Article

Comparison and Selection of Data Processing Methods for the Application of Cr^{3+} Photoluminescence Piezospectroscopy to Thermal Barrier Coatings

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Abstract: Thermal barrier coatings (TBCs) are an indispensable part of the blades used in aeroengines. Under a high-temperature service environment, the thermal oxidation stress at the interface is the main cause of thermal barrier failure. Cr^{3+} photoluminescence piezospectroscopy has been successfully used to analyze the thermal oxidation stress of TBCs, but systematic and quantitative analysis results for use in data processing are still lacking, especially with respect to the identification of peak positions. The processing methods used to fit spectral data were studied in this work to accurately characterize TBC thermal oxidation stress using Cr^{3+} photoluminescence spectroscopy. Both physical and numerical experiments were carried out, where Cr^{3+} photoluminescence spectra were detected from alumina ceramic samples under step-by-step uniaxial loading, and the simulated spectra were numerically deduced from the measured spectral data. Then, the peak shifts were obtained by fitting all spectral data by using Lorentzian, Gaussian and Psd-Voigt functions. By comparing the fitting results and then discussing the generation mechanism, the Lorentzian function—not the Psd-Voigt function that is most widely utilized—was regarded as the most applicable method for the application of Cr^{3+} photoluminescence piezospectroscopy to TBCs because of its sufficient sensitivity, stability and confidence for quantitative stress analysis.

Keywords: thermal barrier coatings; thermal oxidation stress; Cr^{3+} photoluminescence piezospectroscopy; data processing method; fitting function; Lorentzian functions; spectromechanics

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1. Introduction

Thermal barrier coatings (TBCs) have been developed to effectively protect gas turbines and aeroengines by covering the surface of blade substrates with ceramic materials [1–3]. However, during high-temperature service, thermally grown oxide (TGO) will grow at the interface between the ceramic layer and bonding layer [4–7], which causes the generation and evolution of thermal oxidation stress, leading to interfacial and internal cracks and spalling and even the failure of TBCs [8–12]. Therefore, theoretical modeling, numerical simulation and experimental measurement are all indispensable means of analyzing the state, magnitude, distribution and evolution of the stress induced by TGO, which are essential for scientific research and engineering investigations of TBCs. As an optical measurement method, photoluminescence piezospectroscopy can be applied to investigate a mechanical system non-destructively [13].

$\alpha\text{-Al}_2\text{O}_3$ is the main component of TGO; it is formed from the chemical reaction between Al in the bonding layer and oxygen penetrating through the TBC layer during high-temperature service. Because traces of Cr^{3+} inside the bonding layer are doped into $\alpha\text{-Al}_2\text{O}_3$ during its growth, the noncontact Cr^{3+} photoluminescence piezospectroscopy technique is regarded as an effective means of measuring thermal oxidation stress in TGO [14–17]. In 1993, Ma and Clarke found a quantitative relationship between the stress

and the peak position of the Cr^{3+} photoluminescence spectra of some monocrystalline and polycrystalline materials, constructing the theoretical foundation of fluorescence piezospectroscopy in ceramics [18]. By using a fluorescence piezospectroscopy method, the stress of TGO in TBCs produced by electron beam physical vapor deposition (EB-PVD) was determined by Christensen et al. [19], in 1996. In 2001, Nychka et al. [20] further studied the evolution of thermal cycling stress in TGO. Schlichting et al. [21] discovered the relationship between the stress and thickness of the ceramic layer by measuring the average stress in TGO. In 2019, Shen et al. [22] measured the compressive stress of TGO under thermal shock cycles and found that the evolution of the TGO microstructure, cracks, residual stress and element depletion appeared to be relevant to the durability and degradation of TBCs. In 2020, Jiang et al. [23] verified that the residual stress evolution of TGO for air plasma spraying TBCs can be effectively used to indicate interfacial delamination.

The identification of the peak position is one of the key procedures used with Cr^{3+} photoluminescence spectroscopy to characterize the internal stress of TGO. In most published works, the pseudo-Voigt (Psd-Voigt) function has been most widely applied to fit Cr^{3+} photoluminescence spectra, and the stress in TGO was generally at a magnitude of hundreds of MPa and even GPa. For example, the Psd-Voigt function was used to fit Cr^{3+} fluorescence spectra for stress analyses by Clarke et al. [24] and revealed that the compressive stress in the TGO was approximately 3 to 4 GPa during oxidation. Seculck et al. [25] used a Lorentzian–Gaussian (viz. Psd-Voigt) curve to fit the peaks of the Cr^{3+} luminescence spectra, and the measured stress ranged from 1 GPa in tension to 5 GPa in compression. The evolution of thermal oxidation stress in TGO was studied by Manero et al. [26] using the Psd-Voigt fitting function, and the stress detected ranged from approximately 2 to 4 GPa throughout the loading history, with a standard deviation of approximately 78 MPa under the same loading conditions. Jiang et al. [23] employed a Lorentzian curve algorithm to fit the spectrum obtained from TGO and determined the peak position, and the average stress gradually increased from 1.76 GPa until a peak value of approximately 3.45 GPa was reached. Shen et al. [22] discovered that the compressive stress of TGO with a LZC/YSZ top coating reached the highest value of 2.56 GPa at 1000 thermal cycles, but the data processing method was not mentioned. In addition, the interfacial crack propagation behavior induced by thermal oxidation stress is very complicated because of the undulating TGO morphology [27], and the microcracks always nucleate at local undulations, which continuously causes a slight relief in the stress in the TGO [28]. Therefore, only high-resolution stress characterization can sufficiently explain the dynamic evolution mechanism of TBC delamination, which has been effectively presented by the latest numerical model [29]. However, among all the published works, the residual stress measured in TGO varied by at least tens of MPa, which ineluctably made accurately determining the evolution tendency difficult because of the low resolution of the stress measurement [22,23].

Because blades must be in long-term and stable service in extremely hot and humid environments, it is necessary to develop physical-chemical-mechanical models to quantitatively describe the thermal oxidation stress in TBCs and nondestructive methods to reliably evaluate the structural safety of the TBCs, with both measures requiring accurate in situ stress characterization with precision in the order of ten MPa. However, as mentioned above, the resolution and confidence of the stress characterization based on Cr^{3+} photoluminescence piezospectroscopy have generally been in the order of hundreds of MPa.

Cr^{3+} photoluminescence piezospectroscopy is not the only spectromechanical method. Other techniques, such as cathodoluminescence spectroscopy [30,31], Eu^{3+} photoluminescence piezospectroscopy [11,32], and micro-Raman spectroscopy [33–38], have been broadly applied to the stress/strain analyses of different materials and structures. Fitting functions, such as Lorentzian, Gaussian, and Psd-Voigt functions, have been used to identify the positions and intensities of the characteristic peaks in the spectra detected from samples with external or internal stress. However, there is still a lack of specific studies on the effectiveness and applicability of data processing methods for spectrome-

chanical investigations, especially the high-resolution stress analysis of TBCs using Cr^{3+} photoluminescence piezospectroscopy.

In this work, several fitting functions and methods were compared by applying them to identify the peak positions of Cr^{3+} photoluminescence spectra. The fitted spectra were obtained through both numerical experiments and calibration tests under uniaxial loading. Subsequently, the increments of the peak positions corresponding to different stresses were characterized by different data processing methods, including Lorentzian, Gaussian, and Psd-Voigt functions. Then, the piezo-spectroscopic coefficients were linearly fitted based on the correlation between the peak shift and uniaxial stress. The sensitivity and reliability of the different fitting functions were verified and compared through experimental results to obtain the best one for Cr^{3+} photoluminescence piezospectroscopy.

2. Materials and Experiments

The main component of TGO is $\alpha\text{-Al}_2\text{O}_3$, which is formed from the chemical reaction during high-temperature service, and its thickness is lower than 10 μm . Therefore, it is difficult to extract TGO from TBCs separately. However, Cr^{3+} photoluminescence can be obtained from the traces of Cr^{3+} doped in polycrystalline alumina ceramics, which have been applied to the calibration of piezo-spectroscopic coefficients by Ma et al. [18]. An alumina ceramic specimen was produced and used to obtain Cr^{3+} fluorescence spectra under a uniaxial step stress state in this paper. This specimen was prepared by high-temperature sintering and then cut into several $4 \times 4 \times 10 \text{ mm}^3$ samples.

As shown in Figure 1a, the experimental system of the calibration test mainly consisted of three devices, including a self-built micro-Raman/PL system using a 500 mm spectro-scope (Shamrock 500i, Andor, Belfast, UK), a uniaxial loading device (Microtest 5000, Deben, Suffolk, UK) with a load capacity of 5000 N and an electric 2D-stage (RC201ZA100 $\times$ 100, Beijing Ruicheng, Beijing, China). In the spectroscopic system, a 532 nm laser was used to induce Cr^{3+} photoluminescence in the alumina ceramic samples. The spectral resolution was approximately 0.01 nm, and an 1800 L/mm grating was used. A 20 $\times$ objective lens (378-810-3, Mitutoyo, Kawasaki, Japan) was chosen to achieve a sampling spot with a diameter of $\sim 10 \mu\text{m}$. Before the calibration test, an alumina ceramic sample was fixed on the loading device through a compressive preload of 200 N. Then, the sample was loaded step-by-step by compressive forces to 3000 N with a step length of 200 N (according to 12.5 MPa per step for this sample). At each loading step, luminescence spectra were recorded from 20 different sampling spots on the top surface of the sample. Figure 1b shows a typical Cr^{3+} fluorescence spectrum with 2 characteristic peaks, namely, R_1 and R_2 .

Figure 1. (a) The experimental system of the calibration test; (b) a typical Cr^{3+} fluorescence spectrum.

To analyze the applicability of each processing method for accurately identifying the wavenumber increment of the Cr^{3+} luminescence peak caused by stress, numerical experiments were carried out based on actually measured spectra (shown in Figure 1b)

from an unloaded specimen. The procedure used for the numerical experiments is shown in Figure 2. First, a smooth fitting curve (shown in Figure 3a) that had an extreme goodness-of-fit (GOF) over 0.9995 was obtained through multipeak Lorentzian function fitting via the OriginPro 2016 software (OriginLab, Northampton, MA, USA). The GOF in this work was based on the substitution sum of squares of the residuals between the fitted curve and the actual spectrum data. The noise distribution of the actual spectrum relative to the fitting curve is given in Figure 3b. The random distribution follows a normal distribution, whose center is -0.0002 and FWHM (full width at half maximum) is 0.0942 . The data density of the fitted curve was increased to 30-fold that of the experimental data obtained by interpolation.

Figure 2. Procedure used for the numerical experiments.

Figure 3. (a) Smooth curve obtained by multipeak fitting; (b) noise distribution; (c) simulated spectrum with introduced noise.

After that, some overall shifts in the wavenumbers were introduced into the density-increased curve by adding certain increments to the horizontal ordinate data, which was aimed to simulate the effect of stress on the spectral curve. Both the wavenumber-stress coefficients of R_1 and R_2 were regarded as $-1.45 \text{ cm}^{-1}/\text{GPa}$, and the increments were set to a fixed step length of 0.007 cm^{-1} at the beginning, which corresponded to 5 MPa. Then, the incremental step was increased step-by-step.

Finally, the data density of each wavenumber-shifted curve was reduced to a degree consistent with the actually measured spectrum, and random errors at the same level as the error of the actually measured spectrum were introduced using a normal distribution (shown in Figure 3b), achieving the spectral data of the numerical experiments, as shown in Figure 3c.

3. Models and Methods

3.1. The Theoretical Model of Cr^{3+} Photoluminescence Piezospectroscopy

The basis for using piezo-spectroscopic methods for the measurement of stress in crystalline materials is that an applied stress strains the lattice and alters the energy of transitions between electronic or vibrational states [39,40]. Cr^{3+} ions exist in $\alpha\text{-Al}_2\text{O}_3$ corundum in trace impurity form. Cr^{3+} ions can be used to substitute for some Al^{3+} ions, occupying the center of normal octahedral ion sites, since they are similar in ionic

radius. When $\alpha\text{-Al}_2\text{O}_3$ corundum is subjected to pressure, there is an obvious wavenumber increment of Cr^{3+} fluorescence characteristic peak with suitable excitation.

The relationship between an observed shift in a fluorescence line and the state of stress was first described phenomenologically by Grabner [41], who proposed that the change in frequency, $\Delta\nu$, of the fluorescence line can be expressed by the tensorial equation

$$\Delta\nu = \Pi_{ij}\sigma_{ij}^* = \begin{bmatrix} \Pi_{11} & \Pi_{12} & \Pi_{13} \\ \Pi_{21} & \Pi_{22} & \Pi_{23} \\ \Pi_{31} & \Pi_{32} & \Pi_{33} \end{bmatrix} \begin{bmatrix} \sigma_{11}^* & \sigma_{12}^* & \sigma_{13}^* \\ \sigma_{21}^* & \sigma_{22}^* & \sigma_{23}^* \\ \sigma_{31}^* & \sigma_{32}^* & \sigma_{33}^* \end{bmatrix} \quad (1)$$

where Π_{ij} denotes the component of the wavenumber-stress coefficient tensor, σ_{ij}^* is the stress component, and the subscripts i and j represent the crystallographic directions. The Π_{ij} matrix can be simplified by considering the point symmetry of Cr^{3+} ions [39]:

$$\Pi_{ij} = \begin{bmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{22} & 0 \\ 0 & 0 & \Pi_{33} \end{bmatrix} \quad (2)$$

Equation (1) reduces to

$$\overline{\Delta\nu} = \Pi_{11}\sigma_{11}^* + \Pi_{22}\sigma_{22}^* + \Pi_{33}\sigma_{33}^* \quad (3)$$

The main composition of the TGO is polycrystalline $\alpha\text{-Al}_2\text{O}_3$, which satisfies the assumption of macroscopic isotropy. There are enough grains with random crystal orientations in the collecting area during laser excitation in the PL measurement. The spatial orientation of the piezo-spectroscopic relationship can be expressed by the Euler angle transformation matrix, and then, the effect of off-diagonal elements Π_{ij} ($i \neq j$) and σ_{ij}^* ($i \neq j$) vanishes when integrating over the whole space. Therefore, Equation (3) reduces to:

$$\overline{\Delta\nu} = \frac{1}{3}(\Pi_{11} + \Pi_{22} + \Pi_{33})(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (4)$$

Furthermore, when uniaxial stress, σ_U , is applied, the frequency shift, $\Delta\nu$, can be expressed as follows:

$$\overline{\Delta\nu} = \Pi_U\sigma_U \quad (5)$$

where Π_U is the piezo-spectroscopic coefficient under the uniaxial stress state.

3.2. Data Processing Methods

Previous studies have shown that the fluorescence peaks at 14,402 and 14,432 cm^{-1} (shown in Figure 1b) are highly sensitive to stress [42–49]. Lorentzian, Gaussian and Psd-Voigt functions were mostly used to fit the characteristic peaks or bands in the experimental molecular and atomic spectral data, including those obtained by Cr^{3+} photoluminescence [24–26]. In this work, all the luminescence spectra of both actual and numerical experiments were fitted by using Lorentzian, Gaussian and Psd-Voigt functions. The spectral fitting was carried out based on Levenberg–Marquardt algorithm via the software OriginPro 2016.

The line shape accords with the Lorentzian function for the homogeneous broadening of the spectrum caused by spontaneous emission and collision. The expression of the Lorentzian function is as follows:

$$y = y_0 + \frac{2A}{\pi} \times \frac{w}{4(x - x_c)^2 + w^2} \quad (6)$$

where y_0 is the relative base value of the peak, A is the area of this peak, w is its FWHM, and x_c is the peak position.

The line shape accords with the Gaussian function for the inhomogeneous broadening of spectrum caused by the velocity distribution of irradiance particles (viz. Doppler effect). The expression of the Gaussian function is as follows:

$$y = y_0 + \frac{Ae^{-\frac{4\ln 2}{w^2}(x-x_c)^2}}{w\sqrt{\frac{\pi}{4\ln 2}}} \quad (7)$$

where y_0 , A , w and x_c have the same meaning as they do in Equation (6).

The abovementioned homogeneous broadening caused by collision and inhomogeneous broadening caused by the Doppler effect are the main two types of broadening, but spectral lines are always characterized by a variety of broadening mechanisms in general. When considering these above two kinds of broadening mechanisms simultaneously, the Psd-Voigt function, which is the linear superposition of a Lorentzian function and a Gaussian function, can be obtained. The expression is as follows:

$$y = y_0 + A \left[m_u \frac{2}{\pi} \times \frac{w_L}{4(x-x_c)^2 + w_L^2} + (1-m_u) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}w_G} e^{-\frac{4\ln 2}{w_G^2}(x-x_c)^2} \right] \quad (8)$$

where w_L is the FWHM of the Lorentzian curve, w_G is the FWHM of the Gaussian curve, x_c is the peak position, and m_u is the weight of the Lorentzian function.

4. Results and Discussion

The fitting curves of a typical Cr^{3+} photoluminescence spectrum obtained using Psd-Voigt, Gaussian and Lorentzian functions are shown in Figure 4a–c, respectively. The GOFs of different functions for both the measured and simulated spectra are listed in Table 1. Fitting using the Psd-Voigt function can obtain a visually better fitting effect (shown in Figure 4) and a larger value of the GOF (listed in Table 1) than the other two functions. In contrast, the fitting result obtained using the Gaussian function shows the largest shape difference and the lowest GOF.

Figure 4. Typical Cr^{3+} photoluminescence spectra fit using (a) Psd-Voigt, (b) Gaussian and (c) Lorentzian functions.

Table 1. GOF values of different functions used to fit Cr^{3+} fluorescence spectra.

Fitting Function		Psd-Voigt	Gaussian	Lorentzian
GOF	Simulated data	0.9994	0.9808	0.9986
	Measured data	0.9991	0.9804	0.9986

4.1. Results of the Numerical Experiments

All the simulated spectra were fitted by using Psd-Voigt, Gaussian and Lorentzian functions and the simulated spectral data corresponding to specific stress values were exactly the same. In addition, the wavenumber increments, viz., the shifts of the R_1 and

R_2 peaks, were obtained as shown in Figures 5–7. Based on the fitting results, piezo-spectroscopic coefficients Π_U were obtained and are listed in Table 2.

Figure 5. The relation between the peak shift and stress fitted by the Psd-Voigt function: (a) peak R_1 ; (b) peak R_2 .

Figure 6. The relation between the peak shift and stress fitted by the Gaussian function: (a) peak R_1 ; (b) peak R_2 .

Figure 7. The relation between the peak shift and stress fitted by the Lorentzian function: (a) peak R_1 ; (b) peak R_2 .

Table 2. Piezo-spectroscopic coefficients Π_U in numerical experiments based on the results obtained by using different fitting functions.

Π_U	R_1 (cm ⁻¹ /GPa)	R^2	R_2 (cm ⁻¹ /GPa)	R^2
Preset value	−1.45	-	−1.45	-
Psd-Voigt	−1.85 ± 0.16	0.8964	−1.42 ± 0.17	0.8118
Gaussian	−1.45 ± 4.68 × 10 ⁻⁶	1	−1.46 ± 7.45 × 10 ⁻⁵	1
Lorentzian	−1.45 ± 5.99 × 10 ⁻⁶	1	−1.46 ± 7.71 × 10 ⁻⁶	1

Figure 5 gives the results of fitting peak shifts under different uniaxial loadings (equal step length and then increasing step length) by using the Psd-Voigt function. On the whole, the peak shift, whether R_1 or R_2 , maintained a linear relationship with the compressive stress, and the slope of this linear relationship is called the piezo-spectroscopic coefficient, denoted as Π_U . However, such a linear relationship did not exist at the small loading step (corresponding to a ~5 MPa stress pre-step), as shown in the upper right subfigures of Figure 5a,b, where the peak shifts changed with a seemingly random increment. This means that the Psd-Voigt function was not sensitive enough to small stress when fitting the Cr³⁺ photoluminescence spectrum. Moreover, the peak shift began to change monotonically in Figure 5 under the condition of larger loading steps, but the data still obviously fluctuated, and the results were not correct. Specifically, the linear correlation coefficients (R^2) between the peak shift and stress were only 0.8964 for R_1 and 0.8118 for R_2 . In addition, Π_U is -1.85 ± 0.16 cm⁻¹/GPa for R_1 and -1.42 ± 0.17 cm⁻¹/GPa for R_2 , both of which are quite different from the preset value of -1.45 cm⁻¹/GPa.

Figure 6 gives the fitting results obtained by using the Gaussian function, which shows that the shifts of both the R_1 peak and R_2 peak decreased linearly ($R^2 = 1$) with increasing uniaxial stress. Π_U was $-1.45 \pm (4.68 \times 10^{-6})$ cm⁻¹/GPa for R_1 and $-1.46 \pm (7.45 \times 10^{-5})$ cm⁻¹/GPa for R_2 , each of which was nearly equal to the preset value -1.45 cm⁻¹/GPa. A similar phenomenon occurred when using Lorentzian functions. The peak shift, whether R_1 or R_2 , maintained a faultlessly linear relationship with the compressive stress. Π_U was $-1.45 \pm (5.99 \times 10^{-6})$ cm⁻¹/GPa for R_1 and $-1.46 \pm (7.71 \times 10^{-6})$ cm⁻¹/GPa for R_2 .

4.2. Results of the Calibration Experiments

All the experimental spectra were fitted by using Psd-Voigt, Gaussian and Lorentzian functions. The wavenumber increments were obtained, as shown in Figures 8–10. Based on the fitting results, the piezo-spectroscopic coefficients Π_U were obtained and are listed in Table 3. By comparing these results using the three fitting functions, it can be seen that the peak shifts obtained by the Psd-Voigt function had the largest fluctuation; that is, they had the poorest stability. Specifically, the peak shifts of the different sampling spots under the same loading changed over large ranges, with averages of 0.21 cm⁻¹ for the R_1 peak and 0.13 cm⁻¹ for the R_2 peak. The peak shifts changed with external loadings in the linear relationship of low linear correlation coefficients, approximately 0.97 for the R_1 peak and 0.97 for the R_2 peak.

Figure 8. The relation between the peak shift and stress fitted by the Psd-Voigt function: (a) peak R_1 ; (b) peak R_2 .

Figure 9. The relation between the peak shift and stress fitted by the Gaussian function: (a) peak R_1 ; (b) peak R_2 .

Figure 10. The relation between the peak shift and stress fitted by the Lorentzian function: (a) peak R_1 ; (b) peak R_2 .

Table 3. Piezo-spectroscopic coefficients Π_U in numerical experiments based on the results obtained by using different fitting functions.

Π_U	R_1 (cm ⁻¹ /GPa)	R^2	R_2 (cm ⁻¹ /GPa)	R^2
Ma, 1993 [18]	-2.54	-	-2.53	-
Psd-Voigt	-2.91 ± 0.16	0.9684	-2.70 ± 0.13	0.9732
Gaussian	-2.71 ± 0.05	0.9969	-2.50 ± 0.04	0.9966
Lorentzian	-2.71 ± 0.04	0.9970	-2.50 ± 0.05	0.9961

In contrast, the peak shifts fitted by both Gaussian (shown in Figure 9) and Lorentzian (shown in Figure 10) functions decreased linearly with increasing uniaxial stress for both R_1 and R_2 . The piezo-spectroscopic coefficient Π_U obtained by the Gaussian function was almost equal to that obtained by the Lorentzian function, $-2.71 \text{ cm}^{-1}/\text{GPa}$ for R_1 and $-2.50 \text{ cm}^{-1}/\text{GPa}$ for R_2 . Notably, there were few differences between the Π_U results of this work and those in a published work [18], where Π_U was $-2.54 \text{ cm}^{-1}/\text{GPa}$ for R_1 and $-2.53 \text{ cm}^{-1}/\text{GPa}$ for R_2 .

4.3. Discussion

The fitting results above show that, even though it had a visually better fitting effect and higher GOF, the Psd-Voigt function is not suitable for the stress analysis of Cr^{3+} photoluminescence piezospectroscopy, owing to its low sensitivity to small stress changes, and low stability and confidence of peak shifts. Particularly, it did not obviously identify a stress change with a range of 40 MPa, as shown in the upper right subfigures of Figure 5. In contrast, both Gaussian and Lorentzian functions accurately identified the peak shift caused by small stresses and stably described the linear relationship between stress and peak shift. By comparison, the Lorentzian function always achieved a higher GOF, as well as a better visual similarity, than the Gaussian function. Hence, by comparing and contrasting the fitting effect, the Lorentzian function is proven to be most applicable to fit Cr^{3+} photoluminescence spectra for experimental stress analysis.

The applicability of any fitting function to spectral analysis is determined by the generation mechanism of the spectrum. Generally, a characteristic peak corresponding to a single vibration/excitation mode in the Raman/fluorescence spectrum of a crystal, especially that of a monocrystalline material, always presents as a perfect Lorentzian shape, such as the Raman G peak of graphene [50], the first-order Raman peak of monocrystalline silicon [36] and the fluorescence peak of ruby crystals. For polycrystalline materials or eutectic substances with some hybrid structures or multioverlay vibration/excitation modes, the characteristic peaks in their Raman or fluorescence spectra show a Gaussian shape. In the majority of cases, most Raman or fluorescence peaks reflect both Lorentzian and Gaussian characteristics, which are, in fact, the convolution of the two; that is, Voigt shapes. However, it is difficult to realize curve fitting using a true Voigt function for the discrete sequence of spectral data. As an alternative, the Psd-Voigt function is widely used. A Psd-Voigt function is the linear combination of a Lorentzian function and Gaussian function with a certain weight ratio.

The fitting of Raman or fluorescence spectra using a Psd-Voigt function usually obtains a relatively optimal GOF. However, the unilateral pursuit of such a fitting process is to achieve a GOF that is as high as possible by adjusting the Lorentzian–Gaussian weight ratio, which has no physical meaning. Hence, the weight ratios obtained from fitting the spectra of the same sample with different loadings or different positions are uncertain, inconsistent and irregular. Due to the loss of a unified standard for mutual comparison, it is difficult to reflect the small wavenumber changes caused by stress in the fitting results, which makes the Psd-Voigt function insensitive and inaccurate for use in stress analysis.

In fact, the Psd-Voigt function was the most widely utilized function in published works on the application of Cr^{3+} photoluminescence piezospectroscopy [24,26]. In the existing works, the measured thermal oxidation stress was always in the magnitude of hundreds of MPa or even thousands of MPa, showing that the Psd-Voigt function is not sensitive to the stress in the magnitude of tens of MPa. However, with the improvement of engineering requirements for advanced thermal barrier coating technology, accurate calibration of the piezo-spectroscopic coefficient and creditable characterization of residual/processing stress require that the stress resolution of piezo-spectroscopic analysis reach a magnitude of 10 MPa.

The Lorentzian function is more applicable to fit Cr^{3+} photoluminescence piezo spectra. A typical TBC structure is composed of a nickel alloy blade as the substrate, a bonding layer (NiCoCrAlY) and a TBC layer on the surface. During its service under high temperature

(at least 1400 K), thermal oxidation stress is generated and evolves with the growth of TGO [51–53]. With the growth of the TGO, trace amounts of Cr^{3+} ions are introduced into $\alpha\text{-Al}_2\text{O}_3$. When the position of the Al^{3+} ion at the center of the octahedral $\alpha\text{-Al}_2\text{O}_3$ cell is replaced by a Cr^{3+} ion [54], two emission peaks near 693 nm are generated from the energy transition of ${}^2\text{E}-{}^4\text{A}_{2g}$ under laser irradiation. These two peaks are defined as R_1 and R_2 at wavenumbers of approximately $14,403\text{ cm}^{-1}$ (694.30 nm) and $14,433\text{ cm}^{-1}$ (692.86 nm), respectively. Although the $\alpha\text{-Al}_2\text{O}_3$ in the TGO is usually polycrystalline, the line type of the Cr^{3+} fluorescence characteristic peak was more similar to the Lorentzian line type because of the single mechanism of fluorescence generation, which is confirmed by the fitting phenomena shown in Figure 4 and the results listed in Table 1.

In addition, multipeak fitting and the barycenter method were also applied for the identification of peak shifts in some published works [55]. The linear superposition of multiple single-peak functions makes the fitted curve closely fit the measured data, achieving an extremely high GOF of more than 0.999. However, the fitting parameters of the multipeak functions have neither physical significance nor enough stability. Under the same parameter settings, the fitting results at different times are different. They are sensitive to the number of preselected peaks, as shown in Figure 11. The barycenter method takes the barycentric wavenumber of a specific spectral band as its peak position, which is suitable for spectral bands with poor symmetry, such as Eu^{3+} fluorescence peaks [32]. Neither of the above methods are suitable for the data processing of Cr^{3+} fluorescence spectra.

Figure 11. Fitting results of identifying peak positions by the multipeak fitting method: (a) results of R_1 ; (b) results of R_2 .

The bullet point list of our key findings above is as follows:

- The fitting results show that the Psd-Voigt function is not sensitive enough to small stress when fitting the Cr^{3+} photoluminescence spectrum, even though its GOF is relatively high. Both Gaussian and Lorentzian functions can accurately identify the peak shifts corresponding to different stresses.
- The unilateral pursuit of Psd-Voigt function fitting process is to achieve a GOF that is as high as possible by adjusting the Lorentzian–Gaussian weight ratio, which has no physical meaning. Due to the loss of a unified standard for mutual comparison, the Psd-Voigt function is insensitive and inaccurate for stress analysis.
- The applicability of any fitting function to spectral analysis is determined by the generation mechanism of the spectrum. The line type of the Cr^{3+} fluorescence characteristic peak was more similar to the Lorentzian line type because of the single mechanism of fluorescence generation, which is confirmed by the fitting phenomena and the results.
- Comparatively speaking, Lorentzian fitting is proven to be the most applicable method.

5. Conclusions

Methods used to process Cr^{3+} photoluminescence spectroscopic data were studied to analyze the application of stress on the thermally grown oxide layers of TBCs. Numerical experiments and calibration tests were carried out to obtain numerous spectra corresponding to different uniaxial loadings. The results showed that the Psd-Voigt fitting obtained the highest goodness-of-fit, but it had low sensitivity for small stress changes, as well as low stability and confidence of peak shifts, which indicated that it was far from suitable for analyzing stress by Cr^{3+} photoluminescence piezospectroscopy, even though it is very widely utilized in published works. Lorentzian fitting was proven to be the most applicable method, as shown by comparing its fitting results with those of other functions and then discussing the generation mechanism of Cr^{3+} photoluminescence piezospectroscopy.

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