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Yb³⁺ doped Y₃Al₅O₁₂, NaBi(WO₄)₂ and LiNbO₃ crystals as optical temperature sensors

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ABSTRACT

Possibilities of the use the Yb³⁺ doped crystals (Y₃Al₅O₁₂, NaBi(WO₄)₂, LiNbO₃) as materials for optical temperature sensor based on temperature dependences of zero-phonon spectral lines are discussed. Temperature dependences of intensities of zero-phonon transitions between individual Stark states of Yb³⁺ ion due to Debye - Waller factors, homogeneous widths and shifts of the spectral lines in a range from 960 to 1060 nm are investigated. The operation temperature regions and average sensitivities for optical temperature sensors under consideration are determined.

Keywords: Optical temperature sensor, Yb³⁺ doped crystal, zero-phonon spectral line

1. INTRODUCTION

Recently optical temperature sensors (OTS) are in the centre of attention of many research groups, due to their high potential for applications in various fields where conventional techniques cannot be used and/or run to problems representing drawbacks for successful applications. Among the possible applications one should note temperature monitoring in highly corrosive media, electrical power stations, oil refineries, coal mines and building fire detection. Until now a large number of distributed and point OTSs on the base of different rare-earth (RE) ions (Er³⁺, Sm³⁺, Eu³⁺, Pr³⁺) doped glasses, ceramics and fibers have been presented¹⁻⁶. The OTSs on above mentioned materials have the ability to cover a wide temperature range (77 to 1623K) with reasonable measurement resolution^{3,7-9}. However, despite to their attractive properties, such as high temperature mechanical strength, chemical stability and excellent optical property, rare-earth doped bulk single crystals as potential materials for OTSs are less investigated.

Idea of the use of RE³⁺ ions doped materials as optical sensors, including temperature ones is based on temperature dependences of spectroscopic characteristics (absorption coefficients, fluorescence intensities, fluorescence lifetimes etc.) of these materials in the infrared and visible range¹⁻⁹. However, as a rule, they are mainly based on fluorescence intensity ratio (FIR), when it is assumed that temperature dependence is determined only by Boltzmann factor of population of neighboring energy levels. Sensing capabilities of some materials doped with RE³⁺ ions based on FIR are

given in Table 1. Note that the inclusion of the Stark structure of the RE³⁺ ions' optical spectra makes it possible to investigate the temperature dependences of the spectroscopic characteristics of the absorption spectra from excited Stark states, assuming (as in the case of FIR) that their population is determined only by the Boltzmann factor. This, in complete analogy to the FIR, makes it possible to consider OTS based on absorption coefficient ratio (ACR). Thus the capabilities of lithium niobate crystal doped with Yb³⁺ ions as a material for OTS based on FIR and/or ACR are investigated in Ref.¹⁰ (Table1).

Table 1

Sensing materials	Technique: FIR or ACR	Sensitivity at 293 K, % × K-1	Temperature range, K	Ref.
YAG:Nd ³⁺	FIR: ⁴ F _{3/2} , ⁴ F _{5/2} → ⁴ I _{9/2}	1.43	299 - 523	[21]
Silica:Sm ³⁺	FIR: ⁴ F _{3/2} , ⁴ G _{5/2} → ⁶ H _{5/2}	1.84	295 - 748	[21]
Telluride:Pr ³⁺	FIR: ³ P ₁ , ³ P ₀ → ³ H ₅	1.02	273 - 453	[3]
ZBLANP:Nd ³⁺	FIR: ⁴ F _{3/2} , ⁴ F _{5/2} → ⁴ I _{9/2}	1.15	296 - 473	[21]
LiNbO ₃ :Yb ³⁺	FIR: $\nu_5, \nu_6 \rightarrow \nu_4, \nu_1$ ACR: $\nu_1, \nu_2 \rightarrow \nu_5$	0.43 0.48	150 – 400 200 - 400	[10]

In the present paper sensing capabilities of Yb³⁺ doped crystals based on temperature dependences of intensities of the same zero-phonon lines (ZPLs) due to the pure electron inter-Stark transition are discussed. It is assumed that temperature dependences of ZPL's intensities are caused by homogeneous widths, shifts and Debye-Waller factors (DWF) of corresponding transitions. Specific calculations are carried out for two more intense ZPLs caused by transitions from the ground state of excited manifold ²F_{5/2} of Yb³⁺ in LiNbO₃ (LN), Y₃Al₅O₁₂ (YAG) and NaBi(WO₄)₂ (NBW) crystals.

2. SPECTROSCOPIC PROPERTIES OF Yb³⁺ DOPED YAG, LN AND NBW CRYSTALS

The energy spectrum of ion Yb³⁺ (4f¹³ electron configuration) is composed of eightfold degenerate ground multiplet, ²F_{7/2}, and the six fold degenerate excited multiplet ²F_{5/2}, separated from each other by ~10000 cm⁻¹ energy gap. In the crystal field the ²F_{7/2} and ²F_{5/2} multiplets are split into four and three Kramers' doublets, respectively, defining thus the Stark structure of the optical spectrum of Yb³⁺ ion. Energy scheme of Stark states of Yb³⁺ ion in LN, YAG and NBW crystals, plotted on the basis of absorption and emission spectra are given in Fig.1.¹¹⁻¹³ The main spectroscopic characteristics of LN-Yb³⁺, YAG-Yb³⁺ and NBW-Yb³⁺, such as line strengths of inter Stark transitions, probabilities of radiative transitions and so on, are determined in¹⁴⁻²⁰. In particular, temperature dependences of homogeneous widths, shifts and DWFs of the ZPLs YAG:Yb³⁺ are determined in¹⁷ and it is shown that, in accordance to experimental data²⁰, the intensity of the ZPLs on actual wavelengths 1030 nm “dramatically” increases, when

temperature decreases up to the liquid-nitrogen values. The similar pattern is also occurred in the case of *NBW: Yb³⁺* and *LN: Yb³⁺* crystals^{18,19}.

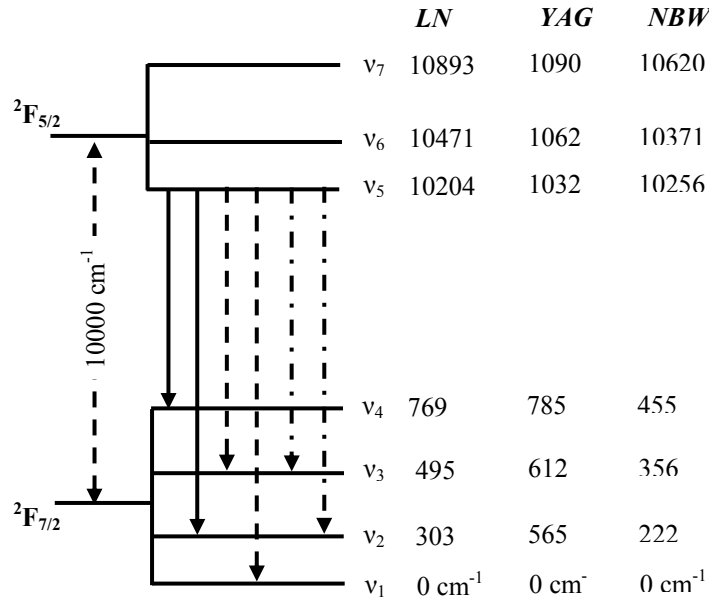


Figure 1. Energy levels schemes of *Yb³⁺* ion and transitions in *LN* (solid), *YAG* (dash) and *NBW* (dash-dot) crystals

As well known within the framework of Franck–Condon approximation the matrix elements of the pure electronic transitions do not depend on the coordinates of the nuclei. Consequently, for weak electron-phonon interactions (EPIs) the profile of the ZPL can be written as

$$I_{if}(\omega, T) = k S_{if} e^{-2M} f(\omega, T), \quad (1)$$

where k is a constant, S_{if} is the line strength of the pure electronic transition $i \rightarrow f$ and $f(\omega, T)$ describes the ZPL, e^{-2M} is *DWF* that expresses the dependence of the ZPL's intensity on the change of nuclei equilibrium positions due to electronic transition. The profile of single spectral line is Lorentzian:

$$f(\omega, T) = \frac{1}{2\pi} \times \frac{\Gamma_{if}}{(\omega - \omega_{if}^{(0)} - \Omega_{if})^2 + \Gamma_{if}^2}, \quad (2)$$

where Γ_{if} , $\omega_{if}^{(0)}$ and Ω_{if} are correspondingly the homogeneous linewidth, the frequency and the shift of the ZPL transition $i \rightarrow f$. Note that in next steps we will examine the temperature dependence of the intensity ratio of the same spectral line at different temperatures. Therefore we will not take into account the temperature dependence due to the Boltzmann factor in population of the initial level of the transition. Thus, it is assumed that the temperature dependence of the ZPLs intensity is determined by the temperature dependences of the homogeneous linewidth and the shift of the spectral line and the DWF. Thereby we can define the relative intensity of ZPL according to expression

$$R(T) = \frac{I(T)}{I(T_0)} = \frac{\Gamma(T)}{\Gamma(T_0)} \times \frac{[\Delta\varepsilon(T_0)]^2 + \Gamma^2(T_0)}{[\Delta\varepsilon(T)]^2 + \Gamma^2(T)} \times \exp[2M(T_0) - 2M(T)], \quad (3)$$

where T_0 is a fixed temperature, $\Delta\varepsilon$ is the temperature shift of ZPL. The numerical values of homogeneous line widths, shifts and *DWFs* of the ZPLs under consideration at $T_0 = 100\text{ K}$ are given on the table 2.

Table 2

Spectroscopic parameters	<i>YAG:Yb³⁺</i>		<i>NBW:Yb³⁺</i>		<i>LN:Yb³⁺</i>	
	1030 nm $\nu_5 \rightarrow \nu_3$	968 nm $\nu_5 \rightarrow \nu_1$	996.6nm $\nu_5 \rightarrow \nu_2$	1010nm $\nu_5 \rightarrow \nu_3$	1010nm $\nu_5 \rightarrow \nu_2$	1060nm $\nu_5 \rightarrow \nu_4$
line width at 100 K, cm^{-1}	0.903	0.732	10.148	2.43	10.962	4.21
Line shift at 100 K, cm^{-1}	3.208	~ 0	-0.373	- 1.19	- 2.123	- 0.681
DWF at 100 K	2.755	0.007	0.942	0.82	0.175	0.352
Linear temperature range, K	30-80	120-300	77-250	50-150	77-350	77-250
work temperature region, K	40-130	100-240	50-400	30-350	150-350	100-350
Average sensitivity, $\% \times \text{K}^{-1}$	3.4	0.02	0.84	1.16	0.97	0.66

3. SENSOR CAPABILITIES OF *Yb³⁺* DOPED *YAG*, *LN* AND *NBW* CRYSTALS

The sensitivity of OTS based on measurement of a temperature dependent spectroscopic characteristic, $R(T)$, is defined by relation¹

$$S_R(T) = \frac{1}{R} \frac{\partial R}{\partial T}. \quad (4)$$

As a temperature dependent spectroscopic characteristic we consider the relative intensity of ZPL defined by Eq. (3). Note, that due to enough complicated temperature dependences of homogeneous widths, shifts and *DWFs*¹⁷⁻¹⁹ the temperature dependence of relative intensity $R(T)$, defined by (3), and therefore the corresponding sensitivity $S_R(T)$ defined by (4) have the quite complex analytical forms. In this case of quantitative characteristics for OTS we use the average sensitivity defined by

$$\bar{S}_R = \frac{1}{\Delta T} \int_{T_1}^{T_2} S_R(T) dT, \quad (5)$$

where $\Delta T = T_2 - T_1$ is the length of the working temperature range, i.e. the region within which the relative intensity $R(T)$ is varied sharply.

The temperature dependences of the relative intensities and the corresponding sensitivities for more intense ZPL of *YAG-Yb³⁺*, *LN-Yb³⁺* and *NBW-Yb³⁺* crystals in the wavelength range 980–1100 nm are given in Fig. 2-4. Temperature ranges within which the dependence $R(T)$ with sufficient accuracy can be approximated by linear functions,

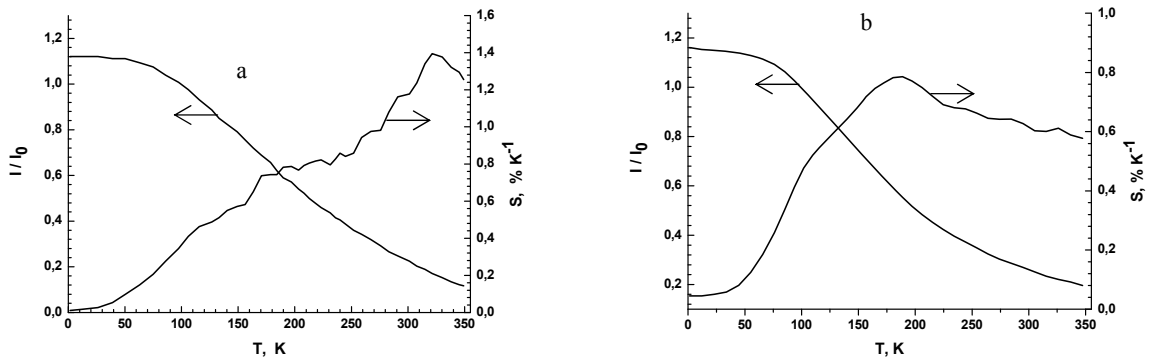


Figure 2. Temperature dependences of relative intensities and sensitivities of OTS based on LN:Yb³⁺: at a) 1010nm, b) 1060nm.

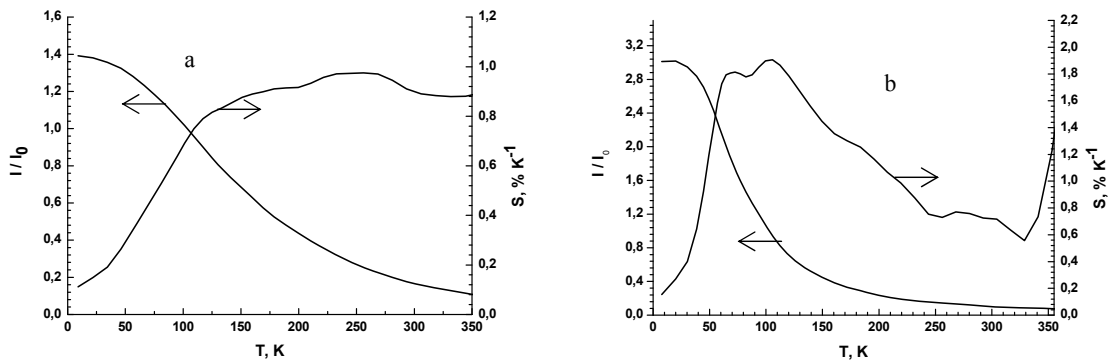


Figure 3. Temperature dependences of relative intensities and sensitivities of OTS based on NWB:Yb³⁺: at a) 996.6nm, b) 1010nm.

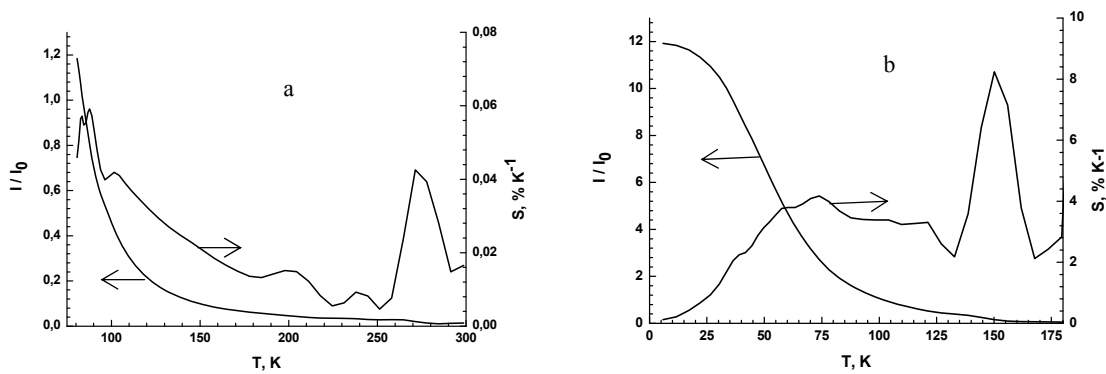


Figure 4. Temperature dependences of relative intensities and sensitivities of OTS based on YAG:Yb³⁺ at a) 968nm, b) 1030nm.

as well as the most favorable to the OTS operating temperature range and the values of corresponding average sensitivities are given in Table 2. It is shown that YAG:Yb³⁺ crystals emitted at 1030 nm are more suitable materials for OTS at the low temperature region 40 -130 K. Indeed, in this temperature range the relative intensity of radiation at the

wavelength of 1030 nm is changed by one order (Fig.4b), while the mean sensitivity is sufficiently high $3.4 \% \times K^{-1}$ (Table 2) and it is not only the highest compared with the average sensitivities for the investigated materials under study in the current article, but about twice exceeds the sensitivities of sensor materials listed in Table 1.

4. CONCLUSIONS

Thus, the Yb^{3+} doped crystals can be considered as quite acceptable materials for the OTSs based on relative fluorescence method and they can be used in the development of optical temperature sensors at low temperature regions.

In the considered temperature range (40 - 200 K) dependence of the relative intensity on the temperature with high accuracy ($\sim 0.1\%$) approximates by a linear function, which increases the attractiveness of these materials as OTS. This mainly concerns to the $YAG:Yb^{3+}$ crystal, the radiation intensity temperature sensitivity of which at the wavelength of 1030 nm is “drastically” high. As a result the expected average sensitivity of the temperature sensor in the temperature range of 40 – 130 K reaches a value of $3.4 \% \times K^{-1}$, which in the considered temperature range on one order of magnitude exceeds the average sensitivity of cooper-constantan thermocouples ($0.31 \% \times K^{-1}$) and is nearly the same as for the chromel-constantan ($2.8 \% \times K^{-1}$) one. At higher temperatures (200-350K) among the considered materials are more convenient $NBW:Yb^{3+}$ and $LN:Yb^{3+}$ crystals emitting at 1010 nm wavelength with average sensitivity of 1.16 and 0.97 $\% \times K^{-1}$, respectively, which are about two times less in comparison with the one for cooper-constantan thermocouples – $2.1 \% \times K^{-1}$. However, compared with thermocouples the OTS are contactless, provide possibilities for distance measurements and temperature monitoring in highly corrosive media, etc. Moreover, it should be noted that at high temperatures due to the Boltzmann factor the population of excited levels can be quite large and therefore OTS based on FIR, seemingly, again can be more suitable (Table 1).

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