



Correlation analysis of spectroscopic data

A.V. Mikheev^{a,b,*}, B.N. Kazakov^b

^a Kazan National Research Technological University, 68 Karl Marx Street, Kazan, 420015, Russian Federation

^b Kazan Federal University, 18 Kremlyovskaya Street, Kazan 420008, Russian Federation

ARTICLE INFO

Article history:

Received 10 October 2016

Accepted 12 December 2016

Available online 16 December 2016

Keywords:

Spectroscopic experiment

Correlation analysis

Correlation spectrum

Luminescence

Up-conversion

Tm³⁺

Yb³⁺

YF₃

ABSTRACT

A method of correlation analysis of spectroscopic data is developed that allows the determination of patterns in experimental results with and without the application of a functional physico-mathematical model. In the latter case the method of correlation analysis allows to determine the regression values that occur in a physico-mathematical model. The method is applicable if the result of an experiment is the relationship between one physical variable and two or more parameters. The key idea of the method is search for particular measuring ranges of one of the parameters, where functional relationships of the physical value and one of the other parameters are either similar to each other or similar to some theoretical relationship. The ranges are found using the maximum of the cosines between two experimental data vectors or between the experimental data vector and the functional physico-mathematical model vector. The concept of a correlation spectrum that plays the major part in the correlation analysis of the experimental relationships between physical values and length or frequency of waves is introduced. The possibilities of the method are illustrated using the correlation analysis of the up-converted luminescence spectra of the YF₃:Yb³⁺ (20 at.%), Tm³⁺ (1 at.%) crystal that were captured at 13 equidistant power values of a laser diode stationary emission: $P \in (P_{min}, P_{max})$, $P_{min} = 253.3$ mW, $P_{max} = 1108$ mW, $\lambda_{ex} = 934$ nm. Using the correlation spectra a strong correlational relationship is determined between ³P₂ and ¹D₂ energy levels populations of the Tm³⁺ ion as well as weak spectrum line of Tm³⁺ (³P₂ → ¹D₂) that is not visible in a regular luminescence spectrum was determined. The properties of the correlation spectrum allows to assert that this line is determined by stimulated emission.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The goal of a spectroscopic experiment is the determination of patterns in the interaction of electromagnetic radiation and matter, and also patterns in the interaction of separate parts of the matter. In order to achieve this goal functional physico-mathematical models that are created to describe the interactions are usually experimentally tested. That said the necessity to change experimental conditions emerges. For example, in the optical spectroscopy temperature, chemical composition of the studied object, wavelength and emission intensity as well as type of the emission modulation (pulse, rectangular, sinusoidal) and time properties of the modulation (pulses duration and period, phase) are changed most frequently. Often, several experimental conditions vary simultaneously. All this makes spectroscopic experiments complicated and expensive.

Results of a spectroscopic experiment are presented as arrays of

numerical data that represent relationships between certain physical values (luminescence/absorption intensity, index of refraction, reflection coefficient, etc.) and other values (wavelength, time, pumping intensity, temperature, impurity concentration, etc.). Currently the most efficient and mathematically strict method of experimental data processing in spectroscopy is regression analysis: determination of functional physico-mathematical model parameters using a set of numerical data. However, the more precisely the functional physico-mathematical model describes an experiment the more parameters it includes and it is more difficult to conduct regression analysis. Apart from this, an increased number of model parameters requires enhanced precision and accuracy of the spectroscopic results. This may require precise and expensive equipment. But even if this equipment is used, interpretation of the spectroscopic experiment using regression analysis can be quite ambiguous. This leads to additional and often more complicated experimental research.

At the same time it is possible to determine patterns in spectroscopic experiment results without regression analysis, without further research and even without functional physico-mathematical model. For example, in order to determine energy emission and absorption process which is a key factor to energy levels

* Corresponding author at: Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation.

E-mail addresses: veehima@gmail.com (A.V. Mikheev), bor300@yandex.ru (B.N. Kazakov).

population of the Ho^{3+} ion in the $\text{LiYbF}_4:\text{Ho}^{3+}$ crystal (0.2 at.%), correlation of relationships between intensities of various luminescence spectrum lines of the Ho^{3+} ion and shift Δz of the laser beam waist with respect to the front face of the crystal was studied in [1]. Luminescence excitation was carried out using 0.755 W semiconductor laser diode, $\lambda_{\text{ex}} = 933$ nm. In [1] it was proposed to use correlation spectrum that is regarded as relationship between λ wavelength and a value proportional to Pearson correlation coefficient to visualize and detect correlations. The correlation coefficient was calculated for a relationship between Δz and luminescence intensity on a fixed λ_0 wavelength and for the same relationship on an arbitrary wavelength λ . Correlation spectra allowed determining the most important excitation mechanisms of the green and red up-converted $\text{LiYbF}_4:\text{Ho}^{3+}$ (0.2 at.%) crystal luminescence [1]. No special experiments to measure the correlation spectra were carried out. They were constructed by the way of computer experiment using 33 $\text{LiYbF}_4:\text{Ho}^{3+}$ (0.2 at.%) crystal luminescence spectra registered at various Δz values. It is important to note that the analysis of the correlation spectra in [1] did not rely on any functional physico-mathematical models.

In this work we propose a new method of analysis of the results of spectroscopic experiments, which is a modified correlation analysis. The method allows checking adequacy of the functional physico-mathematical models that are built to describe the interaction process of electromagnetic radiation and matter as well as the interaction of separate parts of the matter. It turned out that regression analysis is a special case of the correlation analysis. Apart from this, the correlation analysis method allows to determine statistic patterns in any spectroscopic experiment results even without any functional physico-mathematical models.

In the first part of this work the theoretical framework of the method of correlation analysis of the results of spectroscopic experiment is given using calculation and interpretation of the correlation spectra as an example. The definition of the correlation spectrum is used in the wider sense, compared to [1]. The application of the method is demonstrated in the second part of the work using the standard tasks of the activated crystal spectroscopy that is assignment of the observed spectrum lines to various electron transitions of the impurity center in crystal as well as detection of the previously unobserved weak spectral lines.

2. Theoretical framework of the luminescence spectra correlation analysis

The easiest way to give the theoretical framework of the correlation analysis of the results of spectroscopic experiment is to use the luminescence spectra correlation analysis as an example. It is important to know that instead of luminescence spectra any other spectroscopic experiment results including those that are not related to optics could be used. For example, absorption spectra, luminescence decay, relationship between spectral line width and concentration, EPR and NMR spectra, spin-lattice or phase relaxation kinetics, angular or temperature dependence of the frequencies and relaxation times in the EPR and NMR spectroscopy, etc. The correlation analysis method does not depend on the type of the spectroscopic experiment. If spectra (the relationship between physical value and wavelength or frequency) are the object of the correlation analysis application, the correlation spectrum plays a key part in the correlation analysis.

Suppose $\mathbf{J}(\lambda, p)$ is n -dimensional vector whose coordinates are luminescence spectra registered at n various values of the p parameter:

$$\mathbf{J}(\lambda, p) = \{J(\lambda, p_1), J(\lambda, p_2), \dots, J(\lambda, p_n)\},$$

$p \in \{p_1, p_2, \dots, p_n\}$, λ is the wavelength, J is the luminescence intensity. Any physical quantity whose value variation significantly changes the luminescence intensity can be parameter p . For example, time moment t when luminescence decay is registered; the power of the pump radiation; position Δz of the laser beam waist related to the crystal in case of Z-scan; modulation period or duration of a pumping impulse if the rectangular modulation of pump radiation is used. Relationship between luminescence intensity and parameter p can contain important information related to interaction of crystal with the pump radiation that causes luminescence. Particularly, if p is the power of the pump radiation and $\mathbf{J}(\lambda, p)$ is the intensity of up-converted luminescence then $\mathbf{J}(\lambda, p)$ depends from p differently in case of various excitation mechanisms. In case of multistage single-photon absorption this dependence is monotone power function [2], at the same time, multi-quantum absorption of the stimulated radiation (absorption of groups of coherent photons) can lead to nonmonotonic dependence of $\mathbf{J}(\lambda, p)$ from p [3].

Let us suppose that there is the set $\lambda^{(c)}$ of λ wavelengths where the experimentally determined relationship between luminescence intensity and parameter p is proportional to some known function $b(p)$:

$$\mathbf{J}(\lambda, p) = k \cdot \mathbf{b}(p), \quad \lambda \in \lambda^{(c)}, \quad (1)$$

where k is a proportionality factor and $\mathbf{b}(p)$ is a vector whose coordinates are values of the function $b(p)$ at the same values of the parameter p where the intensity $\mathbf{J}(\lambda, p)$ was measured. The vector $\mathbf{b}(p)$ can be a functional physico-mathematical model developed specially to describe the relationship between luminescence intensity and parameter p . In this case, luminescence at $\lambda \in \lambda^{(c)}$ is formed by the interaction processes of luminescence centers with each other and the pump radiation that underline the physico-mathematical model. If $\mathbf{b}(p) = \mathbf{J}(\lambda_0, p)$ is the experimental relationship between luminescence intensity and p , at the particular wavelength λ_0 , then luminescence formation mechanism at $\lambda \in \lambda^{(c)}$ is similar or even identical to the luminescence mechanisms at the λ_0 wavelength. In order to effectively detect the set $\lambda^{(c)}$ in the luminescence spectra easy and convenient criteria of the precise or approximate satisfaction of Eq. (1) is needed.

Because correctness of Eq. (1) means that vectors $\mathbf{J}(\lambda, p)$ and $\mathbf{b}(p)$ are collinear, the cosine of the angle between these two vectors can be used as a criterion of the correctness of Eq. (1):

$$\cos \theta(\lambda) = \frac{\langle \mathbf{J}(\lambda, p), \mathbf{b}(p) \rangle}{\|\mathbf{J}(\lambda, p)\| \cdot \|\mathbf{b}(p)\|}. \quad (2)$$

Here $\langle \mathbf{J}(\lambda, p), \mathbf{b}(p) \rangle$ is the scalar product of the vectors $\mathbf{J}(\lambda, p)$ and $\mathbf{b}(p)$ in the n -dimensional Euclidean space \mathbb{R}^n , $\|\mathbf{J}(\lambda, p)\|$ is the Euclidean norm of the vector $\mathbf{J}(\lambda, p)$. If the angle $\theta(\lambda)$ between the vectors is close to 0 or 180°, then $\cos \theta(\lambda) \approx \pm 1$ and vectors $\mathbf{J}(\lambda, p)$ and $\mathbf{b}(p)$ are almost collinear. This means that the set $\lambda^{(c)}$ can be detected in the luminescence spectrum while building plots of relationships between $\cos \theta(\lambda)$, $\mathbf{J}(\lambda, p)$ and λ together and determining (visually and/or numerically) wavelength ranges where $\cos \theta(\lambda) \approx \pm 1$. Spectral lines for which $\cos \theta(\lambda) \approx \pm 1$ are almost identical with $\mathbf{b}(p)$ relationship between luminescence intensity and p .

After these lines are detected in the spectrum, it is necessary to determine which transitions between the energy levels of luminescence centers are crucial for their appearance. This will help to determine the processes that increase (decrease) populations of energy levels, transitions between which form luminescence in the set $\lambda^{(c)}$. Hence, it is possible to disclose the key mechanisms of the interaction of the luminescence centers with each other and the pump radiation for this crystal under these experimental conditions.

For any linear operator \mathbf{A}_p , that maps space \mathbb{R}^n to \mathbb{R}^n , cosine of

Download English Version:

<https://daneshyari.com/en/article/5398090>

Download Persian Version:

<https://daneshyari.com/article/5398090>

[Daneshyari.com](https://daneshyari.com)