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Dedicated to professor Gh. Marcu at his 80th anniversary

STUDIES ON THE INFLUENCE OF FLUX NATURE ON THE PROPERTIES OF NIOBIUM ACTIVATED YTTRIUM TANTALATE PHOSPHOR

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ABSTRACT. Niobium activated yttrium tantalate ($YTaO_4$:Nb) presents good X-ray absorption and emits in the blue region of the spectrum. The goal of the paper is to study the influence of flux nature on the crystalline structure, morphology and luminescent characteristics of $YTaO_4$:Nb powders. Phosphors samples were prepared by solid state reaction route and theirs properties were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL) measurements and scanning electron microscopy (SEM).

Keywords: yttrium tantalate, phosphors, luminescence, X-ray imaging

INTRODUCTION

Niobium activated yttrium tantalate, $YTaO_4$:Nb is an efficient luminescent material used in medical X-ray imaging applications[1,2]. The characteristic emission spectra consist in a broad band situated in the UV-blue domain of the electromagnetic spectrum with a maximum at 390-410 nm. Performances of $YTaO_4$:Nb phosphor powder are correlated with the crystalline structure, particle size, morphology and luminescence properties.

It is well known that the emission intensity and colour purity of $YTaO_4$-based phosphor are extremely sensitive to crystalline phase composition of the materials [3-5]. Depending on the synthesis conditions yttrium tantalate present different crystalline structures. There are two polymorphs, i.e. high temperature tetragonal (T-$YTaO_4$ phase, scheelite structure) and low-temperature monoclinic (M-$YTaO_4$ phase, fergusonite structure) forms. There is an additional monoclinic phase, designed as M-prime form (M'-$YTaO_4$) that can be obtained in appropriate conditions, namely below 1450°C. The high luminescence performances of niobium activated

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yttrium tantalate phosphor are associated with the monoclinic crystalline structure, where M'-$YTaO_4$ represents the equilibrium phase at room temperature.

The preparation of $YTaO_4$: Nb phosphor is usually achieved by solid state reaction route from synthesis mixtures containing different metallic oxide sources. The monoclinic M' crystalline structure of the $YTaO_4$ host lattice**,** as well as the emission centre formation is substantially improved when the thermal synthesis is flux-assisted by some inorganic salts.

The paper presents several aspects referring to the synthesis of niobium activated yttrium tantalate phosphor ($YTaO_4$: Nb). The influence of the flux nature on the crystalline structure, particle morphology and luminescent characteristics of $YTaO_4$: Nb phosphor is investigated in order to identify an optimal flux reagent that could generate a high performing material.

EXPERIMENTAL PART

Niobium activated yttrium tantalate samples were prepared by solid state reaction route from homogeneous mixtures consisting of raw oxide precursors Y_2O_3 (99.9%), Ta_2O_5 (Optipur), Nb_2O_5 (99%) and Li_2SO_4 (99%) and/or Na_2SO_4 (99%) as flux. The stoichiometric amounts of Y_2O_3, Ta_2O_5, Nb_2O_5 and 30 wt % alkaline sulphates were ball-milled with acetone and dried at 70°C. The powders mixture was calcined in air at 1200°C, for 4 h and slowly cooled to the room temperature. Finally, phosphors samples were water washed, dried and sieved.

The as-prepared phosphors were characterized by fluorescence and FTIR spectroscopy, X-ray diffraction and scanning electronic microscopy.

Photoluminescence (PL) measurements were performed at room temperature, with a Perkin-Elmer 204 Fluorescence Spectrophotometer. The emission spectra were registered under 254 nm excitation and were normalised in comparison with an internal standard. X-ray Diffraction (XRD) analysis was performed on SIEMENS D5000 diffractometer (CuKα radiation). IR absorption spectra were registered on JASCO 610 FTIR Spectrometer (KBr pellets technique). Scanning Electron Microscopy (SEM) analysis was performed using a LEO 1550 microscope.

The interpretation of XRD data was achieved on the basis of powder diffraction files namely, PDF 00-024-1425 for M'-$YTaO_4$, PDF 00-048-0265 for orthorombic-Y_3TaO_7.

RESULTS AND DISCUSSION

Niobium activated yttrium tantalate phosphors ($YTaO_4$:Nb) were obtained by the classic solid state reaction route, from synthesis mixtures containing yttrium oxide and tantalum oxide as generators of the host matrix, niobium oxide as generator of activator ions, and lithium sulphate and/or natrium sulphate as flux. The formation of yttrium tantalate activated with 15 mole % niobium phosphors could be described by the equation (1):

$$Y_2O_3 + (1-x)Ta_2O_5 + xNb_2O_5 \xrightarrow{M_2SO_4,T} 2YTa_{1-x}Nb_xO_4 \quad (1)$$

where: x=0.15

During the thermal synthesis stage, the flux reacts with the mixture of oxides to produce intermediate compounds that are more reactive than the starting oxides. According to the literature, a high calcination temperature facilitates their mutual interaction to give the final product and to regenerate the flux [1,2]. For this reason, the flux compound is considered as catalyst or reactive flux [6].

Photoluminescence (PL) characteristics, crystalline structure, particle morphology and sizes of $YTa_{0,85}Nb_{0.15}O_4$ samples were determined in order to establish the correlation between the phosphors properties and their synthesis conditions.

Luminescence properties

All powder samples are white coloured and exhibit blue luminescence during a 254 nm excitation.

The emission spectra show broad bands with a maximum at around 390 nm (**Fig. 1**). The sample, which was prepared at 12000C with Li2SO4 as flux, presents the highest luminescent intensity. Using a Li_2SO_4 - Na_2SO_4 mixture or Na_2SO_4 as flux, an obvious decrease of the $YTaO_4$: Nb phosphor emission intensity can be observed.

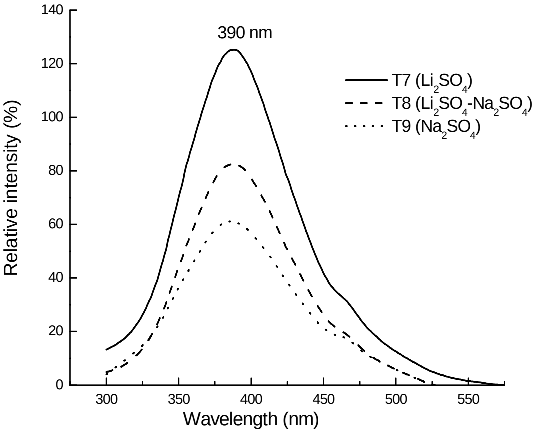

Fig. 1. Emission spectra of $YTa_{0.85}Nb_{0.15}O_4$ samples (λ_{exc}= 254 nm)

The flux-dependence of the luminescence intensity can be partially explained by the crystalline structure or particle morphology and the size of $YTaO_4$-based phosphors obtained in different conditions.

Crystalline structure

The crystalline structure and order degree of phosphors were evaluated on the basis of X-ray diffraction patterns (XRD) and FTIR spectra (**Fig. 2**).

The most homogeneous crystalline phosphor powder was obtained at 1200^0C, by using Li_2SO_4 as flux. Sample T7, $YTaO_4$:Nb [Li_2SO_4; 1200°C] is a single phase material of monoclinic M’ polymorph form. Replacing Li_2SO_4 with Na_2SO_4 (sample T9), additional reflections are observed that can be ascribed to some intermediate compounds, such as the orthorhombic Y_3TaO_7. This shows that at 1200ºC, sodium sulphate does not assure the complete conversion of oxides into yttrium tantalate phase.

Mention has to be made that our experimental data for the compounds obtained in the Y_2O_3-Ta_2O_5-Nb_2O_5 system are in good agreement with the literature XRD data for the Y_2O_3-Ta_2O_5 system. This fact evidences that niobium oxide is well dissolved into the $YTaO_4$ crystalline lattice to form the niobium activated yttrium tantalate phosphor, as suggested by the PL spectra.

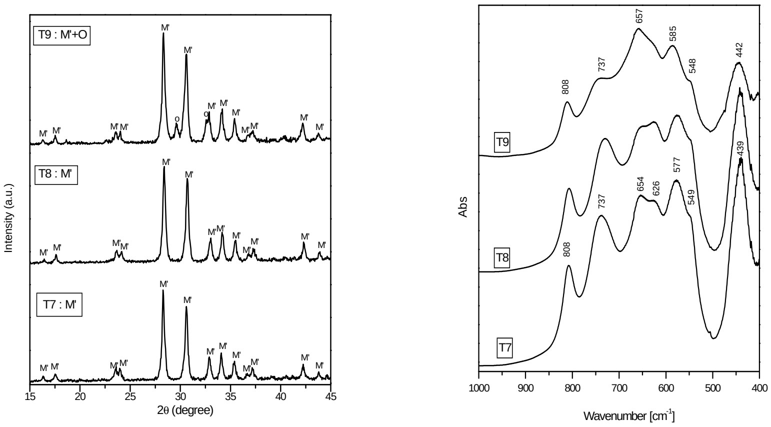

Fig. 2. XRD patterns (left) and FT-IR (right) spectra of $YTa_{0.85}Nb_{0.15}O_4$ samples prepared with different fluxes,T7= Li_2SO_4]; T8= Li_2SO_4+Na_2SO_4; T9= Na_2SO_4 (M’=M’-$YTaO_4$ and O= orthorhombic Y_3TaO_7 structures)

The infrared spectra confirm that flux nature influences the crystalline order degree of phosphors, as it was already illustrated by the XRD patterns. Sample T7 prepared with Li_2SO_4 has a single phase M’- structure, as shown by the well formed 439 and 808 cm^{-1} bands. In sample T9, obtained with Na_2SO_4 as a flux, the M’ phase still exists, but the crystalline structure is less organised, as suggested by the FTIR spectra.

For the Y_2O_3-Ta_2O_5-Nb_2O_5 system, Na_2SO_4 shows reduced flux reactivity as compared to Li_2SO_4. This behaviour is responsible for the weakest luminescence emission observed for T9 samples.

Particle morphology and sizes

SEM investigations were performed with the aim to characterize and compare the particle morphology and sizes for $YTaO_4$:Nb powders obtained in different synthesis conditions (**Fig. 3**)

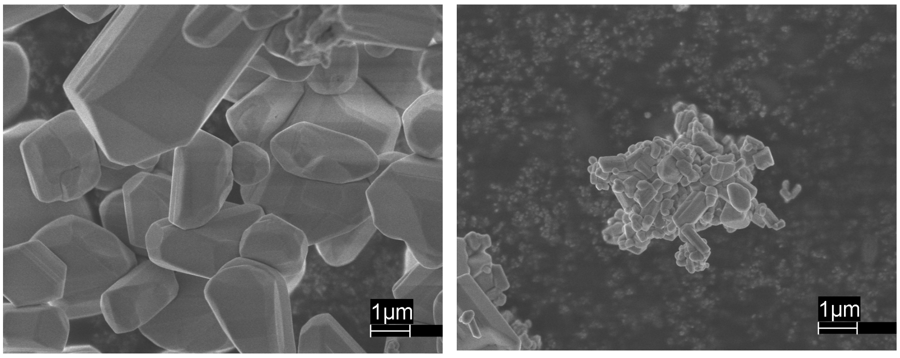

Fig. 3. SEM images of $YTa_{0,85}Nb_{0.15}O_4$ samples prepared with different fluxes: T7 - Li_2SO_4 (left) and T9 - Na_2SO_4 (right)

Using Li_2SO_4 as flux (sample T7), non-agglomerated particles with regular shape are obtained. Most of the polyhedral, elongated crystals are of 2 ÷ 5 μm in length and about 1μm in thickness. The partial or the total replacement of Li_2SO_4 by Na_2SO_4 strongly decreases the particle dimensions. In these conditions, particles with less regulated shape and with aggregation tendency are formed.

The most heterogeneous crystalline powder was prepared with Na_2SO_4, while the most homogeneous powder was obtained with Li_2SO_4 as flux.

Even if Li_2SO_4 (m.p.=884°C) and Na_2SO_4 (m.p.= 860°C) show close melting point values, their behaviour as flux is very different due to the large difference between the two cation sizes. The fact that Li^+ (0.073 nm) is much smaller than Na^+ (0.113 nm) is in the favour of the total conversion of oxides into the M'-$YTaO_4$ crystalline phase.

The general characteristics of $YTa_{0.85}Nb_{0.15}O_4$ phosphors prepared with different fluxes, i.e. the photoluminescence (PL) intensity at peak position, the main crystalline phase and the powder particle dimensions are summarized in Table 1.

Table 1

General characteristics of $YTaO_4$: Nb samples

Phosphor sample	Flux nature (w/w)	General properties		
		PL intensity I_{390} (%)	Crystalline phases	Particle size (μm)
T7	30% Li_2SO_4	125	M'	2.0 ÷ 5.0
T8	15% Li_2SO_4-15% Na_2SO_4	83	M'	0.5÷3.0
T9	30% Na_2SO_4	61	M' + O	0.2÷1.0

where: M' = M'-$YTaO_4$; O = orthorombic-Y_3TaO_7

One can conclude that the highest luminescence intensity of $YTa_{0.85}Nb_{0.15}O_4$ [1200ºC;Li_2SO_4] is associated with the high order degree of the crystalline lattice with M'-$YTaO_4$ structure phase. At 1200ºC, Li_2SO_4 shows the strongest flux reactivity for the Y_2O_3-Ta_2O_5-Nb_2O_5 system.

CONCLUSIONS

The flux nature is an important factor that determines luminescence properties, structural and morphological characteristics of niobium activated yttrium tantalate phosphor. Morphological and structural investigations put in evidence the high crystalline order degree of $YTaO_4$:Nb powders prepared with lithium sulphate as flux. The photoluminescence intensity is strongly affected by the crystalline homogeneity and particle dimensions of the phosphor powders.

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