common O atoms. Then, it is followed by insular (pyroborates and ring metaborates), network and chain-forming structures.



**FIGURE 1.7** Unit cell of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  showing coordination of Sr at various sites.

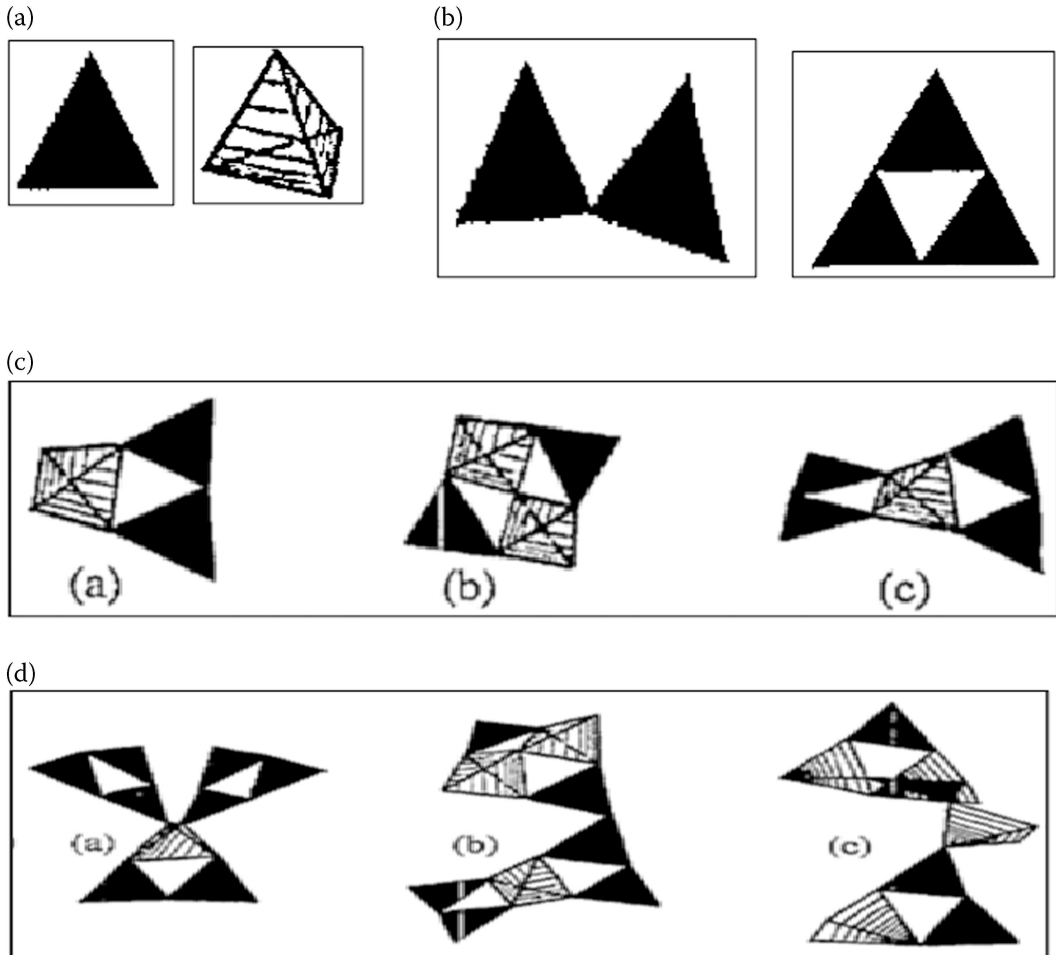
There are more than 50 types of boron-oxygen anions and polyanions in anhydrous borates [40]. However, all of them consist exclusively of three basic types of structural units of different composition. The first set of these basic types identify with  $\text{BO}_3$  triangles ( $\Delta$ ) and  $\text{BO}_4$  tetrahedra ( $\square$ ) as fundamental structural units (FSU), which are shown in Figure 1.8(a). They are isolated in orthoborates and can be merged in pyroborates, metaborates and polyborates.

The second basic type of structural units is usually built up of several FSU (from two to five) joined by sharing common O atoms. There is a rather limited number of these anionic groups. They are shown in Figure 1.8(b) and designated below as combined basic structural units (CSU). Only two of them,  $2\Delta$  and  $3\square$ , can be isolated in the structure of anhydrous pyroborates and some metaborates, respectively. The rest of the structural units of this type are components of various one-, two-, and three-dimensional  $\text{B}_n\text{O}_m$  polyanions by sharing their free O atoms.

Finally, in polyanions of anhydrous borates, it is expedient to distinguish one or more types of structural units. Structural elements of this category are, as a rule, more complex and characterize the borate structures on the whole. It is appropriate to designate these anionic groups as complete radicals of polyanions (CRP). Some of the typical CRP are demonstrated in Figure 1.8(c) and (d). The CRP may be visualized as one or more of the CSU and additional FSU ( $\text{BO}_3$  triangles and/or  $\text{BO}_4$  tetrahedra) joined by sharing common O atoms. Thus, it represents a full repeating fragment of a polyanion corresponding in composition aliquot to the B-O anion part in the structural formula of the borate. It is useful to note that the CRP identifies themselves with the CSU in the anhydrous orthoborate structures, and with the CSU in the pyroborates, metaborates and in some more complex borate compounds.

### 1.4.3 APPLICATIONS OF BORATE HOST MATERIALS AS PHOSPHORS

Solid-state inorganic borates have become a focus of technological interest due to a variety of physical and chemical features exhibited by these compounds [41]. Owing to possible three-, or fourfold coordination of borate atoms, borates form a great number of compounds having diverse structures. Borates intrinsically possess characteristics that are advantageous for optical materials [42], which include wide transparency range, large electronic bandgap, good thermal and chemical stability, low preparative temperature, optical stability with good nonlinear characteristics and exceptionally high optical damage threshold [43–45]. The unique crystal structure of borates determines their enhanced UV transparency, good nonlinearity and relatively high resistance against laser-induced damage. Recent research on inorganic borates has been focused on the synthesis and characterization of compounds with potential application as optical material [46]. Borate compounds currently have been of considerable interest to the scientific community owing to their wide range of applications: Laser, NLO material, phosphor material and scintillator material, etc. Most of the borates are polyfunctional materials with nonlinear optical, piezo-electrical and



**FIGURE 1.8** (a) Configuration of some basic B-O structural units in anhydrous borates: Fundamental structural units ( $\Delta$  and  $\square$  isolated forms occur in orthoborate structure only). (b) Combined basic structural units as insular anions in pyroborate (a) and metaborate (b). (c) Combined basic structural units forming network and framework polyanions: (a)  $2\Delta + 1\square$  (b)  $2\Delta + 2\square$  (c)  $4\Delta + 1\square$ . (d) Combined radicals of polyanions in network and framework polyborate structure: (a)  $(2\Delta + 1\square) + 2(3\Delta)$  (b)  $(4\Delta + 1\square) + (2\Delta + 2\square)$  (c)  $(2\Delta + 1\square) + (2\Delta + 2\square) + 1\square$ .

acousto-electrical properties. Some borates are also suitable as a laser material for miniature laser [47]. Borate crystals with the structure of the naturally occurring mineral huntite  $\text{CaMg}_3(\text{CO}_3)_4$  are widely known as polyfunctional materials having device potential due to their good thermal and chemical stabilities. The general formula of huntite borate is  $\text{LnM}_3(\text{BO}_3)_4$ , Ln = rare earth element and M = Al, Ga, Cr, Fe, Sc. Among them, rare earth aluminium borates  $\text{LnAl}_3(\text{BO}_3)_4$  have attracted considerable attention for their luminescence properties and possible application as single crystal mini-laser [48]. In the following sections, the applications of inorganic borate compounds as LASER and NLO material and phosphor material are discussed.

#### 1.4.3.1 Inorganic Borate as NLO and LASER Material

The NLO materials are materials used to generate new LASER sources of frequencies that cannot be obtained directly from available lasers. Efficient frequency conversion depends on crystal properties such as the effective nonlinear coefficient, refractive indices, phase-matching conditions and damage threshold. The borates with NLO properties form a large family of compounds.

The first NLO borate described was  $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$  [49] in 1975, but intense research on NLO borate materials began with the advent of low-temperature  $\text{BaB}_2\text{O}_4$  and  $\text{LiB}_3\text{O}_5$  which are the most frequently used borate materials. A subsequent search for new borate compounds led to the continued discovery of new borate compounds with improved NLO properties.

Borate materials are also useful as a self-frequency doubling active laser sources. A commercial self-frequency doubling laser source is  $\text{YAl}_3(\text{BO}_3)_4: \text{Nd}^{3+}$ . Many new borates have been recently reported. Borophosphates which contain the borate group and the phosphate group as basic structural units has also drawn attention recently, as new functional materials for application in laser technologies [50]. Complex boron oxide materials attract considerable attention because they can be used as multifunctional optical materials in which the laser effect and nonlinear optical phenomena occur simultaneously. Borotungstate with the general formula  $\text{Ln}_3\text{BWO}_9$ ,  $\text{Ln} = \text{La, Pr, Nd, Sm} - \text{Ho}$  are the promising complex borates [51]. Lanthanide calcium oxoborate  $\text{LnCa}_4\text{O}(\text{BO}_3)_3$ ,  $\text{Ln} = \text{La} - \text{Lu}$  and  $\text{Y}$ , constitute a family of compounds intensively studied since 1997 due to their good NLO properties. These crystals could be doped with rare earth and can be used for self-frequency doubling and self-frequency mixing [52].

#### 1.4.3.2 Inorganic Borate as Phosphor Material

During the past few years, a number of borate materials have been studied extensively due to their unique combinations of large electronic bandgaps, strong nonlinear optical properties, chemical and environmental stabilities and mechanical robustness. Due to their large electronic bandgaps, borate materials are excellent host lattices for luminescent ions. Rare earth borate compounds normally have high UV transparency and exceptional optical damage threshold, which makes them attractive for numerous practical applications such as in lamps and display applications. There are many excellent phosphors in the borate family, for example,  $\text{YBO}_3: \text{Eu}^{3+}$ ,  $\text{GdBO}_3: \text{Eu}^{3+}$  and  $\text{LnMgB}_5\text{O}_{10}$ , etc. which have been applied in the region of UV-excited phosphors and integrated optics [53]. Rare earth borate compounds are an interesting class of luminescent materials. The rare earth borate phosphors were first introduced by R.I. Smirnova et al. [54] and have been of little or no interest for two decades. More recently, due to rising demand for new efficient phosphors for various applications such as lamp phosphor, FPD, PDP, etc. rare earth borates have attracted attention [55,56]. Rare earth orthoborates,  $\text{RBO}_3$  ( $\text{R} = \text{Y, La, Gd}$ ), doped with rare earth ions ( $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ ) are interesting luminescent materials (56). Rare earth borates doped with  $\text{Eu}^{3+}$  are potential red-emitting phosphors. Gadolinium borate phosphors ranging from orthoborates to pentaborates have proved to be potential candidates for practical applications in fluorescent lamps due to their high efficiency [57–59].

Haloborates activated by  $\text{Ce}^{3+}$  ions have been recently shown to be a promising material for detecting thermal neutrons. Strontium haloborates doped with  $\text{Eu}^{2+}$  are well-known X-ray storage phosphors.

Plasma display panels (PDP) are regarded as the most promising candidate for large-sized flat panel displays (FPDs). Phosphors for the application in PDP are required to have high conversion efficiency by VUV radiation of 147 and/or 172 nm from the Xe gas plasma. The inorganic borate compounds have strong absorption in the VUV region [60] and therefore widely used as host lattices of phosphors for PDP applications.  $\text{LnBO}_3$  doped with  $\text{Eu}^{3+}$  has been widely used as a luminescent material in plasma display panels (PDPs) due to the high quantum efficiency and good color coordinates under 147 nm VUV excitation [61]. At present, the most widely used red-emitting phosphor for PDP is  $(\text{YGd})\text{BO}_3: \text{Eu}^{3+}$  [62]. The doped  $\text{YAl}_3(\text{BO}_3)_4$  can be utilized as red PDP phosphor (Tables 1.3 and 1.4).

- Lamp Phosphors
- Led Phosphors
- UV-Based Photo Therapy Phosphors
- PDP Phosphors
- Radiation Dosimetry Phosphors
- Mechno or Layo-luminescent Phosphors
- Nir Quantum Cutting Phosphors
- Neutron Radiography

**TABLE 1.3**  
**Borate host inorganic NLO and LASER materials**

Sr. no.	Inorganic borate	Applications	Ref.
1	CsB <sub>3</sub> O <sub>5</sub>	NLO material to generate deep UV	[63,64]
2	CsLiB <sub>6</sub> O <sub>10</sub>	NLO material for SHG and Higher order harmonic generation	[65–67]
3	YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Nd <sup>3+</sup>	Self-frequency doubling LASER material	[68–77]
4	LiB <sub>3</sub> O <sub>5</sub>	NLO material for SHG	[78–82]
5	NaBe <sub>2</sub> BO <sub>3</sub> F <sub>2</sub> KBe <sub>2</sub> BO <sub>3</sub> F <sub>2</sub>	VUV NLO material used in LASER chemistry and LASER medical science	[65,83–85]
6	BaZn <sub>2</sub> (BO <sub>3</sub> ) <sub>2</sub>	NLO material for SHG	[86]
7	β-BaB <sub>2</sub> O <sub>4</sub>	NLO material	[87–89]
8	Ca <sub>4</sub> GdO(BO <sub>3</sub> ) <sub>3</sub>	NLO material	[90]
9	Ca <sub>4</sub> YO(BO <sub>3</sub> ) <sub>3</sub>	NLO material for THG	[91]
10	K <sub>2</sub> Al <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	New NLO material for THG	[92]
11	YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Yb <sup>3+</sup>	Excellent self-frequency doubling (SFD) material	[93]
12	BiB <sub>3</sub> O <sub>6</sub>	NLO material for SHG and THG	[94]
13	YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Cr <sup>3+</sup>	Tunable LASER gain medium	[95]
14	Ca <sub>4</sub> NdO(BO <sub>3</sub> ) <sub>3</sub>	Mini-laser material	[96]
15	Sr <sub>3</sub> Sc(BO <sub>3</sub> ) <sub>3</sub> :Cr <sup>3+</sup>	LASER material	[97,98]
16	LaBa <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Nd <sup>3+</sup>	Miniature LASER material	[99]
17	NdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	LASER material	[100–106]
18	Ca <sub>4</sub> GdO(BO <sub>3</sub> ) <sub>3</sub> :Nd <sup>3+</sup>	Green-emitting micro-chip LASER	[107–110]
19	Ca <sub>4</sub> YO(BO <sub>3</sub> ) <sub>3</sub> :Yb <sup>3+</sup>	Self-frequency doubling LASER material	[111]
20	LaSC <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	Tunable LASER material	[112]
21	LaSC <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Nd <sup>3+</sup>	Efficient LASER material	[113–115]
22	LaB <sub>3</sub> O <sub>6</sub> :Pr <sup>3+</sup>	Micro-chip LASER material	[116]
23	Ba <sub>3</sub> Y(BO <sub>3</sub> ) <sub>3</sub> :Nd <sup>3+</sup>	LASER gain medium	[117]
24	YbAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	Stoichiometric NLO LASER material	[118]
25	YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Pr <sup>3+</sup>	LASER material in UV region	[119]
26	(Gd <sub>0.5</sub> Y <sub>0.5</sub> )Ca <sub>4</sub> O(BO <sub>3</sub> ) <sub>4</sub> :Yb <sup>3+</sup>	Diode pumping LASER host material	[120]
27	Sr <sub>3</sub> Y(BO <sub>3</sub> ) <sub>3</sub> :Yb <sup>3+</sup>	Femto-second and tunable LASER	[121]
28	Sr <sub>3</sub> La <sub>2</sub> (BO <sub>3</sub> ) <sub>4</sub> :Yb <sup>3+</sup>	LASER material	[122]
29	Sr <sub>3</sub> Gd(BO <sub>3</sub> ) <sub>3</sub> :Nd <sup>3+</sup>	LASER material	[123]

Neutron radiography (NR) is a special application of neutron beams that developed neutron beam applications. The use of neutron beams for radiographic purposes is a relatively new method of non-destructive testing. Neutron imaging has expanded rapidly as a means of non-destructive testing (NDT) of materials. It is possible to develop scintillators, thermo-luminescent, optically stimuable, materials from the borates. These form the basis for the various methods developed for neutron radiography. Various neutron scintillators, phosphors for imaging plates, based on borates are reviewed in detail in chapter 10. Some important applications such as nuclear fuel inspection, bioimaging, dentistry and oral surgery, inspection of mechanical parts, etc. are discussed.

#### 1.4.4 MIXED BORATE PHOSPHORS

Apart from these simple borates, several complex compositions exist involving mixed anions as well as double metal borates. Some of these complex borates show interesting luminescence

**TABLE 1.4**  
**Borate host inorganic luminescent materials**

Sr. no.	Inorganic borate	Applications	Ref.
1	(Ce Gd)MgB <sub>5</sub> O <sub>10</sub>	Red-emitting phosphor in special deluxe lamps	[124]
2	(Ce Gd)MgB <sub>5</sub> O <sub>10</sub> : Tb <sup>3+</sup>	Green-emitting phosphor in tricolor lamps	[124,125]
3	Ca <sub>4</sub> GdO(BO <sub>3</sub> ) <sub>3</sub> :Eu <sup>3+</sup>	Potential red lamp phosphor	[126–128]
4	GdB <sub>3</sub> O <sub>6</sub> : Ce <sup>3+</sup> ,Tb <sup>3+</sup>	Potential green lamp phosphor	[129]
5	SrBPO <sub>5</sub> : Eu <sup>3+</sup>	Storage phosphor	[130,131]
6	CaLaB <sub>7</sub> O <sub>13</sub> : Ce <sup>3+</sup> ,Tb <sup>3+</sup>	Green-emitting phosphor in low-pressure Hg vapor lamps	[132]
7	CaLaB <sub>7</sub> O <sub>13</sub> : Eu <sup>3+</sup>	Red-emitting phosphor in low-pressure Hg vapor lamps	[132]
8	SrB <sub>4</sub> O <sub>7</sub> : Sm <sup>2+</sup>	Optical pressure gauge	[133]
9	(Sr <sub>0.89</sub> Na <sub>0.05</sub> )BPO <sub>5</sub> : Ce <sub>0.05</sub> , Tb <sub>0.01</sub>	Green-emitting phosphor in tricolor lamps	[134]
10	Sr <sub>2</sub> B <sub>5</sub> O <sub>9</sub> Br: Ce <sup>3+</sup>	Potential storage phosphor for thermal neutron	[135–137]
11	SrB <sub>4</sub> O <sub>7</sub> : Eu <sup>2+</sup>	Commercial UV-emitting phosphor in medical lamps	[138,139]
12	Sr <sub>2</sub> B <sub>5</sub> O <sub>9</sub> Cl: Eu <sup>2+</sup>	Blue component of daylight phosphor	[140–144]
13	Sr <sub>2</sub> B <sub>5</sub> O <sub>9</sub> Cl: Eu <sup>2+</sup> ( <b>Thin Film</b> )	Blue component in FED	[145–147]
14	Ba <sub>2</sub> B <sub>5</sub> O <sub>9</sub> Br: Eu <sup>2+</sup>	X-ray storage phosphor	[148]
15	SrB <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> : Eu <sup>2+</sup>	Blue-emitting phosphor	[149]
16	InBO <sub>3</sub> : Tb <sup>3+</sup>	Green-emitting phosphor in CTV screens	[150]
17	La(BO <sub>3</sub> ,PO <sub>4</sub> ): Ce <sup>3+</sup> Gd <sup>3+</sup> Tb <sup>3+</sup>	Green-emitting phosphor in high-quality tricolor lamps	[151]
18	Ba <sub>2</sub> B <sub>5</sub> O <sub>9</sub> Cl:Tb <sup>3+</sup> ( <b>Thin Film</b> )	Green-emitting phosphor in FED	[152]
19	Ba <sub>2</sub> B <sub>5</sub> O <sub>9</sub> Cl:Eu <sup>2+</sup> ( <b>Thin Film</b> )	Blue-emitting phosphor in flat panel display (FPD)	[153–155]
20	YBO <sub>3</sub> : Eu <sup>3+</sup>	Red-emitting VUV phosphor	[156–159]
21	YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Ho,Yb	Upconversion phosphor	[160]
22	CaBPO <sub>5</sub> : Tb <sup>3+</sup>	Green-emitting VUV phosphor	[161]
23	Y <sub>3</sub> BO <sub>6</sub> : Eu <sup>3+</sup>	Red phosphor in vacuum discharge lamps or screens	[162]
24	(YGd)BO <sub>3</sub> :Tb <sup>3+</sup>	Green component in PDP	[163]
25	(YGd)BO <sub>3</sub> :Eu <sup>3+</sup>	Red component in PDP	[164–173]
26	GdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Eu <sup>3+</sup>	Red component in PDP	[174,175]
27	(Y Gd)Al <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Eu <sup>3+</sup>	Red component in PDP	[176]
28	GdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> :Tb <sup>3+</sup>	Green-emitting VUV phosphor	[177]
29	BaZr(BO <sub>3</sub> ) <sub>2</sub> : Eu <sub>3+</sub>	Red component in PDP	[178,179]

properties and are covered in this chapter. These include double borates containing rare earth RM<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, pentaborates LaMgB<sub>5</sub>O<sub>10</sub>, M<sub>3</sub>R<sub>2</sub>(BO<sub>3</sub>)<sub>4</sub>, where M is alkaline earth, mixed anion borates like aluminoborate SrAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, silicate-borates like pekovite, SrB<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, haloborates, M<sub>2</sub>B<sub>5</sub>O<sub>9</sub>X, where M is alkaline earth and X is halogen, phosphate borates, MBPO<sub>5</sub>, where M is alkaline earth. Phosphors based on these compositions find use in various applications like fluorescent lamps, colour TV, plasma display panels, high-intensity discharge lamps based on xenon, optically pumped solid-state lasers, eye-safe lasers and X-ray imaging. This is briefly illustrated in chapter 11.

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## Introduction to Borate Phosphors

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