Journal of Alloys and Compounds 720 (2017) 417–422

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

# Photoluminescence of divalent cobalt ions in tetrahedral sites of zinc orthotitanate

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ARTICLE INFO

*Article history:*
Received 23 March 2017
Received in revised form
8 May 2017
Accepted 19 May 2017
Available online 22 May 2017

*Keywords:*
A. Insulators
C. X-ray diffraction
D. Luminescence

## ABSTRACT

Zinc orthotitanate ($Zn_2TiO_4$) polycrystalline samples doped with $Co^{2+}$ ions were synthesized by solid state reaction and investigated by X-ray diffraction and photoluminescence spectroscopy at room temperature. Two bands were detected in the photoluminescence spectrum in the near infrared range: the most intense, centered at 714 nm assigned to the $^4T_1(^4P)\rightarrow{}^4A_2(^4F)$ and a less intense band, identified as $^4T_1(^4P)\rightarrow{}^4T_2(^4F)$, both generated from spin-allowed electronic transitions. Photoluminescence excitation spectrum at 714 nm exhibits typical transitions of $Co^{2+}$ in tetrahedral coordination. From the transitions observed in emission and excitation spectra and using the Tanabe-Sugano theory, the crystal field parameter $Dq$ and Racah parameters $B$ and $C$ were obtained. The intense and broad emission band in the near infrared makes this system a material with high potential for use as tunable media.

## 1. Introduction

The zinc orthotitanate ( $Zn_2TiO_4$) is a versatile material with high thermal stability and with applications in several fields including catalysis, dielectric materials fabrication, pigmentation, sensing, solid oxide fuel cells development and white light emitting diodes (WLEDs) [1–4], among others. The single phase synthesis can be achieved by solid state reaction at high temperatures [5], chemical process using soft solutions [1], ball milling method [2], solution combustion synthesis [3], regular sol gel [4] and citrate sol gel method [6], following the phase diagram for $ZnO-TiO_2$ systems [5].

$Zn_2TiO_4$ crystal structure belongs to the space group $Fd\bar{3}m$ with cubic symmetry and an inverse spinel structure, which is well known and whose description can be found in several works [1,3,7,8]. This structure has two possible positions for cation occupation, with tetrahedral and octahedral coordination. Divalent and/or trivalent ions can occupy these sites. The usual spinel structure has formula $A^{(4)}\ B_2^{(6)}\ X_4$ (where the superscript 4 indicates the tetrahedral site and 6 the octahedral site; X is the ligand anion), while in the so-called inverse spinel the divalent cations occupy octahedral positions, with formula $B^{(4)}(AB)^{(6)}\ X_4$. With inverse spinel structure, a few Zn ions in zinc orthotitanate are in tetrahedral sites while the remained Zn and Ti cations are randomly distributed in octahedral sites, with formula symbolized by Zn[ZnTi]$O_4$, where the brackets enclose the cations in octahedral coordination [7]. The versatility of the spinel systems resides in the fact that they possess multiple sites in distinct geometries (tetrahedral and octahedral) for dopant occupation [9]. In the point of view of spectroscopic properties, this is interesting because it opens the possibility to obtain emission bands in distinct positions, making them tunable according to the impurity inserted and with the occupation site in the crystal host.

In tetrahedral environment, the luminescence of $Co^{2+}$ is observed at room temperature, in the visible and near-infrared range. The bands are broad and intense, as reported by several authors in distinct ceramic hosts: $ZnGa_2O_4$ [6], $MgAl_2O_4$ [10], $LiGa_5O_8$ [11] and $LiZnNbO_4$ [12]. In octahedral environment, the emission bands are observed in the infrared range (usually above 1500 nm), and at low temperatures mainly due the fact that non-radiative decay play a very important rule in the relaxation process at room temperature. As an example, Henderson and Bartram report that the non-radiative processes in the luminescence of MgO:$Co^{2+}$ are so effective that the emission is completely quenched above 77 K [13,14]. For this reason, the emission of $Co^{2+}$ in octahedral hosts is mainly reported at very low temperatures, as in the $MgF_2$ system [15].

The photoluminescent properties of $Co^{2+}$ incorporated as

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http://dx.doi.org/10.1016/j.jallcom.2017.05.188
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impurity in several crystal hosts has been studied in the last years due to its potential applications in tunable solid state lasers [16], pigments [17] and solar collectors [18]. Systems doped with divalent cobalt as $LiGa_5O_8$ [11], ZnSe [19], $MgAl_2O_4$ [20], $LaMgAl_{11}O_{19}$ [21], $Y_3Sc_2Ga_3O_{12}$ and $Y_3Al_5O_{12}$ [22] have been studied to obtain saturable absorber passive Q-switches for rare-earth lasers. In spinels, the presence of divalent cobalt ions as impurity is characterized by intense and broad emission bands in the visible and near infrared range with short radiative lifetime [10,18,23–25].

In this work are presented the synthesis, the crystal structure analysis and optical properties of $Zn_2$ $TiO_4$ doped with a low quantity of divalent cobalt, replacing divalent zinc ions. Photoluminescence emission, excitation and radiative lifetime experiments were performed and their results were interpreted using the Tanabe-Sugano (TS) theory. From the transitions observed in these spectra, the crystal field parameter *Dq* and Racah parameters *B* and *C* were obtained using the Tanabe-Sugano energy matrices and diagrams. Two approaches were used for these calculations and the results were compared. From our knowledge, this is the first work where the energy levels are studied and the energy parameters calculated for the tetrahedral $Co^{2+}$ in zinc orthotitanate. The intense and broad emission band in the near infrared makes this system a material with high potential for use as tunable media.

## 2. Experimental

The samples were prepared from conventional solid state reaction. Zinc oxide (ZnO), titanium oxide ($TiO_2$) and cobalt carbonate ($CoCO_3$) in powder form with high purity level were weighed according to the following stoichiometric reaction:

$$2(1-x)ZnO + TiO_2 + 2xCoCO_3 \rightarrow Zn_{2(1-x)}Co_{2x}TiO_4 + 2xCO_2 \tag{1}$$

The masses of the reactants were calculated to obtain 2 g of $Zn_{2(1\text{-}x)}Co_{2x}TiO_4$, with $x = 0.001$. The powder oxides were manually grinded in an agate mortar with pestle during 2 h for powder homogenization. After this, the powder was compacted into disks with 13 mm diameter, 1 mm thick and mass about 0.6 g under pressure of 4 tons. The pellets were deposited in alumina crucibles and suffered a thermal treatment being heated at 1200 °C with a furnace-heating rate of 12 °C/min. during 10 h in an electric furnace under atmospheric pressure. At the end of the thermal synthesis, the furnace was switched off and left to cool until room temperature by inertia. The pellets were removed from the furnace at room temperature and one of the pellets was reground until a homogeneous, thin powder was obtained for X-ray diffraction experiments.

The sample chemical composition was verified through the elemental analysis by X-Ray Fluorescence technique, using a *Bruker* portable micro-XRF spectrometer, model ARTAX 200 with a molybdenum anode, operating under 40 kV and 250 $\mu$A. The spectra were collected in three distinct spots in one pellet during 100 s. Powder X-Ray diffraction pattern of the sample was carried out at room temperature, using a *Bruker-AXS* D8 Advance diffractometer with unfiltered Cu-K$\alpha$ radiation ($\lambda = 1.54056$ Å), 40 kV, 25 mA and a LynxEye XE position sensitive detector with energy discrimination. Data were collected in a Bragg-Brentano geometry, with a step size of 0.01°.

The X-ray diffraction data were refined using the Rietveld method, with the *Fullprof* package [26]. The Rietveld refinement provides information about the space group, lattice parameters and phase quantification. The observed data were compared to the files extracted from ICSD (Inorganic Crystal Structure Database).

Photoluminescence experiments (emission, excitation spectra and emission decay) were performed at room temperature using in a *PTI 300 QuantaMaster* spectrofluorimeter equipped with a 75 W pulsed Xenon lamp at 200 Hz. All data were corrected by the apparatus sensitivity response.

## 3. Results

### 3.1. Elemental analysis and crystal structure

The X-ray fluorescence spectrometry is a technique widely used for the determination of both major quantity and traces of chemical elements in a wide range of materials, especially due to its non-destructive features. The X-ray fluorescence spectrum of the one of the spots selected in the disc sample is depicted in Fig. 1. It was identified peaks at 2.7859 keV, 4.5088 keV, 4.9141 keV, 6.8903 keV, 8.6132 keV and 9.5506 keV. The peaks at 4.5088 keV and 4.9141 keV are characteristic of Ti presence in the sample; the peaks at 8.6132 keV and 9.5506 keV are related to Zn atoms. The peak at 6.8903 keV is related to Co atoms. At last, the peak at 2.7859 keV is characteristic of Ar, due to its presence in the atmospheric air. All spectra recorded in distinct spots in the sample exhibit the same behavior and for this reason they were not showed in this paper. The presence of spurious peaks related to other elements was not observed, confirming the purity of sample and its chemical composition.

Fig. 2 shows the powder diffractogram of the sample recorded at room temperature. Measured peaks were assigned to zinc orthotitanate single phase. It was not detected peaks of secondary phases related to the cobalt carbonate, indicating that the $Co^{2+}$ ions were homogeneously mixed and effectively inserted in the host lattice. The Rietveld refinement was performed using the data of cubic $Zn_2TiO_4$ (ICSD code 80851) as input. The sample crystallizes at $Fd\overline{3}m$ space group, with cubic symmetry and lattice parameter $a = 8.46879$ Å.

Further details of the Rietveld refinement can be seen in Table 1. Input data related to the experimental conditions and the structural data were introduced in the *Fullprof* software in order to compare data with the experimental diffractogram. The pseudo-Voigt profile function was used during the refinement. Agreement factors and the difference between the calculated and observed profiles were evaluated at each refinement cycle to determine the refinement quality, and their values are also presented in Table 1. The

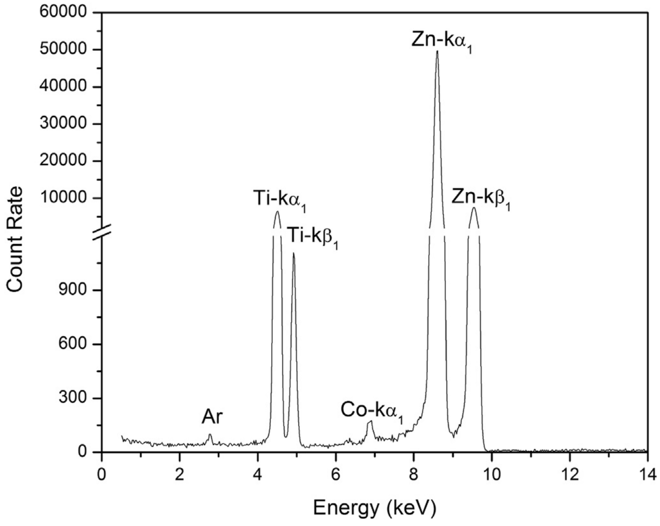

**Fig. 1.** The X-ray fluorescence spectrum of $Zn_2TiO_4$:$Co^{2+}$. Ti, Co and Zn peaks are identified in the spectrum. The Ar peak is measured due to its presence in the atmospheric air.