Journal of Luminescence 129 (2009) 430–433

Contents lists available at ScienceDirect

Journal of Luminescence

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

Synthesis and optical properties of $KZnLa_{0.99}Nd_{0.01}(VO_4)_2$ triple vanadate(V)—New promising laser materials

Marcin Sobczyk *

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, Wrocław 50-383, Poland

ARTICLE INFO

Article history:
Received 6 July 2008
Received in revised form
29 October 2008
Accepted 4 November 2008
Available online 7 December 2008

PACS:
78.55.−m

Keywords:
Synthesis
Absorption spectra
Luminescence spectra
Lifetimes
Nd^{3+}
Vanadates

ABSTRACT

In an attempt to find a neodymium–vanadate system with long lifetime of $^4F_{3/2}$ level and relatively strong $^4F_{3/2}\rightarrow{}^4I_{11/2}$ emission for laser applications, the optical properties of Nd^{3+} in a new $KZnLa(VO_4)_2$ host is reported. The crystalline samples were obtained at 900 °C in air. The samples were crystallized in monoclinic system and were isostructural with $KZnLa(PO_4)_2$. $KZnLa_{0.99}Nd_{0.01}(VO_4)_2$ strongly emits in the near infrared range with the maxima at 871.6 and 1057 nm upon excitation through the $^4F_{5/2}$ level (808 nm) or by the charge transfer bands of VO_4^{3-}. The lifetime of $^4F_{3/2}$ level of Nd^{3+} ion is larger than that observed in other neodymium–vanadates systems.

1. Introduction

$LnVO_4$ (Ln—trivalent lanthanide ions) are well-known and popular non-linear materials. The neodymium ions doped into series of orthovanadates (V) YVO_4, $GdVO_4$ and $Y_{1-x}Gd_xVO_4$ are excellent diode-pumped laser materials as they have good properties, such as, large absorption as well as emission cross-section, water resistance, hardness, etc. Difference of ionic radii of Y^{3+} and Nd^{3+}, however, strongly limits Nd concentration in the YVO_4 laser crystals. This problem is not observed when Nd^{3+} substitutes La^{3+} ions. It is very interesting that the fluorescence lifetimes of $^4F_{3/2}$ laser levels of Nd^{3+} ion-doped $LaVO_4$ is longer (137 μs) than that in the other Nd^{3+}-doped $LnVO_4$ crystals (where Ln = Y, Gd, Lu) [1,2]. In this work the synthesis of triple orthovanadate(V), $KZnLa_{0.99}Nd_{0.01}(VO_4)_2$, and its optical properties are presented. The recorded lifetime of $^4F_{3/2}$ excited level was about twice longer than those recorded for Nd^{3+}-doped laser crystals $LaVO_4$ [2], YVO_4 [3,4], $GdVO_4$ [5].

2. Experimental

The chemicals used were K_2CO_3, ZnO, NH_4VO_3 (all of analytical grade), La_2O_3 and Nd_2O_3 (99.999%). The starting materials were mixed together stoichiometrically and placed in a platinum crucible; heated in an electric furnace for 24 h at 300 °C and next 24 h at 900 °C in air. The obtained powders were slightly yellow.

The X-ray powder diffractograms of the products were recorded on a DRON-2 X-ray diffractometer using Ni-filtered copper-radiation ($\lambda = 1.5418$ Å). The analysis was performed in the $2\theta = 10$–120° range and with 0.05° step. The unit cell parameters were obtained by least-squares fitting of all the observed reflections. For this purpose, the Crysfire Powder Indexing System and Chekcell Graphical Powder Indexing Cell and Space Group Assigment software were applied [6]. The powder density was determined with a pycnometer using carbon tetrachloride (CCl_4).

The infra-red spectrometer (model BRUKER 113v FTIR) was used to measure the sample IR spectrum covering the wavenumber range 4000–400 cm^{-1} with KBr as diluent.

Absorption spectra of $KZnLa(VO_4)_2$:Nd^{3+} pellet were recorded on a Cary 5E spectrometer in the 3800–50,000 cm^{-1} range at room temperature. Luminescence spectra were obtained using laser diode (808 nm) and GDM monochromator with a spectral bandwidth of 0.5 cm^{-1}. Luminescence decay curves were recorded on a Tektronix TDS 3052 digital oscilloscope following the

* Tel.: +48 71 3757333; fax: +48 71 3282348.
E-mail address: marcin@eto.wchuwr.pl

0022-2313/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2008.11.020

Table 1
Observed and calculated d spacing and observed relative intensities for $KZnLa(VO_4)_2$.

h	k	l	d_{obs}	d_{calc}	I/I_0	h	k	l	d_{obs}	d_{calc}	I/I_0
2	0	0	3.3986	3.4058	61	0	2	3	1.8611	1.8623	9
1̄	2	0	3.2065	3.2125	100	3̄	2	2	1.8399	1.8427	22
0	2	1	3.1620	3.1780	10	3̄	0	3	1.8159	1.8174	16
2̄	1	0	3.0974	3.0854	14	1	3	2	1.7958	1.7992	35
2̄	1	1	3.0765	3.0779	20	1̄	4	0	1.7572	1.7597	16
1̄	2	1	3.0356	3.0291	7	3	2	1	1.7447	1.7468	4
0	1	2	2.9666	2.9683	85	1̄	4	1	1.7294	1.7277	3
1	2	1	2.7610	2.7509	5	4̄	1	1	1.7144	1.7124	5
2̄	0	2	2.7283	2.7261	26	4̄	0	2	1.6967	1.6979	15
2̄	1	2	2.5546	2.5532	32	4̄	1	0	1.6571	1.6582	15
1	1	2	2.5062	2.5141	29	1̄	1	4	1.6381	1.6380	9
1̄	2	2	2.4340	2.4368	70	0	0	4	1.6222	1.6251	21
3̄	0	1	2.3364	2.3382	7	2̄	1	4	1.5990	1.5991	20
1̄	3	0	2.2907	2.2876	4	2̄	3	3	1.5839	1.5826	8
0	3	1	2.2685	2.2751	23	3	3	1	1.5406	1.5396	5
3̄	1	1	2.2308	2.2264	34	4̄	2	2	1.5360	1.5390	4
2	2	1	2.1893	2.1907	17	2̄	4	2	1.5132	1.5145	7
3̄	1	0	2.1642	2.1677	6	2̄	2	4	1.4956	1.4947	7
2	0	2	2.0971	2.0981	5	3	2	2	1.5222	1.5189	4
2	1	2	2.0129	2.0161	47	3̄	4	1	1.4356	1.4370	4
3	0	1	1.9878	1.9906	6	3̄	4	0	1.4201	1.4208	14
2̄	3	1	1.9755	1.9755	14	1̄	3	4	1.3811	1.3822	9
0	3	2	1.9474	1.9455	46	0	4	3	1.3938	1.3943	29
3̄	2	0	1.9241	1.9269	31	3	4	1	1.3447	1.3438	12
1̄	2	3	1.9088	1.9064	9	2̄	5	1	1.3380	1.3391	25

excitation by a Continuum Surelite I optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser and detected by a S-20 photomultiplier.

3. Results and discussion

The X-ray examination of $KZnLa(VO_4)_2$ and Nd^{3+}:$KZnLa(VO_4)_2$ powders revealed presence of a single phase. The powder pattern of sample was indexed on the basis of a monoclinic cell, $P2_1/n$ space group, with the lattice parameters: $a = 7.045(1)$, $b = 7.283(1)$, $c = 6.722(1)$ Å, $\beta = 104.85$, and $V = 333.4$ Å^3, respectively. For $LaVO_4$ the crystallographic parameters are: $a = 7.047(1)$, $b = 7.286(1)$, $c = 6.725(1)$, $\beta = 104.85$, and $V = 333.8$ Å^3, respectively [7]. The observed and calculated d spacings and observed relative intensities are listed in Table 1. The calculated and measured densities are equal to 4.713 and 4.524 g cm^{-3}, respectively. The XRD shows that $KZnLa(VO_4)_2$ has unit cell dimensions very similar to monoclinic $LaVO_4$ and $LaPO_4$ [7,8] and is isomorphous with $KMLa(PO_4)_2$ (where M = Zn or Mg) triple phosphates [9,10]. With 1 mol% activated Nd^{3+} ions of La^{3+}, there has not been significant influence on the structure of the matrices studied.

Infrared spectra of monoclinic lanthanide phosphates were studied in detail and reported in Refs. [10,11]. The IR spectra of $KZnLa(VO_4)_2$ and $KZnLa_{0.99}Nd_{0.01}(VO_4)_2$ are similar to the monoclinic $LaPO_4$, $KMgLa(PO_4)_2$ and $KZnLa(PO_4)_2$, respectively [10–12]. For the monoclinic forms of phosphate and their orthovanadate(V) analogues with C_s site symmetry of the PO_4 and VO_4 groups usually four bands appear in the ν_4 region (460–530 cm^{-1}) and five or six bands in the ν_3 region (750–850 cm^{-1}). The observed peaks are shown in Fig. 1 together with their assignments listed in Table 2.

Fig. 2 shows the room-temperature absorption spectrum of the Nd^{3+}-doped $KZnLa(VO_4)_2$ powder disk. Free Nd^{3+} ion has a $4f^3$ configuration with a $^4I_{9/2}$ ground state level. The Nd^{3+} ion occupy the position of La^{3+} ion with a low site symmetry (C_s) and $^4I_{9/2}$ level splits into five Kramers doublets. In the 3800–20,000 cm^{-1} spectral range, relatively sharp and well-separated bands of

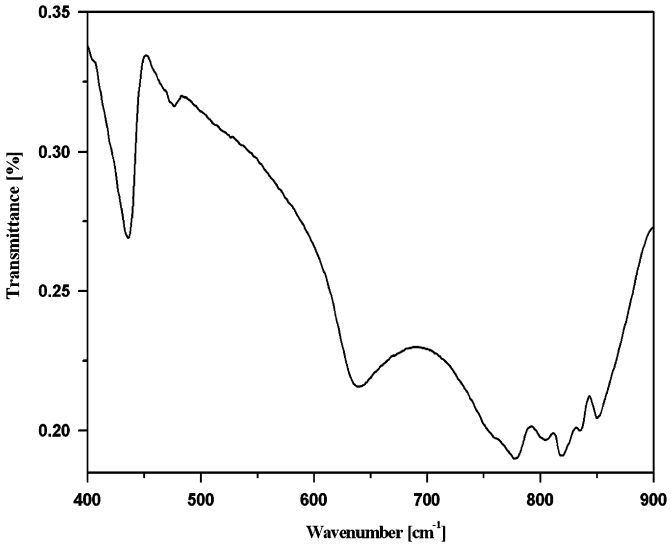

Fig. 1. IR spectrum of $KZnLa(VO_4)_2$ in the KBr pellet at room temperature.

Table 2
Infrared spectra of $KZnLa(VO_4)_2$, $KMgLa(PO_4)_2$ and $LaPO_4$.

Ref.	$KZnLa(VO_4)_2$ This work	$KMgLa(PO_4)_2$ [10]	$LaPO_4$ [11]
Symmetry			
ν_2	436	494	487
ν_4	462	530	532
	475	558	559
	508	572	575
	524	617	621
ν_1	640	948	946
ν_3	757	988	980
	778	1006	1010
	804	1030	1025
	816	–	1053
	835	1069	1075
	847	1086	1087

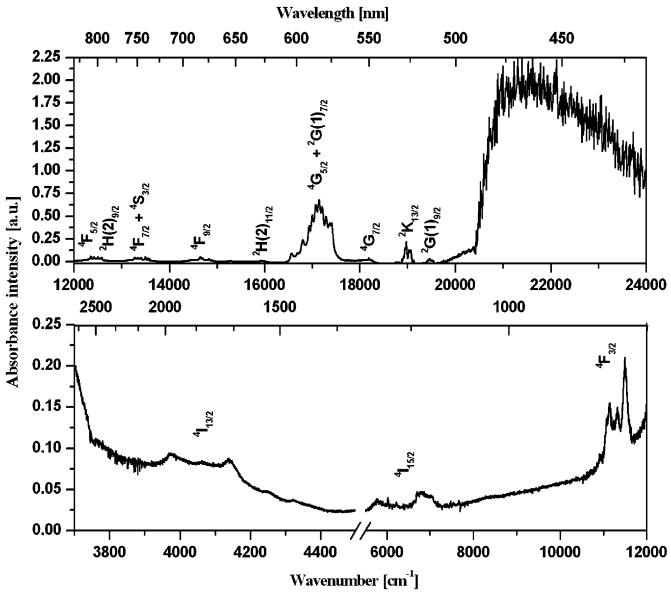

Fig. 2. Room-temperature absorption spectrum of the Nd^{3+}:$KZnLa(VO_4)_2$ pellet.