ABSTRACT

Strontium Titanate ($SrTiO_3$) doped with Praseodymium (Pr) as an oxide compound phosphor show a potential application for a field emission display (FED). Addition of Aluminum ions (Al^{3+}) has been attracting interest as a sensitizer to improve the luminescent efficiency of phosphors. In this study, the influence of Al^{3+} as a dopant on the crystallization, surface morphology and luminescent properties of $SrTiO_3$:Pr,Al nanophosphors were investigated. Nanophosphor with the nominal composition of $SrTiO_3$ undoped and doped with Pr^{3+} and Al^{3+} were synthesized at relatively low temperature by the sol-gel method. The crystal structures and average grain sizes were examined using x-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns indicated that crystalline $SrTiO_3$ which has been synthesized at calcining temperature of 800°C for 2 h present a cubic structure. Moreover, the improvement of single crystalline phase is confirmed by increasing the temperature. SEM micrographs indicate that the addition of Pr^{3+} and Al^{3+} influence the texture and morphology of the samples. Nanoparticles samples with various sizes of 25-55 nm were obtained as a function of Pr and Al concentration using Scherrer's equation. Fourier Transform Infrared (FTIR) spectra from $SrTiO_3$ doped and undoped are also reported. The effect of doping on the infrared spectral of $SrTiO_3$ structure is clearly shown in the low-frequency regions but overlapped with O-Ti-O bending mode. Raman spectroscopy was employed to investigate the evolution of the cubic phase in the nanocrystals during annealing and doping concentration. By addition of dopants, Raman spectra show formation of second-order Raman Scattering of $SrTiO_3$. The luminescent properties of $SrTiO_3$:Pr,Al phosphor were investigated by Photoluminescence (PL) spectroscopy. Under 325 nm excitation, $SrTiO_3$:Pr,Al phosphor exhibited a strong red emission, peaking at about 615 nm. The intensity of emission spectra was enhanced by the addition of Al^{3+} ions.

ABSTRAK

Strontium Titanate ($SrTiO_3$) didop dengan Praseodymium (Pr) sebagai sebatian fosfor oksida mempunyai potensi tinggi dalam penggunaan paparan pancaran medan (FED). Penambahan ion Aluminium (Al) sebagai pemeka bertujuan untuk meningkatkan kecekapan pendarcahaya bahan fosfor. Dalam kajian ini, pengaruh Al^{3+} sebagai bahan dop ke atas penghabluran, morfologi permukaan dan sifat pendarcahaya nanofosfor $SrTiO_3$: Pr telah dikaji. Nanofosfor dengan komposisi nominal $SrTiO_3$ tidak berdop dan dop dengan Pr^{3+} and Al^{3+} telah disintesis pada suhu rendah menggunakan kaedah sol-gel. Struktur hablur dan purata saiz zarah diperiksa menggunakan pembelauan sinar-X (XRD) dan mikroskopi imbasan elektron (SEM). Corak XRD menunjukkan bahawa hablur $SrTiO_3$ yang telah disintesis pada suhu pengalsinan 800^{o}C selama 2 jam menghasilkan struktur kubus. Tambahan lagi, penambahbaikan fasa satu hablur disahkan dengan peningkatan suhu. Mikrograf SEM menunjukkan bahawa penambahan Pr^{3+} dan Al^{3+} mempengaruhi tekstur dan morfologi sampel. Sampel berzarah nano dengan pelbagai saiz antara 25-55 nm diperolehi dengan kebergantungan pada kepekatan Pr^{3+} dan Al^{3+} menggunakan persamaan Scherrer. Spektrum Transformasi Fourier Infra merah (FTIR) untuk $SrTiO_3$ yang berdop dan tidak berdop juga turut dilaporkan. Kesan pendopan pada struktur $SrTiO_3$ dalam spektrum inframerah jelas ditunjukkan dalam kawasan frekuensi rendah tetapi bertindan dengan mod pembengkokan O-Ti-O. Spektroskopi Raman digunakan untuk mengkaji evolusi fasa kiub dalam hablur nano semasa pengalsinan dengan kepekatan bahan dop berubah. Dengan penambahan bahan dop, spektrum Raman menunjukkan pembentukan Sebaran Raman Urutan Kedua. Sifat pendarcahaya fosfor $SrTiO_3$:Pr,Al dikaji menggunakan Spektroskopi Fotopendarcahaya. Di bawah pengujaan 325 nm, fosfor $SrTiO_3$:Pr,Al menunjukkan pancaran merah yang kuat pada puncak 615 nm. Keamatan spektrum meningkat dengan penambahan ion Al^{3+}.

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4 RESULTS AND DISCUSSIONS

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Luminescence is a science related to spectroscopy. First observed in an extract of Ligrium nephiticiem by Monardes in 1565, it took until 1852 to be fully described by Stokes who reported the theoretical basis for the mechanism of absorption (excitation) and emission. Today luminescence, in its varied forms, is one of the fastest growing and most useful analytical techniques in science. Applications can be found in areas as diverse as materials science, environmental science, microelectronics, physics, chemistry, biology, biochemistry, medicine, toxicology, pharmaceuticals, and clinical chemistry. This rapid growth occurred only in the past couple of decades and is principally driven by the unique needs of the life sciences.

Luminescence is defined as the generation of light without heat which usually occurs at low temperatures, and is thus a form of cold body radiation. It can be caused by the movement of electrons within a substance from more energetic states to less energetic states. Examples of luminescence in nature that had been observed from ancient times are fireflies, insects, fishes, mushrooms and luminescent bacteria. A luminescent material is often called phosphor, which means 'light bearer' (Joseph, 2001). Phosphor is a substance that exhibits the phenomenon of phosphorescence (sustained glowing after exposure to energized particles such as electrons). Of course we are familiar with phosphor; we meet them everyday. If this should come as a surprise, switch on the fluorescent lamp, relax in front of the television set or take a look at the screen of our computer. All of that are the examples of phosphor application in our daily life. Research on phosphors and their applications requires the use of a number of fields in science and technology. For advanced application, phosphors are widely used in plasma display panels (PDPs), field emission displays (FEDs), luminous paint and safety indicator.

The long afterglow phosphors are a special kind of luminescent materials with long persistent phosphorescence lasting for several hours at room temperature. As novel functional materials, these long afterglow phosphors are drawing more and more attention in recent years because of a constantly growing market for their applications. In the early time, Co and Cu doped zinc sulphide (ZnS: Cu, Co) was considered a main kind of phosphorescent materials. However, the material itself is not stable enough during its application. It can only maintain phosphorescence no more than a few hours. Sulfide absorb the moisture from the surrounding environment to form sulfate that causes the destruction of sulfide lattice, and thus the material no longer shows long afterglow (Chang and Mao, 2004). Therefore, it is substituted by the strontium aluminates. In the past decade, new kinds of long persistent phosphors, which overcome the shortcoming of the above mentioned sulfides, were invented. In the mean time, titanate-based phosphors also were increasingly investigated due to the potential interest of these materials.

Phosphors based on oxide matrices are attractive host materials for the development of advanced phosphors due to their ease of synthesis and stability. Titanium dioxide (TiO_2) could be a possible candidate among oxide compounds which have been known to exhibit an absorption band in the soft ultra violet (UV) range, because TiO_2 has served as a photonic catalyst in this energy range. Recently, perovskite titanate $MTiO_3$ (M=Mg, Ca, Sr, Ba) have attracted great interest both in scientific and technological field. The oxide perovskite strontium titanate ($SrTiO_3$) is expected to be chemically stable and good candidates for optical host materials. $SrTiO_3$ is a well-known material because of its good properties, such as high dielectric constant, high charge storage capacity, good insulating property, excellent chemical and physical stability and excellent optical transparency in the visible range. In addition, $SrTiO_3$ is suitable for host matrix as phosphors (Guo *et al.*, 2006; Yamamoto *et al.*, 2002).

Up to now, rare earth ion doped luminescent materials, due to their characteristic emission bands ranging from ultraviolet to visible, to infrared wavelength region, have attracted much attention and become an interesting topic in the field of luminescent material. The luminescence properties of titanate perovskite doped with trivalent praseodymium were increasingly investigated since the mid-1990s due to the potential interest of these red emitting phosphors for display applications. Several studies have already reported on the luminescence of Pr^{3+} doped $SrTiO_3$ powder samples. The addition of Al^{3+} or Ga^{3+} into $SrTiO_3$: Pr reported to greatly enhance the emission intensity.

Traditionally, phosphor are synthesized in powder form by procedures involving crushing, grinding, ball milling and high-temperature solid state reactions. However, it is difficult to obtain reliable emission intensities with such methods, probably because of inhomogeneous distributions of metal ions, phase separations or the accumulation of impurities. Moreover as luminescent materials, the phosphorescent properties are greatly affected by the grain size, when the grain size reaches nano scale, many new properties can be obtained. For this reason, recent investigations have addressed the development of alternative synthetic procedures and more homogenous materials with improved emission efficiency achieved by using sol-gel process.

The sol-gel method, possessing advantages of well controlling the stoichiometry, particle size and morphology, is a potential method for preparing inorganic materials. The sol-gel method of phosphor preparation is regarded as a wet method. A kind of metal organic compounds known as alkoxides of metals is used as precursors. These metal-organic alkoxides could either be in liquid form or are soluble in certain organic solvents. Through the use of the appropriate reagents, the processes of hydrolysis and gelation can be induced to produce homogeneous gels from the mixture of alkoxides. To obtain powder or ceramic samples, gels can be baked, sintered and powderized as in other traditional methods. The sol-gel method is advantageous in as much as thin films or coatings of the phosphor can be formed on substrates directly and/or the sol-gel can be molded into designated forms. In this study, the sol-gel method was utilized for preparing $SrTiO_3$ phosphors.

1.2 Statement of problem

Many works on luminescence properties of other materials like aluminates, silicates and phosphate via sol gel method were done. Even though there are several reports on luminescence properties of $SrTiO_3$:Pr, Al, there is no clear-cut understanding on the relation between luminescence properties and structure. Thus, in this study we present the luminescence spectra of this system which is prepared via sol-gel method and indicate the close relationship between such emission and the molecular arrangements in the respective structures.

1.3 Objectives of study

The objectives of this study are as follows:

- To synthesize nano-particle phosphor strontium titanate doped with rare-earth or transition metal.
- To determine the crystalline phase and structure of host material.

- To determine the influence of the dopant concentration on luminescent characteristic of phosphor system.
- To determine the mechanism of luminescence of $SrTiO_3$; Pr, Al.

1.4 Significance of the study

In the fast growing field of luminescent material, there are lots of these material applications in many fields such as painting, safety sign and so on. In this research, we want to develop phosphor based titanates because of its promising luminescence performance.

By the end of this research, we expected to have a system that has excellent properties as phosphor materials which has low calcination temperature, nanoscale size and high intensity.

This study also looks forward to find out the knowledge base of phosphor properties and applications in scientific and technological field.