Materials Letters 64 (2010) 650–653

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Second harmonic generation in Er^{3+}–Yb^{3+}:YBO_3

P. Haro-González [a], F. Rivera-López [a], I.R. Martín [a], A.D. Lozano-Gorrín [b], C. González-Silgo [c], V.M. Sánchez-Fajardo [d], C. Guzmán-Afonso [d], M.E. Torres [d],*

[a] Departamento de Física Fundamental y Experimental, Electrónica y Sistemas, Universidad de La Laguna, Tenerife, Spain
[b] Servicio Integrado de Difracción de Rayos X, Universidad de La Laguna, Tenerife, Spain
[c] Departamento de Física Fundamental II, Universidad de La Laguna, Tenerife, Spain
[d] Departamento de Física Básica, Universidad de La Laguna, Tenerife, Spain

ARTICLE INFO

Article history:
Received 13 October 2009
Accepted 9 December 2009
Available online 24 December 2009

Keywords:
YBO_3
SHG
Crystal structure refinement

ABSTRACT

Polycrystalline samples of pure and erbium and ytterbium-codoped yttrium borates have been obtained via solid-state reaction and characterized by X-ray diffraction. An appreciable Second Harmonic Generation (SHG) under pulsed excitation at 1064 nm was observed in both compounds matrix. Doping enhances the observed second harmonic generation, which is compatible with a better profile matching refinement in a non-centrosymmetric space group.

1. Introduction

Many red-emitting Eu^{3+} phosphors have been studied with a view to be used in new-generation flat-panel display phosphors (PDPs) technologies. Among them, Yttrium and Lanthanide Orthoborates have proved to be promising candidates for such applications, whereas solid solutions of YBO_3 and $GdBO_3$ are already currently in use [1]. Despite extensive research on the characteristics of Eu^{3+} luminescence in these compounds, fundamental questions remain unanswered regarding the relation between the crystal structure of the host and the resulting Eu^{3+} spectral features, particularly in the case of the vaterite YBO_3 system. High-resolution luminescence spectrum does not permit to unambiguously distinguish between the alternatives of having either two or three cation sites in the structures [2,3]. The structure has been solved by single-crystal X-ray diffraction (which yields space group $P6_3/m$) and by neutron powder diffraction (which yields space group C2/c). Both structures are compatible with three and two cations sites, respectively [4,5].

In this work we report the existence of second harmonic generation in Er^{3+}–Yb^{3+} codoped YBO_3 host crystals. In addition, the profile matching refinement for pure and codoped YBO_3 from X-ray powder diffraction was analyzed in order to establish a relationship with the crystal structure.

2. Experimental

High purity crystalline powder samples of YBO_3 and $Er_{0.1}Yb_{0.1}Y_{0.8}BO_3$ were synthesized by solid-state reaction. The starting materials were Y_2O_3, H_3BO_3 and Er_2O_3, Yb_2O_3 for the doped compound with 99.99% purity in adequate proportion. The Er_2O_3, Yb_2O_3 and Y_2O_3 powders were preheated at 600 °C for 5 h. The preheated powders were then weighed, mixed, ground and pressed into pellets for heating treatment at 850 °C into a platinum crucible for 48 h. Whatever the synthesis route used, routine X-ray powder patterns have clearly shown that undoped YBO_3 and doped YBO_3 Er^{3+}, Yb^{3+} phases exhibit the same structure already described previously. Powder X-ray diffraction was carried out in a PANalytical X'Pert PRO diffractometer with X'Celerator detector using $CuK\alpha$ radiation, in the angular range $10° < 2\theta < 100°$, with a step size of 0.02°. Data analysis and profile matching refinement were performed using the WinPlotr and FullProf computer programs [6,7] respectively. The starting lattice constants, in several space groups ($P6_3/m$, Cmcm, and C2/c), were obtained from the ICSD data base [8].

The SHG measurements of Er^{3+}–Yb^{3+}-doped YBO_3 and pure samples were performed by pumping the samples with high energy pulses of about 5 ns of duration at 1064 nm by using a frequency-doubled Nd-YAG pulsed laser and by using the Kurtz powder technique [9]. High pure KDP crystalline powder was used as a standard sample.

3. Results and discussion

3.1. X-ray powder diffraction

From the profile matching refinement, it is easy to ensure that the crystal lattice is monoclinic C2/c instead of hexagonal or orthorhombic

---

* Corresponding author.
E-mail address: manuel.torresbetancort@gmail.com (M.E. Torres).

0167-577X/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2009.12.016

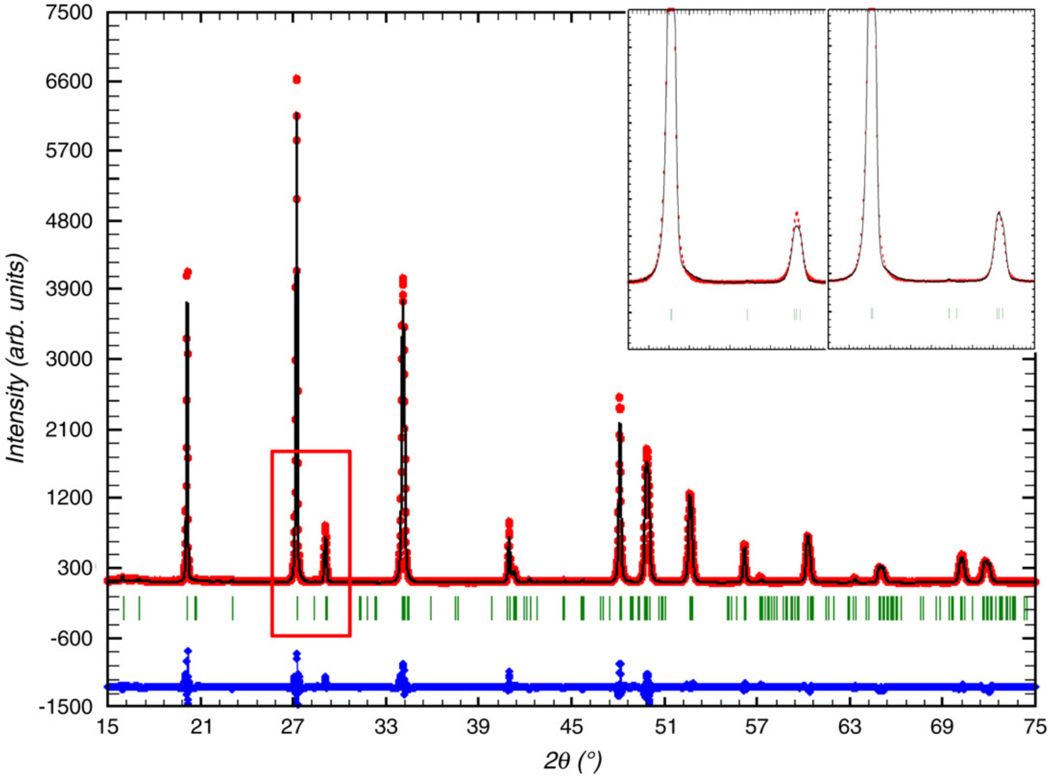

Fig. 1. Profile matching fit of pure YBO_3 crystal structure refinement in the non-centrosymmetric space group (C2) from X-ray powder diffraction. The observed data points (red points), calculated profile (black line), and difference curves are shown (blue line). The green ticks correspond to the Bragg peaks. The insets show two refinements: C2 (left) and C2/c (right).

space group. However, profile parameters of some weak reflections have been better refined in a non-centrosymmetric space group (C2), indicating that the yttrium atom positions are close to those expected for the more symmetric space groups and these intensities are originated largely of B and O atoms. Fig. 1 shows the profile matching fit of the pure compound using a Thompson–Cox Hasting pseudo Voigt peak shape function in the C2 space group. In the inset figures the non-centrosymmetric refinement and the centrosymmetric one are compared (left and right, respectively). There are no significant differences between both refinements. Table 1 shows similar standard deviation of the refined parameters and reliability factors. However, an improvement of the non-centrosymmetric space group profile matching for the doped compound can be observed in Fig. 2. Also, from Table 1, standard deviation of profile parameters and reliability factors are better for the C2 space group refinement, especially R-Bragg and RF factors which are sensible to the space group selection (i.e. to the structural model) [7]. We have seen that the refinement of the reflections (00l) and (h0l) with odd l (systematic absences in the C2/c space group) helps us to reach a better fit, using the C2 space group. In Fig. 1 (left inset) we have showed the (203) and (003) reflection fitting (they are marked in the Fig. 2), but in other regions of the diffraction pattern something similar happens.

On the other hand, it is observed that the cell parameter of the doped compound is shorter than the pure borate. This is well explained because the ionic radii of ytterbium and erbium atoms are shorter than the yttrium one.

In our study, this dissimilarity from the previous results [4] is essential and has important consequences for the optical properties in this type of compound. For example, with this non-centrosymmetric space group, the second harmonic generation and the enhancement of this signal when the sample is doped could be explained because the crystalline structure of the doped compound is more distorted than the pure borate (systematic absences are less weak). Also, in the C2 space group there are non-equivalent sites for the yttrium atom, which is compatible with the majority of the spectroscopic results [2,3].

Definitely, the framework of triangular BO_3^{3-} groups (and or tetrahedral polyborates $B_3O_9^{3-}$) gives rise to superlattice reflections, most of these peaks are impossible to differentiate by conventional X-ray because of the weak scattering power of boron and oxygen and, in the acentric (or less

Table 1
Crystallographic data of the pure and Er^{3+}–Yb^{3+} codoped YBO_3 crystals.

Empirical formula	$Er_{0.1}Yb_{0.1}Y_{0.8}$ BO_3		YBO_3	
Space group	C2/c	C2	C2/c	C 2
Unit cell dimensions *a*, *b*, *c* and *β*	11.3251(3) Å	11.3254(3) Å	11.3675(3) Å	11.3646(3) Å
	6.5379(2) Å	6.5400(2) Å	6.5497(2) Å	6.5512(2) Å
	9.5622(2) Å	9.5631(2) Å	9.5824(2) Å	9.5810(2) Å
	112.942(1) °	112.945(1) °	113.137(2) °	113.090 (2) °
Reliability factors (conventional Rietveld factors)	$\chi^2 = 1.75$	$\chi^2 = 1.61$	$\chi^2 = 1.84$	$\chi^2 = 1.85$
	Rp = 18.2	Rp = 16.8	Rp = 17.8	Rp = 17.9
	Rwp = 15.6	Rwp = 14.7	Rwp = 15.3	Rwp = 15. 8
	Rexp = 11.81	Rexp = 11.61	Rexp = 12.6	Rexp = 12.6
	R-Bragg = 1.18	R-Bragg = 0.7	R-Bragg = 1.6	R-Bragg = 1.73
	RF = 1.34	RF = 0.87	RF = 1.47	RF = 1.55