



Optical and structural properties of chromium impurities in niobium–gallium oxide



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HIGHLIGHTS

- Cr³⁺ doped niobium–gallium oxides were prepared by solid state reaction and wet chemical method.
- We show bands in red region.
- Spectra are associated to Cr³⁺ ions in octahedral sites.

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ABSTRACT

In this work, the optical properties of the gallium–niobium oxide doped with chromium ions were investigated. The samples were obtained by wet chemical and solid-state methods, investigated by X-ray powder diffraction and the data were refined by Rietveld methods. The morphology was determined by scanning electron microscope (SEM) images. The photoluminescence, excitation and photoacoustic measurements showed broad and intense bands in the red region of the spectrum, associated with energy transitions of chromium ions in octahedral sites. From the optical spectra and using the crystal field theory, the energy parameters were obtained.

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1. Introduction

Light emitting materials present a large number of applications, such as: cathode rays tubes [1], tunable lasers [2,3], special lamps [4], electroluminescent devices [5], devices to X ray images [6], broadband amplifiers [7], devices for radiation detection [8], light emission sources [9], optical sensors [10], luminescent plastics [11] and luminescent paper [12], among many others. Some of these applications use toxic elements as emission activators, which sometimes are expensive as well [13,14]. So, it is important the development of non-polluting low cost materials with durability and stability. Nowadays, the research about new luminescent materials point to oxides phosphors, because many of these materials present the qualities above [14]. On the other hand, oxides systems

doped with Cr³⁺ are investigated because they eventually can present broad emission and absorption bands at visible and near infrared regions, due to the impurity–host ions interactions. Some examples of the potential applications of Cr³⁺-doped oxides materials are: the Al₂O₃:Cr³⁺ used as a thermographic phosphor for the surface temperature measurements [15], the ceramic scintillator Gd₃Ga₅O₁₂:Cr,Ce [16] and the Mg₂SiO₄:Cr³⁺,Li from which have been obtained a continuous-wave laser and pulsed laser, tunable from 1030 to 1180 nm [17].

Following the interest in investigating the properties of Cr³⁺ doped-oxides as luminescent materials and taking into account the previous studies about Cr³⁺ in octahedral sites of Ga³⁺ in magnesium–gallium oxides [18–20], we present in this paper a study on the preparation, structural characteristics and optical properties of the Cr³⁺ in octahedral sites of Ga³⁺ in niobium–gallium oxides. We used the solid-state and the wet chemical methods for reaction between Nb₂O₅, Ga₂O₃ and Cr₂O₃ oxides. The reaction produced GaNbO₄, GaNb₁₁O₂₉ and quantities of non-reacted Ga₂O₃ and in solid-state method, Nb₂O₅ also.

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The GaNbO₄ has been investigated because it presents some relevant physical properties. For example, the compound was studied as a new potential semiconducting material, where the energy bands structure, physicochemical and photophysical properties were recently reported [21]. The GaNbO₄ is also investigated as a photo-catalytic material for use in photo-dissociation of aqueous methanol to produce H₂ [21]. In earlier works, G. Blasse et al. showed the GaNbO₄ luminescence at low temperature and at atmospheric pressure, located at 460 nm and 420 nm [22] and at high pressure, at 465 nm and 485 nm [23]. The emissions were attributed to the Nb–O distance and the presence of defects in the crystal structure.

Another important characteristic of the oxide materials is the thermal stress, because above a determinate value, the material breaks. This thermal stress depends directly on the coefficient of thermal expansion (CTE). The mean CTE of GaNbO₄ ($=5 \times 10^{-7}/^{\circ}\text{C}$) was obtained by Dejneka et al. [24], a value considered low, and consequently, interesting for applications as catalytic material. Tabero [25] showed that the crystalline structure is responsible for the anisotropy of thermal expansion coefficients of the GaNbO₄.

The GaNbO₄ was described as a compound which crystallizes in a monoclinic system, space group C2/mn with unit-cell dimensions $a = 12.660 \text{ \AA}$, $b = 3.7921 \text{ \AA}$, $c = 6.6147 \text{ \AA}$ and $\beta = 107.90^{\circ}$ and which presents two different distorted octahedral sites, occupied by the cations Ga³⁺ and Nb⁵⁺ [25,26].

The gallium oxide Ga₂O₃ is studied for several applications, as for example, optoelectronic devices due to their mechanical, optical, thermal and chemical properties [27]. The Ga₂O₃ was described as a monoclinic structure with lattice parameters $a = 12.23 \text{ \AA}$, $b = 3.04 \text{ \AA}$, $c = 5.80 \text{ \AA}$ and $\beta = 103.7^{\circ}$ with distorted octahedral Ga³⁺ sites [28,29].

The compound GaNb₁₁O₂₉ was reported in a previous work as an orthorhombic structure isostructural with the Ti₂Nb₁₀O₂₉ compound with cell dimensions related to this material, $a = 28.5 \text{ \AA}$, $b = 3.805 \text{ \AA}$, $c = 20.51 \text{ \AA}$ and $\beta = 90^{\circ}$, space group *Amma* [30]. In the GaNb₁₁O₂₉ the Ga³⁺ ions are octahedrally coordinated by O²⁻ ions [31].

The gallium oxides have appropriate sites to be occupied by the impurity ion Cr³⁺ due to the fact that Ga³⁺ and Cr³⁺ have the same valence and similar ionic radii $r_{\text{Ga}^{3+}} = 0.620 \text{ \AA}$ and $r_{\text{Cr}^{3+}} = 0.615 \text{ \AA}$ [32] which facilitates the substitution. On the other hand, the difference of the valence and ionic radii does not favor the substitution of Nb⁵⁺ ($r_{\text{Nb}^{5+}} = 0.78 \text{ \AA}$) by Cr³⁺ ions.

In Fig. 1 we can see the splitting of energy levels of d³ ions in the octahedral crystalline field, described in the Tanabe–Sugano diagram [33,34], which is the electronic configuration of the Cr³⁺ ions. The fundamental energy level ⁴F is splitted into the ground energy level ⁴A₂ and two excited energy levels ⁴T₂ and ⁴T₁. The first excited level, ⁴P is transformed by the crystal field in the ⁴T₁ (⁴P) level and the higher level ²G is splitted in ²E, ²T₁, ²T₂ and ²A₁. The transitions at the visible region of the spectrum occur between these levels. The transitions between states with the same spin multiplicity are allowed, generating intense bands, while transitions between states with different spin multiplicities are forbidden, producing weaker bands. The energy levels ⁴T₂ and ⁴T₁ are dependent of the crystal field energy parameter Dq . Therefore, the transitions from and to these states generates broad optical bands, while transitions between the fundamental energy level ⁴A₂ and the ²E and ²T₁ (²G) energy levels generates narrow bands, because these states are not dependent from the crystalline field. The transitions between the ⁴F splitted energy levels are precisely those which make interesting the research about Cr³⁺-doped materials, for the possibility of producing tunable intense bands.

The crystallographic and optical data of the Cr³⁺-niobium–gallium oxide system are show in this paper, as a new

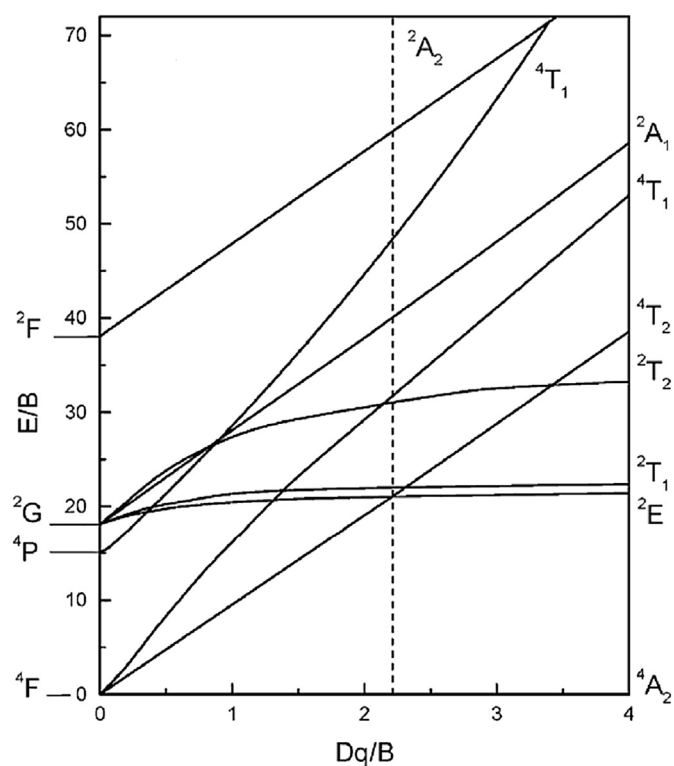


Fig. 1. Tanabe–Sugano energy-level diagram for d³ electronic configuration.

system with potential applications on tunable material at room temperature. A very attractive luminescent sustainable material.

2. Experimental

Two polycrystalline samples of the niobates were prepared using different methods. One was prepared by conventional solid state reaction, while the second was made by wet chemical method. In procedures, the highly pure (99.9%) niobium oxide (Nb₂O₅), gallium oxide (Ga₂O₃) and chromium oxide (Cr₂O₃) powders, were weighed with adequate stoichiometric proportions to obtain 1 g of the Ga_{0.99}Cr_{0.01}NbO₄ compounds. The sample obtained by the solid state method was prepared as follows: after the powders were weighed, the mixture was milled by hand in an agate mortar during three hours and then pressed. Afterwards, the material was placed into a furnace to react at 1000 °C for 12 h.

In order to compare the effect of sample preparation on the optical properties, besides the sample obtained with the solid state method, another sample of the same compound was prepared through the wet chemical method. In this case, adequate oxide stoichiometric proportions were mixed and dissolved into 5 ml of water solution with 50% of glacial acetic acid (CH₃COOH). The mixture was slowly heated during 25 min to fully evaporate the water. After the evaporation the solution volume was reduced, leaving the final solution with a green color. Finally, the green solution was completely dried at 100 °C in a furnace during 12 h. During this step the oxides are dissociated and the metal ions are mixed in the network with a better distribution than the one obtained by the mechanical method. In the second step, the solid solution was put into an alumina crucible to receive thermal treatments inside a furnace. The first treatment was made at 800 °C during 12 h and the final synthesis at 1200 °C for 12 h. After the synthesis, the mixture was reground until a homogeneous and fine powder was obtained, ready for pressing (the sample) in pellets. A

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