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Influence of crystalline structure on the luminescence properties of terbium orthotantalates

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ABSTRACT

Terbium orthotantalate powders were produced with M-fergusonite type (I2/a) and M′-fergusonite type (P2/a) structures. The samples were studied by X-ray diffraction, Raman scattering, and photoluminescence measurements (emission and decay curves). The results showed that crystalline materials were obtained with all the 18 Raman-active modes predicted by group theory calculations. Also, it was observed through photoluminescence decay curves that the Tb^{3+} ions occupies only one-symmetry site in both crystallographic arrangements. Photoluminescence emission curves exhibited some variation in spectral shape, peak position, and relative intensity as a consequence of their different crystalline arrangements. The dominated emission of Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$) is centered with a maximum intensity at 549.2 nm (M-type) and 543.0 nm (M′-type). Fluorescence lifetimes for M-$TbTaO_4$ and M′-$TbTaO_4$ were determined as 33.4 μs and 1.25 ms, respectively. M′-type materials seems to be the most suitable for luminescent devices and could be a potential green luminescent material due to the strongest emission if compared with the M-fergusonite type.

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1. Introduction

The development of luminescent inorganic materials has been subject of extensive research in the past years because of their applications in devices involving the artificial production of light [1]. In this respect, rare earths are good candidates for luminescence center due to their special 4f intra-shell transitions [2]. Particularly, terbium ions are widely used as efficient emission centers in many oxide-based compounds, having relatively high transition probabilities originating from the 4f electron configuration [3]. The strong green emission with high glow purity and stability make terbium-doped phosphors to be suitable for many technological applications, such as cathode-ray tubes, fluorescence lamps, X-ray image devices, scintillators, light emitting diodes, and field emission displays [4]. Then, a large number of studies have been devoted to terbium-doped oxide matrices [5–12]. Among them, Tb^{3+} activated tantalates have attracted much attention because it is a promising alternative phosphor for X-ray intensifying screen [13]. The fluorescent properties of rare earth tantalates and niobates were firstly reported in [14]. Undoped tantalates and niobates themselves have been well known as self-activated luminescent materials [15]. Nevertheless, to the best of our knowledge, no work concerning terbium orthotantalates in self-activated materials was previously reported in the literature so far.

In the present work, M-$TbTaO_4$ and M′-$TbTaO_4$ self-activated ceramics were prepared by solid-state reaction. It is well known that the synthesis parameters strongly influence on the degree of the crystalline order of the ceramics and in the same cases it might results in different structural arrangements [16,17]. Furthermore, the crystal structure is directly related with the luminescence performance of the materials [6]. In this work, specific conditions of temperature and time were employed to compounds crystallized in monoclinic structures with two different arrangements in agreement with the previous work by Siqueira et al. [16]. In this case, the compounds crystallize in M-fergusonite (M-type) structure with space group I2/a (#15) when processed at high temperatures, and M′-fergusonite (M′-type) with space group P2/a (#13) for compounds obtained at low temperatures. The crystalline structures were investigated by X-ray diffraction (XRD) and Raman scattering. Furthermore, the photoluminescence (PL) properties of each sample were studied in detail by both PL emission and decay time measurements, in order to correlate these characteristics with the corresponding crystalline structures. Finally, we will compare the optical properties of self-activated terbium orthotantalates studied in this work with other Tb^{3+}-doped materials.

2. Experimental

$TbTaO_4$ ceramic powders were prepared by solid-state reaction. The starting materials employed were Tb_4O_7 and Ta_2O_5 ($>99.9\%$ Sigma-Aldrich), which were thoroughly mixed in a

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mortar according to the desired stoichiometric ratio. The experimental processing conditions were 1300 °C/6 h to produce M-$TbTaO_4$, and 1200 °C/6 h to obtain M′-$TbTaO_4$. The crystalline structures of the as-synthesized samples were studied by XRD using a Shimadzu D-6000 diffractometer with graphite monochromator and a nickel filter in the range of 10–60°2θ (15 s/step of 0.02°2θ), operating with FeK_α radiation (λ=0.1936 nm), 40 kV and 20 mA (the results were automatically converted to CuK_α radiation for data treatment and manipulation).

Raman spectra of the as-synthesized powders were collected in backscattering configuration using an Horiba/Jobin-Yvon LABRAM-HR spectrometer with the 632.8 nm line of a helium-neon laser (effective power of 6 mW at the sample's surface) as excitation source, diffraction gratings of 600 and 1800 grooves/mm, Peltier-cooled CCD detector, confocal Olympus microscope (100 × objective), and experimental resolution typically 1 cm^{-1} for 10 accumulations of 30 s. Appropriate interference filter for rejecting laser plasma lines, edge filter for stray light rejection were used. All resulting spectra were corrected by Bose–Einstein thermal factor [18].

The emission spectra were acquired at room temperature on a DIGIKROM480 Tzerny Turner monochromator with resolution of 1 nm, excited by a He–Cd laser (325 nm, 40 mW). The luminescence signal was acquired by a photomultiplier model (R928), operating in the range from 400 to 900 nm or an InGaAs detector, in the range from 800 to 1700 nm. Signal was amplified by a SRS 530 lock-in with reference signal provided by an optical chopper (SR540), operating in the range from 5 to 4000 Hz and collected by a computer. Luminescence decay curves were obtained in the same experimental setup of the luminescence experiments, where the SRS lock-in was substituted by a SR445A 350 MHz Preamplifier and the amplified signal was collected by a computer. The excitation laser was pulsed by the use of a chopper, with frequencies in the range from 10 to 100 Hz.

3. Results and discussion

The terbium orthotantalates produced were studied through XRD and Raman scattering and the results are presented in Fig. 1. The samples crystallized in fergusonite-type structures, but with different arrangements as a function of the synthesis temperature (Fig. 1a). At high temperatures (1300 °C), the powders exhibited the M-type structure, belonging to the space group I2/a (C_{2h}^6, #15), with Z=4. On the other hand, at low temperatures (1200 °C) the powders exhibited the M′-type structure, space group P2/a (C_{2h}^4, #13), and Z=2. XRD patterns were indexed according to ICSD-109187 and ICSD-415434 for M-$TbTaO_4$ and M′-$TbTaO_4$, respectively. For the polymorphs studied in this work, it is well known that the atoms occupy different Wyckoff positions. For the M-$TbTaO_4$ (I2/a, #15) material, the atoms Tb and Ta occupy the position 4*e* while the two oxygen occupy the 8f sites. For the M′-$TbTaO_4$ ceramic (P2/a, #13), the Wyckoff positions are as follows: Tb=2f, Ta=2e, O(1) and O(2)=4g. Due to these occupation sites, the Raman-active modes for these two systems can be decomposed according to the irreducible representation (i.r.) of the C_2 point-group. Then, using the site-group method of Rousseau et al. [19] we obtained the same distribution of the degrees of freedom at Brillouin-zone center in terms of the i.r. for the two arrangements, as following:

$$\Gamma_{TOTAL} = 8A_g + 10B_g + 8A_u + 10B_u \quad (1)$$

Fig. 1b presents the Raman spectra for the samples investigated: the blue spectrum corresponds to the M-$TbTaO_4$ ceramic, while the black spectrum is related to the M′-$TbTaO_4$ sample. Although the materials exhibited an equal number of Raman-active modes, they present different Raman signatures. All the 18

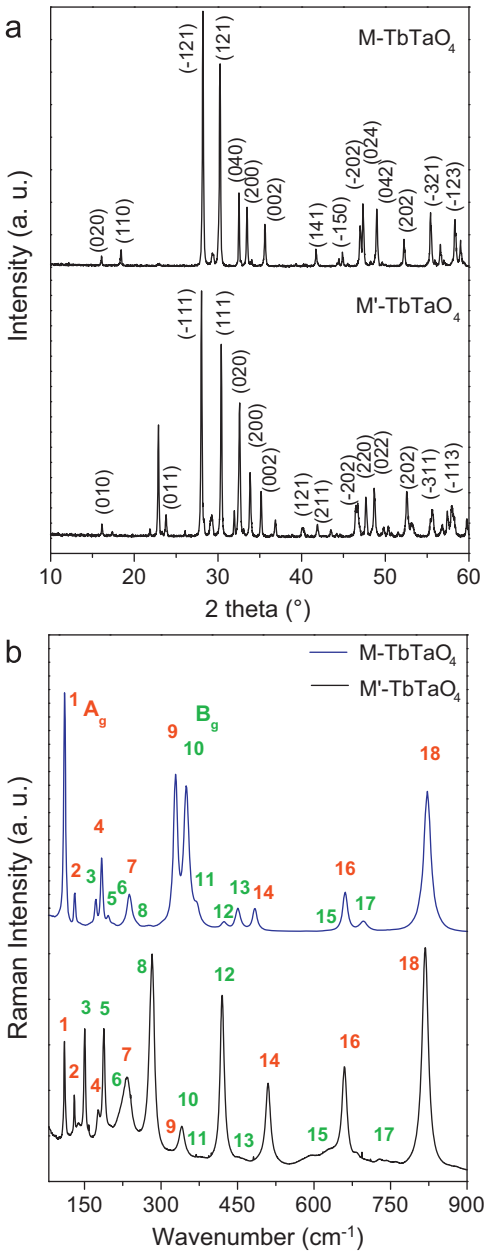

Fig. 1. (a) XRD patterns for M-$TbTaO_4$ and M′-$TbTaO_4$ with the respective crystallographic planes indexed. (b) Raman spectra for the M-type (blue) and M′-type (black) compounds in the region 60–900 cm^{-1}. The Raman-active modes are numbered for better visualization and assignment. Red numbers represent the A_g modes, while green numbers correspond to the B_g modes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

active modes can be visualized and were numbered (Fig. 1b) for better visualization and assignment: red numbers correspond to the A_g modes, while green numbers correspond to the B_g modes. If we compare the spectra of M- and M′-$TbTaO_4$, we can observe a change of the relative intensities of the modes through the transition from M-fergusonite to M′-fergusonite. This difference could be attributed to the new structural arrangement assumed by the sample when it changes from one structure to another. Furthermore, if we observe the assignment to the active Raman modes of these fergusonite-type structures (see Fig. 1b), we can assume that the crystalline arrangement regarding the M-type structure seems to favor the A_g modes, while the arrangement observed in M′-type structures seems to favor the B_g modes.

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