

Chapter 1

Introduction to Perovskite oxides and their properties

1.1 Perovskite oxides

Oxides with general ABO_3 , where A is either alkali or alkaline earth or rare earth elements and B is either transition metal or group IV elements, are known as Perovskite oxides. The perovskite structure is one of the most extensively studied structures in Solid State Chemistry, Solid State Physics, Materials Science, and Geology. German Chemist and Mineralogist Gustav Rose discovered the mineral perovskite, $CaTiO_3$, in 1839. Rose named $CaTiO_3$ after Lev Alexeievitch Perovsky, a Russian Military official. Although the term 'perovskite' was initially reserved for $CaTiO_3$, it was later applied to synthetic compounds with a similar stoichiometry and crystal structure to the mineral. Goldschmidt extensively studied the first synthetic perovskites and pioneered many principles that remain applicable to the structure even today [1].

The ideal simple perovskite oxide, for example, $SrTiO_3$ has cubic symmetry as depicted in Figure 1. It has three dimensional structure of corner sharing TiO_6 octahedral with Sr^{2+} ion at the body centre surrounded by 12 oxygen ions.

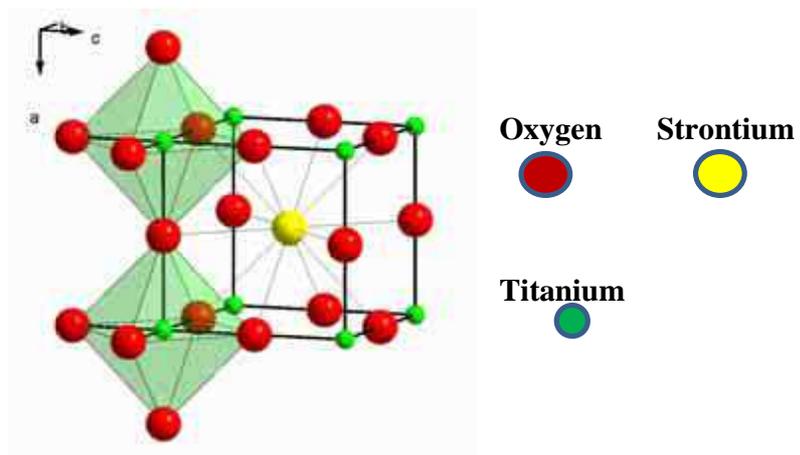


Figure 1.1 Ideal cubic perovskite structure of $SrTiO_3$.

1.2. Properties and Applications of Perovskite oxide materials

1.2.1 Electric and magnetic properties of perovskite oxides

Since the perovskite structure can accommodate a variety of cations and anions that change its structure and properties, this class of materials has attracted large interest. Perovskite materials are widely known for their dielectric properties. Materials with high dielectric strength and low dielectric loss are ideal for use as capacitor materials and electrical insulators. Polycrystalline cubic BaHfO₃ films appear to be promising candidates for future memory capacitor applications [2].

Ferroelectric oxides with perovskite structure have been currently of great technological interest due to their excellent properties for various related applications in recent years. However it is well known that most of the ferroelectric materials at present are lead based perovskite that are toxic. Naturally, lead free materials are of interest because of their obvious health and environmental advantages in future applications. BaTiO₃ is a well known ferroelectric material used in high dielectric constant capacitor of the discrete and multi-layer type [3]. Barium strontium titanate BaSrTiO₃ (BST) is commonly used to replace silicon dioxide (SiO₂) as the dielectric in advance memory devices. The high dielectric constant combined with a low dissipation factor makes BST one of the promising candidates for dynamic random access memory (DRAM) applications [4].

Many examples of perovskite compositions with various interesting properties can be found in the literature. For example, many compounds exhibiting colossal magnetoresistance (CMR) are the perovskite related $\text{La}_{1-x}\text{A}_x\text{MnO}_{3+\delta}$ materials where A^{2+} is Ca, Sr, Ba, or Pb

[5]. Compounds exhibiting CMR have potential uses in data storage technologies, such as computer hard drives and floppy disks. Different perovskite compositions also result in a wide variety of electrical behaviours. For example, SrFeO_3 is a metallic conductor at room temperature [6], BaBiO_3 is a semiconductor [7] and stoichiometric LaMnO_3 is an insulator [8]. In addition to their diverse electrical properties, perovskites have been extensively examined for superconductivity. $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($0.05 < x < 0.31$) discovered in 1975 is a superconducting oxide with a critical temperature (T_c) of 13 K [7]. Since then, a number of superconductors with $T_c > 77$ K including the well known $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been discovered [9].

Certain perovskite oxides, for example solid solutions of PbZrO_3 and PbTiO_3 , exhibit piezoelectric properties and are used for numerous applications including microphones, stereo speaker fuses (for lighters) and ultrasonic cleaners [10, 11]. Ba/Pb free dielectric materials with giant dielectric constant and good thermal stability have particularly attracted ever increasing attention for their practical applications in microelectronics such as Internal Barrier Layer Capacitors (IBLC). Recently, there has been a great interest in synthesis and characterization of calcium copper titanate $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, commonly called CCTO [12].

Multiferroics have become an object of growing interest due to the coexistence of magnetic order and ferroelectric polarization combined in a single-phase material. The interest is motivated not only by the rich physics that is expected in this class of solids, but also by their great technological potential. Indeed, multiferroic materials with significant magnetoelectric (ME) coupling might open promising opportunities for designing novel

microelectronic and spintronics devices. An enhancement of the magnetization was reported in epitaxial BaFeO₃ films [13], under the application of a high magnetic field, thus indicating possible ways to suppress the spin modulation.

Naturally occurring MgSiO₃ and CaSiO₃ make up a large percentage (50-90%) of the perovskite rich lower mantle and are believed to be the most abundant minerals within the earth. Numerous studies on the pressure stabilized perovskite form of MgSiO₃ and CaSiO₃ have been carried out by geophysicists [14] in an effort to understand their properties of thermal stability. The phase stability and single crystal elastic properties of CaSiO₃ at higher temperature and pressure have been studied by Li Li et al [15] and Shieh et al [16] respectively. The elastic properties are essential for interpreting seismic wave velocities and their lateral variations, as well as for understanding seismic anisotropy in the mantle.

1.2.2 Photoluminescence in perovskite oxides

Photoluminescence (PL) in solid materials usually result from radiative decay of electronic transitions. In semiconductors, the PL comes from band to band transition or excitonic states, while in insulators from transition metal or rare earth ions present as impurities. Pr-doped perovskite type titanates ATiO₃, where A is one of the alkaline earth elements, have been attractive as red phosphor materials for a potential flat panel display and field emission display[17-22]. Alkaline earth stannates or zirconates with perovskite structure show intense photoluminescence under UV excitation at room temperature [23, 24]. Since the crystal structure of these perovskite phosphors is simple, they are regarded to be model host lattices for phosphors and luminescence mechanisms. The perovskite phosphors are also promising for the development of not only light-emitting thin film devices but

multifunctional optoelectronic devices as some of them exhibit ferroelectric and superconducting properties. In addition, they are deposited epitaxially on perovskite single crystal substrates.

Conventionally luminescence of wide gap materials(e.g. oxides) result from the presence of intrinsic defects and also by impurity doping. However, in so called 'self-activated phosphors,' luminescence under photo excitation can be observed even in high quality pure materials. Such a property is inherent to the ABO_3 perovskite crystal family, which reveals a broadband emission in the visible spectral region (so called 'green' luminescence). Some examples of such oxides are $SrTiO_3$ [25], $BaTiO_3$ [26], $KNbO_3$ [27], $KTaO_3$ [28] and $PbTiO_3$ [29]. The nature of this wide-band visible luminescence universal for ABO_3 perovskite type oxides is still a subject under intense discussion. Various mechanisms, such as donor–acceptor recombination [30], and charge transfer vibronic exciton (CTVE) [31] have been proposed to understand the luminescence behaviour.

1.2.3 Thermoluminescence in perovskite oxides

Whenever the perovskite oxides are irradiated with ionizing radiation, the defects are produced in the materials thereby generating traps and trap centers in the forbidden energy gap. Hence they show thermoluminescence properties. Premkumar et al. have studied the thermoluminescence properties of γ -irradiated $YAlO_3:Ni^{2+}$ and $YAlO_3 : Cr^{3+}$ nanophosphors [32, 33]. Thick films of nickel oxide (NiO) and perovskite type $LaFeO_3$ were investigated for γ -radiation dosimetry purposes by Arshak et al. [34].

1.3 Preparation methods of perovskite oxides

Different preparation methods of the perovskite oxides result in different physical or even chemical properties of these materials. To obtain perovskite materials, conventional ceramic methods based on solid phase reactions at high temperatures are commonly used.

In the conventional synthesis of ceramics by solid phase reactions, the metal oxides or the corresponding salts, such as for example carbonates, are repeatedly ground and heated before calcinations. Thus this method has following drawbacks.

1. Inhomogeneity of the products
2. Incorporation of chemical impurities during repeated grinding and heating operations.
3. Coarseness of particles which makes them unsuitable for coatings.
4. Presence of defects which interferes with luminescence.

To avoid these disadvantages, several new methods have been developed. These improved synthesis methods give pure phases by mixing reactants at molecular level. Under such conditions, the reaction temperatures are significantly lower leading to homogeneous fine powders. Some of the novel synthesis routes are briefly described below.

1.3.1 Co-precipitation method

The precipitation of metal salts is a classical chemical method which is often used for the synthesis of simple oxides. Adding a chemical reagent that determines the decrease of the solubility limit leads to precipitation. Co-precipitation occurs when different cations in solution precipitate simultaneously [35]. The control of the concentration, temperature, pH and solution homogeneity is essential for the simultaneous precipitation of all cations and to obtain perfectly homogeneous products. Some of the popular reagents used for precipitation are ammonia, ammonium carbonate or ammonium oxalate and urea. The

thermal decomposition of the hydroxides, carbonates or organic salts leads to the corresponding oxide compounds, insoluble in solutions.

1.3.2 Hydrothermal synthesis

The principle of hydrothermal synthesis is based on a reaction in the aqueous solution or suspension of the precursors at high temperature and pressure. Crystalline powders can be obtained in this method without calcination. The particle size and shape can be modified by the reaction temperature, pH, time and concentration of reactants [36].

1.3.3 Pechini method

'Pechin' method [37] allows the synthesis of oxides, with a very good control of the stoichiometry of the reactants and reaction products. Good homogeneity and high reproducibility of the reaction mixture are some of the merits of this method. The Pechini method is also called "the polymeric precursor method" or "the method of mixed liquids". The basic principle of the method consists in the formation of a chelate by the reaction of different cations introduced into the system as soluble salts (commonly used are nitrates) with a carboxylic acid (most commonly citric acid). The resulting aqueous solutions containing citric acid and metal salts when mixed with a desired polyol (most often ethylene glycol) and heated at 80 - 100 °C, gives a clear solution. By further heating between 150 - 250 °C, a condensation reaction occurs involving COOH and OH groups, leading to the formation of a polyester "resin", in which metallic cations are distributed uniformly in the resin mass.

1.3.4 Sol-gel method

Sol-gel alkoxide route is a prominent method in the field of ceramics. The starting materials, the metallic alkoxides are commercially available for a large variety of metals. By reactions in the presence of organic compounds, hybrid materials are obtained [38]. The

processing of oxide compounds by alkoxide route is based on the hydrolysis and polycondensation of metallic alkoxides. Sol-gel process in aqueous medium uses inorganic salts and chelating agents of carboxylic acids or polyol as precursors. Sol gel method has been widely used to prepare nanosized materials, but its application is limited by the stability of its precursor system and it is difficult to control the chemical composition of complex oxides.

1.3.5 Low temperature solution combustion method

The low temperature combustion synthesis (LCS) [39] technique has proved to be a novel, extremely facile, time saving and energy efficient route for the synthesis of ultra fine powders. LCS is based on gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous and fluffy product with large surface area. Because of the several advantages of this method, low temperature combustion synthesis has been adopted in the preparation of CaSiO_3 ceramic powders investigated in the present research work. A detailed description of combustion synthesis is presented in the next chapter.

1.4 Introduction to CaSiO_3 perovskite ceramics

This thesis work presents the preparation and investigations carried out on CaSiO_3 nano ceramic powders. This section presents a brief introduction to CaSiO_3 and its importance in materials research.

CaSiO_3 also called Wollastonite has good prospects as a raw material in the ceramics industry. It is a white mineral having a chain structure, with 48.25 % CaO and 51.75 % SiO_2 content. The lower half of the earth's transition zone and lower mantle (depths between 500 and 2900 km) comprises of 6-12 weight % of mineral CaSiO_3 . The wollastonite containing materials are used for the production of sanitary components,

porcelain materials, lining bricks, glaze and flux [40]. CaSiO_3 with high temperature strength, creep resistance, chemical inertness, thermal stability, low thermal expansion and low thermal conductivity, is a suitable material for variety of applications. Wollastonite and its additives form a dielectric phase having high electrical resistivity. This property can be used for making high frequency electronic component. Lead silicate and wollastonite have been used to prepare a material with ultrahigh electrical resistivity, applicable in electrical and radio engineering.

Wollastonite has a fibrous structure in the form of needle shaped crystals, which makes it possible to use it as a filler in paints [41]. The needle shaped wollastonite crystals facilitate a better and more homogenous distribution of paints over the surface of an article. It is also used as well in the synthesis of pigments applied as underglaze paints to majolica products. A specific feature of natural wollastonite is the fact that wollastonite articles do not undergo significant volume changes in the course of their manufacture. Wollastonite is added to ceramic mixtures in making facing tiles [42]. Its use contributes to a decrease in the linear shrinkage, water absorption and ensures high thermal resistance. The quality of wollastonite and wollastonite based materials improve when its concentration is high. Wollastonite ceramics are also used as a biomaterial in medical industry for artificial bone and dental root because it shows good bioactivity and biocompatibility [43].

The colour and the structure of wollastonite make it usable as a strengthening filler for polymers. Wollastonite is used as a 50 % filling pigment in the production of polyether, vinyl, and epoxy resins. The addition of wollastonite to ceramic mixtures makes it possible to shorten the firing time, to decrease the firing temperature, to reduce shrinkage and to

impart strength to materials. [44,45]. This possibility of obtaining stronger materials based on wollastonite opens new application areas. The high strength and porosity, low thermal conductivity and non-wettability in aluminum alloys makes ceramic materials based on natural wollastonite useful for the production of heat insulating ceramics for lining of casting equipment and checkers in metallurgy and the automobile industry.

1.5 A brief review of the structural, dielectric and luminescence properties of CaSiO₃

1.5.1 Structural properties of CaSiO₃

The compound CaSiO₃ exhibits polymorphism. It has two phases, namely β -CaSiO₃ (Wollastonite) and α -CaSiO₃ (Pseudowollastonite) at lower and higher temperatures respectively. Azarov et al.[46] have reported that Pseudowollastonite crystallizes in to a pseudo-hexagonal structure, whereas β -phase has a triclinic or monoclinic structure. At a temperature of 1125°C, wollastonite is irreversibly transformed into pseudowollastonite with an insignificant change in the volume.

Although CaSiO₃ perovskite is thought to be the major calcium silicate component of the lower mantle, its structural properties are still poorly understood. Even the structure that CaSiO₃ assumes at high pressures is not well defined. Experimentally, CaSiO₃ perovskite is generally reported to have a cubic structure [47]. Shim et al. [48] reported a lower symmetry structure based on high resolution synchrotron data, and proposed several possible tetragonal structures. Theoretical calculations have predicted small symmetry lowering distortions of the cubic structure which yield tetragonal or even orthorhombic symmetries [49]. Caracas et al [50] have predicted a multitude of structural instabilities

with minor distortions of the cubic lattice that would be barely discernable in X-ray data. These symmetry lowering distortions are accomplished by rotation or distortion of the SiO_6 octahedra.

Henriques et al. [51] have studied the structure of CaSiO_3 to be triclinic, using a quantum mechanical first principles approach. Unit cell parameters have been optimized using the local density approximation (LDA) within the density functional theory (DFT) formalism in order to minimize the total energy. A comparison was made between these theoretical results and X-ray data. They have also calculated the electronic band structure, density of states, and optical absorption. Chakradhar et al. [52] have found that CaSiO_3 synthesized by solution combustion process, attains its β - and α -phases at $950\text{ }^\circ\text{C}$ and $1200\text{ }^\circ\text{C}$ respectively.

Hexiong Yang et al. [53] have studied the structure of pseudowollastonite (α - CaSiO_3) and predicted it to be monoclinic with $C2/c$ space group. Tangboriboon et al. have reported that both β - and α - CaSiO_3 phases have triclinic structure. With increasing temperature perovskite structures generally transform in the following series: triclinic or monoclinic, rhombohedral, tetragonal or orthorhombic, cubic perovskite structure [54].

1.5.2 Dielectric studies in CaSiO_3

In the conventional printed circuit board technology, low temperature co-firable ceramic (LTCC) technology is one of the new technologies to manufacture integrated multifunctional electronic chips. It can be utilized for the integration of passive components into a monolithic, high reliable and robust LTCC module. These modules consist of several

layers of substrate material with buried components such as capacitors, inductors, resistors, resonators and filters. They are interconnected with 3D strip line circuitry. Utilization of low dielectric constant LTCC substrate materials and associated high conductivity metallizations such as Au and Ag are found to have potential applications in the area of wireless communication.

The microwave components working at higher frequency, such as antennas and baluns required the ceramic with a permittivity less than 10. Among several LTCC glass-ceramic systems, CaO-B₂O₃-SiO₂ system has been reported as a promising material for use in microelectronic packaging because of low firing temperature and low dielectric loss [55, 56]. Commercially available Ferro A6 LTCC system is a typical example.

The synthesis (by Sol-gel method) and microwave dielectric properties of CaSiO₃ nanopowder have been investigated by Huanping Wang et al. [57]. Compared with CaO-SiO₂ ceramics prepared by solid-state process, the CaSiO₃ ceramics made from nanopowders calcined at 1000 °C achieved more compact structure for pellets at the sintering temperature of 1320 °C, and then had excellent microwave dielectric properties: relative dielectric constant $\epsilon_r = 6.69$, quality factor $Q_f = 25398$ GHz. CaO-MgO-SiO₂ submicron powders were prepared by Huanping Wang et al. [58] at low temperature by sol-gel method. The crystallization temperature was observed to be enormously reduced by the introduction of Li-Bi liquid phase sintering aids. The system was found to have excellent microwave dielectric properties: $\epsilon_r = 7.16$ and Q_f (Quality factor) = 25630 GHz. Tsang-Tse Fang et al. [59] investigated the role of Si ions in the microstructure change, the electrical conduction, and the dielectric responses of CaSiO₃-doped CCTO. They have

found that the system possesses ultra high dielectric constant of about 10^4 – 10^5 at radio frequency and slightly below room temperature.

Ming He et al. [60] have calculated the permittivity (dielectric constant) of the wollastonite ceramic matrix. The dielectric constant of the crystalline wollastonite (estimated to be 6.2 at 1 MHz frequency) was used to evaluate the dielectric properties of the wollastonite ceramic matrix. In this study, the Clausius Mosotti model was used to calculate the permittivity of the crystalline wollastonite from molecular polarizability.

1.5.3 Photoluminescence and Thermoluminescence studies in CaSiO_3

CaSiO_3 gel samples were obtained by Andric et. al [61] by Alkoxy sol-gel technique, through hydrolysis-condensation reactions of tetraethylorthosilicate as silica source. In this work they have studied the process of crystallization of Eu^{3+} activated CaSiO_3 gel and decomposition of organic precursors by means of thermal analysis and stretching of O-Si-O and Si-O modes of vibration by infrared spectroscopy. Results of scanning electron microscopy and energy dispersion spectrometry were used to check chemical composition and morphology of synthesized material. Emission spectra and emission life-time measurements were performed to investigate luminescence properties of Eu^{3+} doped CaSiO_3 powder.

Nanocrystalline porous CaSiO_3 ceramic powders were synthesized by a novel low temperature initiated self-propagating, gas producing solution combustion process by Nagabhushana et al. [62] and they were characterized by XRD, SEM and EDS. Porosity, surface area and thermoluminescence (TL) studies were also undertaken. The effect of

temperature on crystalline phase formation and particle size of porous CaSiO_3 was investigated. Single phase $\beta\text{-CaSiO}_3$ and $\alpha\text{-CaSiO}_3$ were formed at 950 and 1200 °C respectively. The phase transformation temperatures of combustion derived CaSiO_3 were found to be lower compared to the powders obtained via solid state reaction method. The micro structure and morphology were studied by SEM and it is interesting to note that with increase in calcination temperature, the samples became more porous and the pore diameter increased from 2 to 10 μm . The samples calcined at 950 °C for 3 hours had 17.5 % porosity. However the porosity increased to 31.6 % on calcination at 1200 °C for 3 hours. The surface area of as-formed and calcined at 950 and 1200 °C CaSiO_3 samples were found to be 31.93 m^2/g , 0.585 m^2/g and 3.48 m^2/g respectively. The TL intensity in powdered sample was more when compared to the pelletized CaSiO_3 and it was further observed that there was a shift in glow peak temperatures in pelletized sample. This was attributed to the inter particle spacing and pressure induced defects.

In the work done by Frank et al. [63], calcium silicate phosphors activated with varying amounts of manganese luminesce yellow to orange under cathode-ray excitation, but did not respond to UV excitation at 253.7 nm. If a small amount of lead is added with the manganese, the resulting material responds to 253.7 nm excitation, to give the same colour as that produced by cathode rays. In addition to the visible luminescence, there was an ultraviolet band at 340.0 nm wavelength. The spectral distribution in the visible region is dependent upon manganese concentration and temperature. If lead alone is used as an activator, the product gives emission entirely in the ultraviolet region. Three emission bands are evident at approximately 300.0 nm, 334.0 nm, and 350.0 nm wavelengths, any one of them may be predominant depending upon the conditions of preparation. CaSiO_3 : Pb, Mn phosphors are cathodoluminescent materials of commercial importance.

Sol-gel synthesis route was employed by Lei Zhou et al.[64] by using novel silicate sources in order to study the photoluminescence of $\text{CaSiO}_3 : \text{Eu}^{3+}$ nanophosphors. Different silicate precursors were used to adjust the microstructure and size of the resulting phosphors. The crystallite size of phosphors was in the range of 30-35 nm and some of them showed regular microstructure after high temperature thermolysis. The photoluminescence properties showed that all of them exhibit the characteristic fluorescence resulting from $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) transitions of the Eu^{3+} ion. The strongest one was the red emission at 610 nm. Furthermore, the emission quantum efficiency (η) of the $^5\text{D}_0$ excited state of Eu^{3+} has been calculated to be around 33 % from the emission spectrum. The lifetime of the Eu^{3+} first excited level ($\tau, ^5\text{D}_0$) has also been calculated.

The luminescence behaviour of Eu^{3+} in $\text{CaSiO}_3 : \text{Eu}^{3+} (\text{Bi}^{3+})$ was studied by Jinghai Yang et.al.[65]. When the $\text{Eu}_{0.08}^{3+}\text{Bi}_{0.02}^{3+}$ samples were excited with wavelength of 350 nm, the emission intensity of electronic dipole transition at 609 nm originated from $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions. This transition was stronger than magnetic dipole transition at 587 nm originated from $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu^{3+} ions mainly due to the lower symmetry and the distortion of the structure.

The luminous materials of $\text{CaSiO}_3 : \text{Pb}, \text{Mn}$ were synthesized by sol-gel method and ultrasound technology by Yang Liangzhun et. al.[66]. The effects of factors such as the synthetic material compositions, ultrasound time and annealing temperature on phosphorescent brightness of sample were studied and the optimum synthetic conditions were determined. The results showed that compared with the sample made by the high

temperature solid state reaction, the luminescent intensity of the CaSiO_3 : Pb, Mn sample increased by about 200 % and the mean diameter of particles of the sample decreased by about 300 nm.

Energy transfer among Ce^{3+} , Eu^{2+} and Mn^{2+} in CaSiO_3 , was studied by Shi Ye et al[67]. Co-doping $\text{Ce}^{3+}/\text{Mn}^{2+}$ or $\text{Eu}^{2+}/\text{Mn}^{2+}$ is an effective approach to enhance the orange reddish emission of Mn^{2+} . The ion size compensation effect between Eu^{2+} to Mn^{2+} causes more Eu^{2+} to be doped into the CaSiO_3 lattice, which benefits the increase in energy transfer efficiency from Eu^{2+} to Mn^{2+} . Additionally, the suitable spectrum overlapping of the Eu^{2+} emission with the first excited state ${}^4\text{T}_1$ of Mn^{2+} as well as the formation of $\text{Eu}^{2+}/\text{Mn}^{2+}$ clusters may be other causes of the enhanced Mn^{2+} luminescence. $\text{Eu}^{2+}/\text{Mn}^{2+}$ co-doped samples can be very well excited by near-UV. The excitation spectrum of Ce^{3+} covers a different wavelength range from that of Eu^{2+} (normally blue shift occurs). Thus, replacement of Ce^{3+} for Eu^{2+} makes phosphors to be excited by shorter wavelengths.

1.6 References

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