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APPLICATION OF TERNARY PHOSPHORS FOR VISUALIZATIONS AND LIGHTING

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The suitability of ternary phosphors is disscused for their application in phosphor – liquid crystal displays inorganic electroluminescent device and phosphor-converted-white light emitting diodes. The electroluminescent mechanism color-by blue concept for achieving full-color inorganic electroluminescence display is discussed.

INTRODUCTION

Ternary compounds of general formula II-III_2S_4 (where II-Ca, Sr, Ba; III-Ga, Al) form an extensive class of semiconductors and present luminescence properties, when doped with rare-earth elements [1-3]. Introduction of rare-earth element impurities is necessary to achieve a higher quantum yield during optical and electric pumping of II-III_2S_4 crystals and ensure an efficient energy transfer from excited carriers to 4f-electrons. Rare-earth elements can be excited via wide absorption bands of the host, which in turn lowers the excitation threshold, thus increasing the luminescence efficiency.

II-III_2S_4 are semiconducting materials with a large band gap (>4eV) exhibiting an orthorhombic and cubic crystalline structure. These compounds are effectively excited by the action of different external factors: electric field, vacuum ultraviolet, X-rays, and cathode and gamma rays. However there is a basic distinction between visualization of shorter-waves (ultra-violet, X-rays, γ-quanta) and very long-waves (infra-red and mm) radiations. They efficiently transform ultra-violet radiation to visible. The high value of quantum efficiency and peak position make these phosphors rather interesting for display applications. The high performance of these compounds, in comparison with commercial phosphors, is also related to their high stability.

The ternary compounds II-III_2S_4 doped with Eu^{2+} and Ce^{3+} ions are very attractive for lighting and display applications. The Eu^{2+} doped II-Ga_2S_4 (II- Sr, Ca) and $BaAl_2S_4$ compounds is an efficient green and blue emitting phosphors, with excellent color coordinates, high lumen equivalent and fast luminescence decay. The low saturation effects of Eu^{2+} doped materials make it very advantageous for applications where high beam currents are required to achieve the wanted brightness levels, as in field emission displays (FEDs). Furthermore this phosphor allows efficient acceleration of charge carriers up to optical energies under high electric fields leading to high electroluminescent efficiency in inorganic Thin Film Electroluminescent (iTFEL) devices.

II-Ga_2S_4 :Eu^{2+} phosphor is a promising candidate in phosphor converted, light emitting diodes (LED) for solid state lighting (SSL). High quality powders or films are required for all these device applications.

Inorganic thin-film electroluminescent (iEL) devices are expected to be a very interesting candidate for full-colour flat panel displays. The lack of a blue phosphor with suitable colour coordinates, high enough luminance and efficiency was one of the main difficulties to commercialise full colour devices. These last years, binary and ternary sulphide phosphors have been investigated, like SrS:Ce [4], Ca and $SrGa_2S_4$:Ce [5], SrS:Cu [6], SrS:Cu,Ag [7], and CaS:Pb [8] . Unfortunately not any one of these phosphors provides suitable performances for full colour display application.

Recently a breakthrough was made in 1999 who have reported on a new thin film EL phosphor, $BaAl_2S_4$ doped with Eu^{2+}, which gives a higher brightness of 65 cd/m^2 at 50 Hz and good colour coordinates, x= 0.12 and y=0.10 [9]. Greater brightness that 700 cd/m2 at 120 Hz has been

obtained using the thick dielectric technology at iFire Company [10]. This performance allows iFire Company to announce a full colour 34-inch iEL HDTV screen for the 2006 timeframe using the Colour-By-Blue (CBB) technique [11].

The first report concerning this $BaAl_2S_4:Eu^{2+}$ phosphor was presented by Donohue and Hanlon [12]. The cubic structure with a lattice parameter of 1.2588 nm was established. At 300K, a blue band peaked at 475 nm was obtained with a decay time of the order of 0.45 μs. In this pioneer paper, it was pointed that this phosphor will be efficient due to a wide band gap leading to a low interaction between the excited states of Eu^{2+} and fundamental edge. This cubic structure was precised by Eisenmann et al. [13] and some luminescence properties were presented in [14, 15]. In this paper we will discuss present and potential application of these ternary materials.

I. PHOSPHOR-LIQUID CRYSTAL DISPLAY

Usually, liquid crystal displays LCDs shows a narrow viewing angle and reduced brightness, because it is a passive emitting display device and it is based on the switching of polarized light. In a color LCD, a large energy loss occurred when combining the white backlight and color filter. We suggest that the combination between a ultraviolet (UV) backlight and UV-excited phosphor layers could generate color pixels without the use of filters. This means that phosphor LCDs can ideally have three times higher light output than conventional color LCDs. To attain a significant improvement in brightness for a phosphor LCD, the quantum efficiency of phosphors should be high under UV excitation. The choice between backlight phosphor and front RGB phosphor combinations will critically affect the brightness of phosphor LCDs. Thus, the selection of the backlight phosphor and RGB phosphors becomes an important factor determining optical properties (brightness, color gamut, and contrast). Figure 1 shows the basic structure of a phosphor LCD display. The phosphor LCD consists of a near-UV backlight to excite phosphors and pixelated phosphor layer to generate color image by multiplexing or active-matrix addressing LC system. The light modulated by the conventional LCDs transmits directionally by the switching of polarized light, while the light emitted from the phosphor pixel of a phosphor LCD transmits isotropically into free space. Since the UV backlight in a phosphor LCD does not pass through a color filter, the light attenuation of conventional LCDs caused by the color filter can be significantly reduced so, this basic structure of the phosphor LCD offers a simple solution to enlarge viewing angle and increase light efficiency.

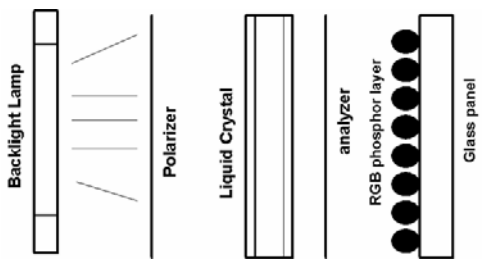

Fig.1. Basic structure of a novel phosphor LCDs.

Phosphor LCDs are an interesting device which combine the merits of CRTs and LCDs. The quantum efficiency, color gamut, and optical properties of several potential RGB ternary phosphors suggest that phosphor LCDs will be an alternative way to resolve the demerits of conventional LCDs, such as narrow viewing angle, low brightness, and restricted color gamut.

II. ELECTROLUMINESCENT DEVICES

EL devices can be grouped in different types depending on the form of the phosphors (powder vs. thin film) and of the driving voltage (DC vs. AC). Two of these types, viz., AC driven thin films electroluminescent devices are commercially available. Due to its good performance (brightness, viewing angle, ruggedness) ACTFEL is the most important EL device type and is the longest lasting and most reliable flat panel display technology on the market. In this paper, the requirements of materials used in thin-film EL devices with double-insulating-layer structure are discussed in terms of optical, electrical, and physical characteristics. There are two device structures used in practical thin-film EL panels: a). a conventional device structure and b) in inverted device structures. Figure 2 shows the conventional device structure consisting of metal electrode/ insulating layer/phosphor layer/insulating layer/transparent electrode/glass substrate. On the other hand, Fig.3 shows the inverted device structure consisting of transparent electrode/insulating layer/phosphor layer/insulating layer/metal electrode/glass substrate and color filters on the covering glass substrate.

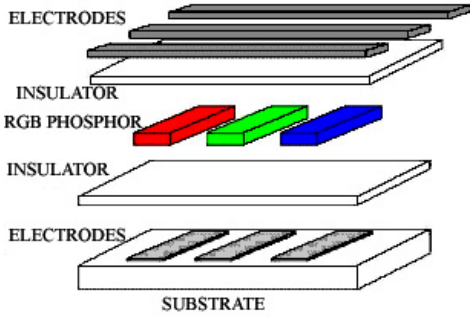

Fig.2. Device structure of a conventional thin-film EL device with patterned phosphors.

PHOSPHOR LAYERS

All phosphors consist of a host material and a luminescent centre. The requirements for the phosphor host materials are as follows:

- They have a large enough band gap (>4eV) to emit visible light from the doped luminescent centers without significant absorption.
- They must hold a high electric field of the order 10^8 V/m without electric breakdown and they must have insulating characteristics below the threshold voltage. They must withstand a post annealing temperature of 550^0C. Phosphor host materials satisfying the above requirements are limited to II-VI compounds, such as CaS, SrS and alkaline earth thiogallates and

thialuminate, $CaGa_2S_4$, $SrGa_2S_4$, $BaGa_2S_4$, and $BaAl_2S_4$.

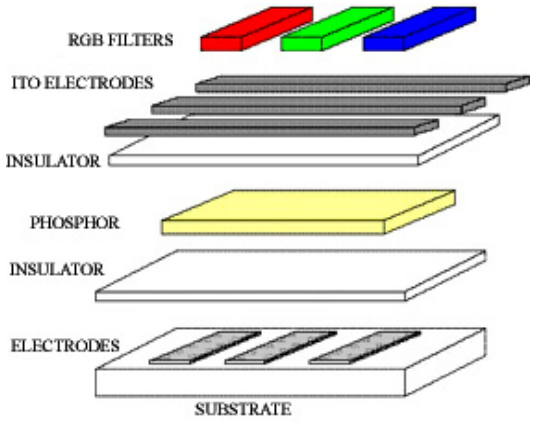

Fig.3. Device structure of an inverted thin-film EL device with patterned color filters.

METAL ELECTRODES

The requirements for the rear electrode materials in the conventional thin-film EL structure shown in Fig.3 are as follows:

- Good adhesiveness to the insulating layer.
- No metal-ion migration at high electric field.
- An ability to prevent breakdown spread when dielectric breakdown of the phosphor layer or insulator layer occurs.
- Low resistivity.
- High-temperature resistance not to be deformed above 550^0C during annealing, i.e. high melting point.
- Thermal expansion coefficient that matches that of glass substrate. Small reflection coefficient in the visible light region to obtain good contrast.

INSULATING LAYERS

The most important role of the insulating layers is to protect the phosphor layers from electric breakdown in the electric field of more than 10^8 V/m, so that insulating layer films must have no significant defects in areas in excess of 200 cm^2. The following properties are required to produce reliable and efficient thin-film EL devices:

- High dielectric constant.
- High dielectric breakdown electric field.
- Small number of pinholes and defects.
- Good adhesiveness.

THE DOUBLE-INSULATING-LAYER TYPE EL DEVICES HAVE THE FOLLOWING ADVANTAGES:

- Double-insulating layers can protect the phosphor layer against impurities and moisture from outside to ensure higher stability.
- Direct electric fields from electrodes to the phosphor layer are prevented resulting in it's a high breakdown values.
- Trapped charges at the phosphor layer/insulating layer interfaces cause internal polarization, with increases the effective EF under ac drive conditions.
- As a result, luminous efficiency and luminance are increased.

ELECTROLUMINESCENT MECHANISM

Above the threshold voltage, electrons are injected from the interface states between the phosphor and insulating layers by high-field-assisted tunneling. The injected electrons are accelerated and gain kinetic energy large enough to excite luminescent centers or the host lattice.

High-energy electrons, which are called hot electrons, directly excite luminescent centers through the impact excitation mechanism. When these electrons in the excite state of the luminescent centers make radiative transitions to the ground state, EL emission is realized. The high energy electrons travel through the phosphor layer and are finally trapped at the phosphor layer/insulator layer interface states on the anode side, causing polarization. When the polarity of the ac voltage wave forms is reversed, the same process takes place in the opposite direction in the phosphor layer.

The development of inorganic EL technology began with the discovery of high-field electroluminescence in 1936[16]. Then various technologies were invented, such as luminescence from molecular centers, LUMOCEN[17], high-luminance and long-lifetime ac thin-film EL displays, multicolor emission from CaS-and SrS-based thin-film EL[18] and alkaline earth thiogallates[19,20]. A full-color display requires three colors: red, green, and blue. "Triple-patterned phosphor" technology, which emits three colors in a pixel, and "Color-by-White" technology, which changes white light into three colors by the use of a color filter, can be used to obtain a full-color display. But they have some problems; for example, the process is complex and the efficiency is bad, respectively. Recently iFire technology developed CBB technology [21] by applying the principle of color conversion technology, which changes the blue color into red and green colors through color-changing materials. CBB technologies have some advantages: a simpler process, less expensive, and higher yield. Brighter blue-phosphor materials are needed in order to make CBB technology practicable.

NOVEL METHOD TO ACHIEVE FULL-COLOR INORGANIC EL DISPLAY, COLOR-BY-BLUE

The Color-by-blue (CBB) concept for achieving full-color inorganic EL display is based on the idea of color reproduction by optical down-conversion. The production of color by down-conversion has been known for many years and is most commonly achieved by the use of UV light as the primary radiation, usually termed as a pump that is absorbed by phosphor layers which then convert it to RGB colors. Due to the recent progress in inorganic EL technology and the available of efficient and saturated blue EL phosphors, the production of full-color inorganic EL displays by the utilization of the CBB concept could be a viable route for achieving full-color EL displays with high luminance levels and excellent color quality. The CBB approach offers an elegant solution to all of these challenges. More specifically, it eliminates the need for etching the blue phosphor layer as well as the subsequent phosphor patterning processes thus simplifying the full-color production process immensely. Secondly, since the colors in all of the three sub pixels in the CBB approach

are generated from a primary blue-emission source, only one single thin film blue phosphor is required instead of three. As, a result, the need for threshold matching for the three phosphor films as previously required in the triple-patterned panels is eliminated. In order for the CBB approach to function effectively, the chief requirement is an efficient blue EL device. Resent improvements in the blue EL phosphor material system of $BaAl_2S_4$: Eu, have made it an excellent blue pump and enabled the utilization of the CBB approach in inorganic EL displays. To achieve efficient conversion of blue light into red and green used inorganic photo luminescent phosphor and organic florescent dyes and pigments. Material screening and selection for potential display applications were based on three criteria:

1. High conversion efficiency of the blue light into either red or green emissions. This is obtained when there is a strong coupling between the blue EL emission and the excitation peaks of the potential phosphors or florescent dyes and pigments. In addition to having a strong absorption coefficient, these converts must have high quantum efficiency yields in converting the blue light into either red or green light.
2. Color saturation of the emitted light of the photoluminescent materials is essential in order to avoid the need of color correction by filtering.
3. Color and luminance stability under strong blue excitation are crucial as well.

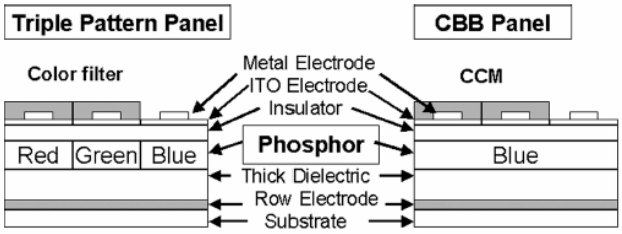

Fig.4. Structure of the TDEL panels using triple pattern and CBB technology.

Figure 4 shows the structure of TDEL panels for the combination of conventional triple-pattern technology and CBB technology. The panels consist of the substrate, printed row electrode, screen-printed thick-dielectric, phosphors, upper insulator, ITO, metal column electrode, and color filters or color-conversion materials (CCM).They are simple structures and can produce panels cheaper than other flat-panel displays because they do not require a fine structure like that for a TFT-LCD.

PHOSPHOR –CONVERTED WHITE LED

There has been much interest in light emitting diodes (LEDs) that emit light from ultraviolet to infrared. Major developments in wide band gap III-V nitride compound semiconductors have led to the commercial production of high efficiency LEDs [22, 23]. Development of white LEDs is important for expanding LED applications toward general lighting, where the opportunities are enormous. Green and blue InGaN technology makes possible the first white light LED in which white lights is obtained by mixing the outputs of red, green, and blue LEDs. Unfortunately, combining multiple LEDs produces a poor white.

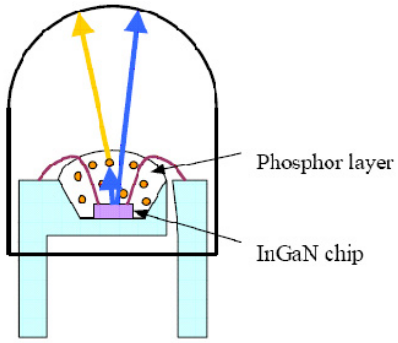

Fig.5. InGaN based luminescence conversion white LED.

Using one or more phosphors excited by an LED can also be made to generate white light. The simplest version of a phosphor-converted (PC) LED arises from a combination of a part of the primary blue light of the LED and a yellow phosphor, conceptually copied from the color correction scheme of high pressure discharge lamps, in which a blue excitable yellow phosphor is used in combination with incompletely absorbed blue. Such a phosphor ($YAG:Ce^{3+}$) is used now by LED manufacturer's together with a blue LED emitting at 450-475 nm. Much better results-greater variability of the chromaticity and better color rendering -can be expected by combining a blue LED with suitable phosphors, (Figure 5) excited by part of the blue LED emission.

However the emission peaks have to be at the correct wavelengths and suitable broad, and be excitable by the same LED wavelength. Alternatively, excitation could be caused by cascading, meaning a green emission could be used to excite a red-emitting phosphor. We postulate the dipole-allowed 5d-4f transition of Eu^{2+} can be shifted into the right spectral position by a suitable choice of a $II-III_2S_4$ compound. For example, $SrGa_2S_4$ shifts the emission of Eu^{2+} to 537 nm peak wavelength, while SrS shifts it to 620 nm. The excitations spectra consist of extremely broad bands that extend well into the visible region. The efficiency of $SrGa_2S_4$:Eu is very good as well. A cathodoluminance of 100 cd/m^2 and efficacy of 1 lm/W were obtained at an accelerating voltage of 5 kV with a current density of 60 $\mu A/cm^2$, along with an intrinsic luminous efficacy η_{int}=18.8 lm/W [24].

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