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Temperature dependence of the optical properties of Bi_2O_3. A theoretical approach basing on the Kramers-Kronig transformation for polynomial mixed terms models

Research Article

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Abstract: The Kramers-Kronig transforms (KK) constitute a powerful tool to validate experimental data. The present study is implemented for Bi_2O_3 thin films deposited by thermal vacuum evaporation at different temperatures of the glass substrates. Since the extraordinary properties of this fabric allow us to consider particular analytical approach as it was previously shown, the reflectance properties of Bi_2O_3 as a function of temperature could be studied.

The novelty of this article is the studying of a global effective analytical representation, based on polynomial functions, in order to obtain a general model that includes temperature dependence of the optical properties, using the Kramers-Kronig transformation type. In the mathematical expressions, were included mix combined term in order to avoid the effects of Runge phenomenon. As a case study was chosen Bi_2O_3 – a substance less studied in literature. In the last part are the presented and commented the results obtained for a series of eight studied models.

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Keywords: optical properties of Bi_2O_3 films • Kramers-Kronig transformation • numerical applications.

1. Introduction

Theoretical research methods have been presenting a growing importance in the last decade. The investigations of the optical proprieties of various types of samples are, by this, a great area of continuous research, because of the significant applicative impact of the optical proprieties in the fields of industry and health. As a straight proof, we should be consider the rising impact factor of related literature journals. Moreover, considerable attention has been devoted to the inverse problem of determining the constitutive parameters of complex media from optical parameters [1–3]. To overcome this problem, an alternative method of Kramers-Kronig analysis of the experimental

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spectra can be applied [3].

The possibility of applying the Kramers-type transformation was discussed in the literature Kronig by a long series of authors [2, 3, 5, 7, 8] for a wide range of substances with different optical properties.

The often raised problem is related to the necessary and sufficient conditions which allow for the implementation of Kramers-Kronig transformation. In particular, the most common problem which is invoked is linked to limitation of the measurement range – the limitation will affect the apparent quality of the interpolation and that the estimated values outside the measurement range.

Although in the small wavelength domain the measurements can not be performed because of equipment limitations, it seems that because the general trend of reduction for the reflectance spectra found in this area, the contribution of this interval is reduced. In this respect, within some reasonable approximations which are common in the literature [1–5] we could consider for the analysis as sufficient the wavelength domain covered by the IR, visible and in the near UV measurement range. In this respect, the main contributions of the spectrum thus are conveniently captured [6].

In order to apply the KK method for a certain sample, one needs first to acquire the reflectance spectrum $R = R(\omega)$ then has to extrapolate the experimental spectrum into a large enough spectral range, in order to perform the computations of this expression.

Generally speaking, the interpolation methods used in the literature are based on the use of Chebyshev polynomials or specific types of spline functions, which can achieve a more faithful interpolation of the measured spectrum [1–5]. Another common method is to consider the partial interpolation functions, which directly result in an increase in reflectance spectrum obtained approximation quality [5–7]. Thus, a promising method that would help quite a faithful interpolation would be based on the use of neural networks approach with a suitable training algorithm backpropagation [4]. The research results will be straightforward.

The use for these methods above presented implies a series of specific problems. Besides the advantage of increase the accuracy of approximation by using spline functions or partial portions functions on the interpolation process, there is the great disadvantage of increasing difficulty in building a global model that includes temperature dependence. Also, when using polynomials Chebyshev it is met difficulties in achieving a reliable fitting to capture the optical properties change depending on temperature [8, 10]. This difficulty is even greater of their optical properties change is greater, as in the case study chosen for this article.

All these issues highlight a number of difficulties which come together if the aim is to realize a global mathematical model. This approach is not simple. In this sense, this paper aim is to present such a model to demonstrate the possibility of achieving effective purpose. The present case study is considered for Bi_2O_3 fabric which hasn't been thoroughly studied in the literature. This aspect is related to the fact that we wanted to investigate a new strategy, different from other approaches in the literature. The necessarily implemented algorithm is simple: first it performs an interpolation of the values obtained for reflection data set and, based on this interpolation is calculated using the known KK relations, optical magnitudes of interest, especially the refraction index. The interpolation function and the calculated values obtained based on the KK transformation should be investigated in the last stage, on criteria to be considered related to statistical analysis. The presented results are obtained for a recursive optimization due by successive evaluations.

2. Theoretical notions

In the KK method, one starts from the complex reflection amplitude of a normal incident electromagnetic wave, used in the Kramers-Kronig analysis, is defined as follows [1].

$$\Re^{1/2} = \frac{(n-1)+i\kappa}{(n-+1)+i\kappa} = R^{1/2} \exp i\phi, \tag{1}$$

where R is the reflection factor of simply the reflectance at a certain frequency, ω or wavelength λ and ϕ is the phase, being related to the reflectance by the following equation:

$$\phi(\omega) = \frac{\omega}{\pi} \int_0^\infty \frac{\log(R(\beta))}{(\beta^2 - \omega^2)} d\beta - \pi. \tag{2}$$

Integrating by parts, moreover, the spectral regions in which the reflectivity is constant do not contribute to the value of ϕ, due to the second term in integral. Thus the spectral region to be studied can be limited.

Correspondingly, the refractive index n and the absorption coefficient κ can be expressed, according to the KK analysis, by the following relations:

$$n = \frac{1-R}{1+R+2\sqrt{(R)}\cos(\phi)}, \tag{3}$$

$$\kappa = \frac{-2\sqrt{(R)}\sin(\phi)}{1+R+2\sqrt{(R)}\cos(\phi)}. \tag{4}$$

Thus, in order to apply the KK method for a certain sample, one needs first to acquire the reflectance spectrum $R = R(\omega)$ by using a certain spectrometer device, then is has to extrapolate the experimental spectrum into a large enough spectral range, in order to perform the computations of the expression (2). After computing the phase factor ϕ , one has to simply apply Equations (3) and (4) in order to compute the main optical parameters, namely the refractive index and the absorption index, from which other important parameters can also be worked out [1–4]. Instead, the classical method of finding n and κ is to acquire both the transmittance spectrum $T = T(\omega)$ and the reflectance spectrum $R = R(\omega)$ of the same sample, then, by knowing the thickness of the sample, one can compute first the absorption coefficient, α as:

$$\alpha = \frac{1}{d}\left(2\log\left(1-R\right) - \log(T)\right), \tag{5}$$

from where the absorption coefficient will be given by

$$\kappa = \frac{\alpha\lambda}{4\pi}, \tag{6}$$

and then, in order to find the refractive index n (Figure 2), one has to apply the next formula for the reflectance at normal incidence:

$$R = \frac{(n-1)^2+\kappa^2}{(n+1)^2+\kappa^2}, \tag{7}$$

where the refractive index n will be computed as

$$n = 1 + \frac{\sqrt{(1+R)^2-\kappa^2(1-R)^2}}{1-R}. \tag{8}$$

3. Experimental details and analysis methods

The Bi_2O_3 films were deposited by classical vacuum evaporation on glass substrates maintained at different temperatures. The starting material was high purity bismuth trioxide powder (99,999%), inserted in a quartz crucible surrounded by tantalum wire, from electrical current, in order to achieve the necessary heating. The substrates were facing downwards, the distance between the top of the crucible and the substrate being maintained at 8 centimetres. The pressure inside the evaporation chamber was around 8.10^{-2} torr.

The film thickness was estimated by using a Linnik type of interferential microscope and it resulted each time in the range of the nanometers. Both the transmittance and the reflectance spectra were acquired with a Perkin Elmer Lambda 35 spectrometer with a 190–1100 nm available spectral range. Still, the experimental data was affected by detector noise and thus, the useful spectral range was narrower, between 350 and 1100 nm.

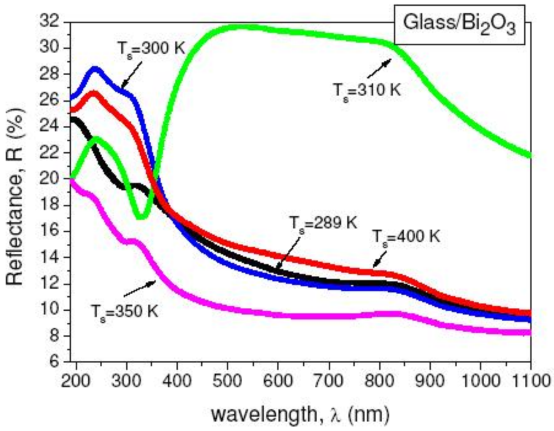

Figure 1. The measured reflectance magnitudes at different temperatures for Bi_2O_3.

The Equations (3), (4) and (5) shows that if the reflectivity is measured over the whole frequency spectrum, then the phase angle ϕ could be calculated. In order to apply the KK method, integration by parts.

4. Results and discussions

Figure 1 shows the Bi_2O_3 reflectance spectra measured in the 190–1100 nm domain at different temperatures. It should be noted the existence of areas between the measured values are high, especially in the wavelength range 190–400 nm. On the other hand is easy to see the existence of a clear trend of decrease for the reflectance magnitude for the small wavelength domain – under 190 nm respectively in the large wavelength domain, over 1000 nm.

These trends are found in all data sets measured for all the temperatures. There is still a significant change in measured values of the spectrum in the 300–500 nm wavelength range. In this regard, it was desirable to obtain a representation of these spectra, against temperature and wavelength (Figure 2), in order to make a more suggestive representation.

In this order, it was performed a sequential representation of the reflectance measured spectra, depending on the wavelength and the temperature (Figure 2). This representation could be obtained using statistical analysis program StatSoft Statistica 10. In this way you can see the existence of a significant change in the optical properties due to a temperature dependence and therefore it is presented a high sensitivity of this physical parameter for the optical properties. We could identify two areas of temperature, at around 330 K and 295 K respectively, in

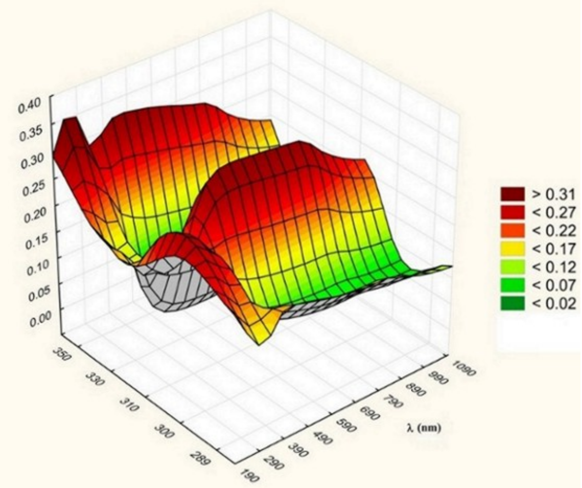

Figure 2. The measured reflectance magnitudes against wavelength (nm) temperatures (K) for Bi_2O_3.

which the subject property to major changes. In a future paper will be presented the required analysis for these observations. In conclusion, it may highlight the need to identify a mathematical model to highlight these changes in reflectance with the temperature which would be extremely interesting. In this respect, we should develop a mathematical model building process to interpolated spectra measured at different temperatures.

Figure 3 shows the measured refractive index values for Bi_2O_3 in the 190–1100 nm domain, measured at different temperatures. In a similar way, we could observe the existence of significant changes in the measured values, for 310 K temperature nearby. On the other hand is easy to see the existence of a clear trend of decreasing refractive index values for the smallest wavelength that in the large wavelength over 1000 nm.

Naturally, based on the obtained determinations, we could make a sequential representation of the refractive index spectrum, against on the wavelength and the temperature (Figure 4). This representation was obtained using statistical analysis program StatSoft Statistica V.10. Similarly, it could be noticed a change in refractive index values depending on temperature underlining a great sensitivity to the physical parameter. It is a great interest for a mathematical model building to highlight these changes of the optical proprieties with the temperature.

For a complete discussion of the mathematical model present proposed it has to consider the following steps: first it was made an interpolation of measured spectra at different temperatures, the polynomial approach being considered, for related to the unitarity treatment reasons: in the second step, we make assessments of refractive index obtained on the KK transformation; in the third step

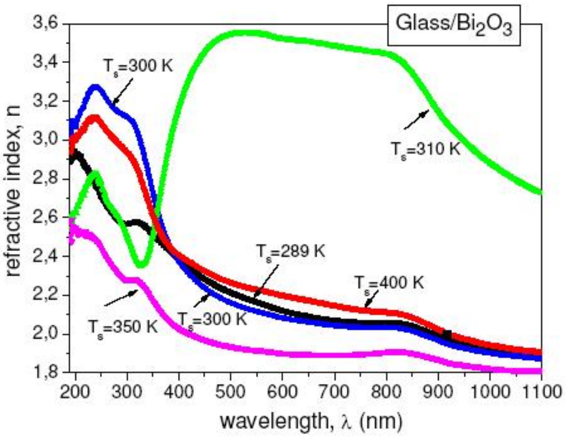

Figure 3. The measured refractive index magnitudes for Bi_2O_3 at different temperatures.

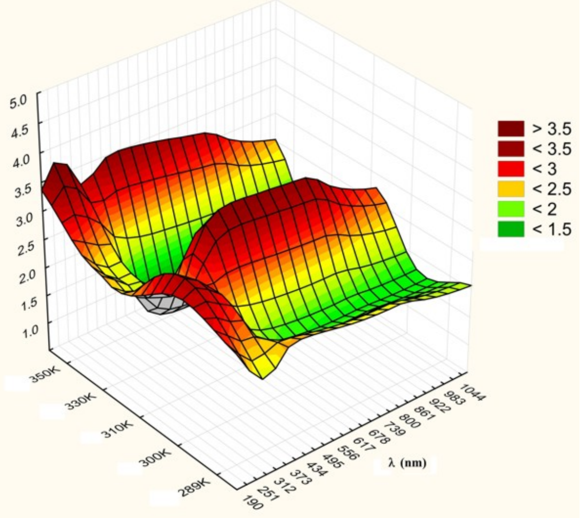

Figure 4. The measured refractive index magnitudes against wavelength (nm) temperatures (K) for Bi_2O_3.

a statistical analysis was made for the results, in order to made a model refinement. In this respect, the analysis was done gradually and the polynomial mixed terms were included in order to capture the temperature dependence. The used procedure to obtain the polynomial model coefficients was based on a regressive type multidimensional analysis. The computations were made using a specific MATLAB script unit. We considered expressions of the form:

$$\begin{aligned} R(\lambda, T) = a_0 + a_1\lambda + \ldots + a_n\lambda^n + b_{1,1}T\lambda \\ + \ldots.b_{m,k}T^m\lambda^k + \ldots. + c_1T + \ldots \end{aligned} \tag{9}$$

The coefficients' evaluation was done using the least

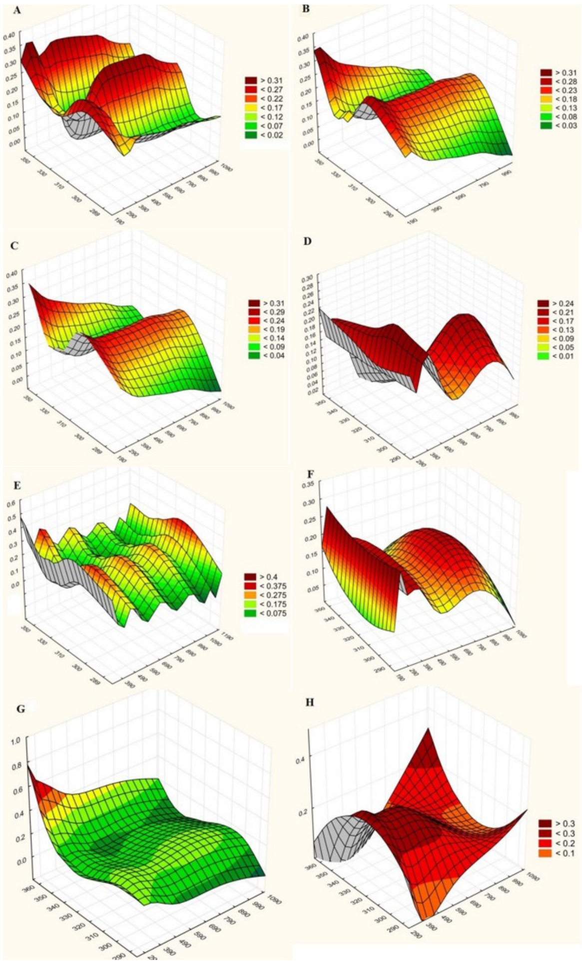

Figure 5. The theoretical reflectance results for Bi_2O_3 against wavelength (nm) and temperature (K) for the considered analytical models.

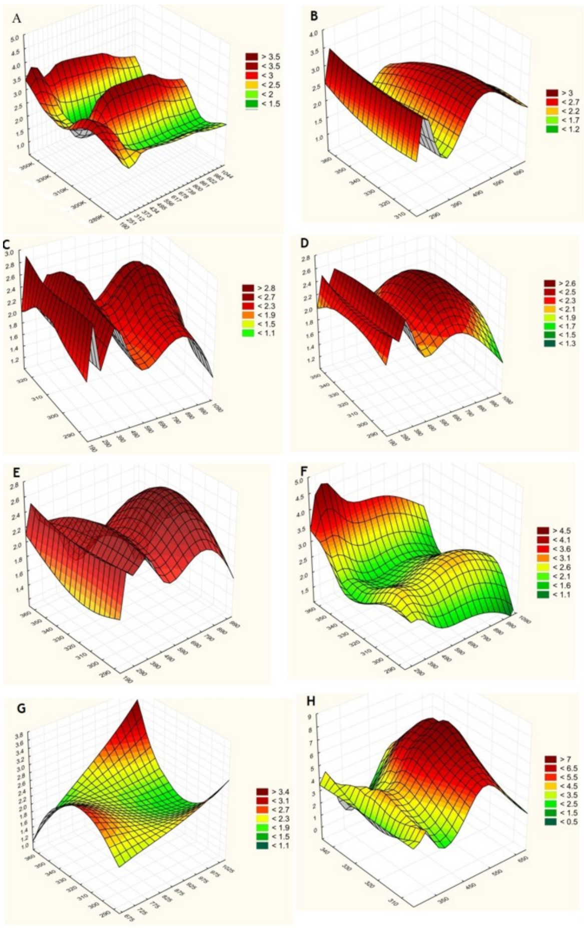

Figure 6. The theoretical refractive index results for Bi_2O_3 against wavelength (nm) and temperature (K) for the considered analytical models.

squares method. It was chosen for such an approach because of the reliability process argument. For each considered model was calculated the correlation coefficient r.

For the investigation of the reliability of the mixed term polynomial approach, was chosen the particular case study of Bi_2O_3. It having been studied a number of 15 models and in this paper we presented only preliminary results for a series of 8 different analytical expressions of the form (9).

Generally speaking, the experimental values of the reflectivity have to be extrapolated in a spectral domains large enough to consider that the zero limit and respectively infinity limit are attained, aiming to obtain the reflectance spectral on the complete spectral domain. Such wrap, over the whole spectral range – from zero to infinity is possible using certain extrapolation techniques, which could describe the optical behaviour in these ranges.

By applying the algorithm described above has led to reflectance representations depending on the wavelength and temperature (Figure 5), respectively to Kramers-Kronig transformation results for refractive index evaluation (Figure 6).

In our approach, we considered, after some successive tries, a ninth rank polynomial function named L9M12T3, of the form

$$\begin{aligned} R(\lambda, T) = a_0 + a_1\lambda + \ldots + a_9\lambda^9 + b_{1,1}T\lambda \\ + \ldots.b_{1,2}\lambda T^2 + \ldots. + c_3T^3 \end{aligned} \tag{10}$$

The reflectance representation is given in (Figure 5b). We could note that this model reproduces with enough accuracy the main trends for the optical properties which depend on the temperature. The related Pearson product-moment type correlation coefficients r were evaluated for

Table 1. The correlation coefficients for L9M12T3 model.

temperature	T1	T2	T3	T4	T5
T(K)	289	300	310	330	350
Pearson correlation	0.804	0.965	0.979	0.971	0.9807

Table 2. The correlation coefficients for L10M12T3 model.

temperature	T1	T2	T3	T4	T5
T(K)	289	300	310	330	350
Pearson correlation	0.7132	0.859	0.7551	0.7525	0.8085

each temperature value a part and are presented in Table 1.

For the computed refractive index values, the results for this are not impressive.

The second example is for a tenth rank polynomial function named L10M12T3, of the form

$$R(\lambda, T) = a_0 + ... + a_{10}\lambda^{10} + b_{1,1}T\lambda + ...b_{1,2}\lambda T^2 + ... + c_3 T^3\,. \qquad (11)$$

The obtained results for reflectance magnitudes are shown in (Figure 5c). We can note that it reproduced with enough accuracy the main trends for the optical properties depending on the temperature. The related Pearson product-moment type correlation coefficients r were evaluated for each reference temperature value a part and are presented in Table 2. The quality is lower as we could easily see.

For the computed refractive index values, the results are presented in Figure 6b. Even for this model results are not satisfactory, the Pearson correlation coefficients being weak.

Next were analysed higher order models to investigate the ability of obtaining a representation that can reproduce the temperature dependence of optical properties. In this way, it could be investigate an eleventh rank polynomial (Figure 5d) and a twelfth rank model (Figure 5e). For the refractive index related magnitude, the results are represented in (Figure 6c) and respectively (Figure 6d). It should be noticed that both of them seem to reproduce with some accuracy the main trend change for the temperature dependence. The related Pearson product-moment type correlation coefficients r for the twelfth rank model hows that the quality of the approximation is lower as we could easily see.

The last four analysed models, had a higher rank and higher degree mixed terms gradually included. In this way, expressions for the last four models considered are presented in relations (12–15):

$$R(\lambda, T) = a_0 + a_1\lambda + ... + a_{13}\lambda^{13} + b_{1,1}T\lambda + ...b_{1,2}\lambda T^2 + ... + c_3 T^3, \qquad (12)$$

$$R(\lambda, T) = a_0 + a_1\lambda + ... + a_{13}\lambda^{13} + b_{1,1}T\lambda + ...b_{2,2}\lambda^2 T^2 + ... + c_3 T^3, \qquad (13)$$

$$R(\lambda, T) = a_0 + a_1\lambda + ... + a_{13}\lambda^{13} + b_{1,1}T\lambda + ...b_{2,2}\lambda^2 T^2 + ... + c_4 T^4, \qquad (14)$$

$$R(\lambda, T) = a_0 + a_1\lambda + ... + a_{13}\lambda^{13} + b_{1,1}T\lambda + ...b_{2,3}\lambda^2 T^3 + ... + c_4 T^4. \qquad (15)$$

The related reflectance values determined are presented in Figures 5f,g respectively 5h. For the last model, described by the Equation (15), due to extremely low values for the Pearson correlation coefficient, was not made graphical representation of reflectance. At this stage, considered expressions were investigated in a desire to investigate whether, with increasing of the polynomial interpolation model rank it improves the quality of computed results and consequently the quality refractive index assessment using KK method.

For this reason we investigated the pattern of expression (12). The results reveal the existence of a danger, known as the Runge phenomenon (Figure 5f), due to the pronounced tendency of oscillation when the representation polynomial function is high. For this reason, many papers considered spline interpolation functions, in that order polynomial on very small on each portion domain. Figure (6e) represented values for the refractive index calculated from the KK transformation basing on the expression (12). Approximation quality analyzed basing on Pearson coefficients shows that is the best from previous cases. For these reasons we continued to investigate these models – described by expressions (13–15) were included the higher order mixed terms. The aim was to investigate the possibility to avoid the Runge phenomenon along the wavelength axis. The results for these models (13) (Figure 5g) and (14) (Figure 5h) highlight the emergence of a type similar to Runge phenomenon along the temperature axis. To our surprise, the refractive index obtained values for the expression (13) and represented in (Figure 6f) was the best results. For example, could be considered the comparison for the refractive index at two different temperatures using specific polynomial approach for each temperature value (Figure 7). For model (14) the refractive index obtained values are represented in (Figure 6g) and for the model (15) the refractive index obtained values are represented in (Figure 6h) with the worst Pearson correlation coefficients.

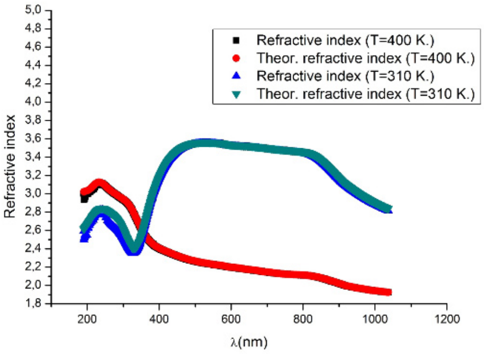

Figure 7. Comparison for refractive index magnitudes for Bi_2O_3 at $T = 310$ K and $T = 400$ K.

This determines that there is a very specific limited rank domain to provide optimum conditions for application of the polynomial method, by maintaining a low enough rank for the model parameters' polynomial and by including enough related mixed terms that provide an increase in quality results. At this point it should be noted however that increasing high rank polynomial will not automatically lead to an increase in model performance for the reflectance interpolation and then to an increase for the refractive index of the quality assessment based on interpolation relations.

5. Conclusions

In this paper, we present a reliable approach for theoretical evaluation of optical magnitudes and we introduce a discussion over the polynomial rank of fitted function.

Bismuth trioxide wasn't studied so far in a systematic forthcoming and a theoretical approach is welcomed. We consider such a technique, since this powerful mathematical relation was proved productive for de for the determination of optical proprieties and is frequently used in the extraction procedures of optical constants, mainly in the mid-IR spectral region [1–4].

This advance involves misassumptions regarding the spectrum in the spectral range beyond the measurement limits. The extrapolations have to be made with care, due by the important contributions of extrapolated covered domains. In the same time, a significant concern has to be shown for the chosen reflectance spectra interval. A good selection of the studied domain guarantees an unfailing established function.

Several investigations [1–4] have emphasized the need to extrapolate the truncated experimental spectrum to lower wave numbers in order to obtain a better estimate of n via the KK procedure. In specially books attempts are exposed to succeed in reaching good assessment of this extrapolating gathering as linear or polynomial extrapolation [1], domain splitting [2], *etc*.

The entire procedure, which is the present case study, is based on the polynomial extrapolation method.

In this way, in order to succeed in computing the refractive index – n using this technique, there should be followed the next steps [5–10]:

1. One calculates the phase function $R(\lambda)$ from the extrapolated reflectance spectra.
2. One determines the optical constants $n(\lambda)$ and respectively the absorbtion coefficient $\kappa(\lambda)$ from $R(\lambda)$ and $\phi(\lambda)$.

In this respect, the polynomial method should be applied carefully in conditions which decrease want a convergence of factors that could destroy the integral of (2). The main idea was to extend the study and to consider the analytical expression of the polynomial model by including mixed terms, in order to succeed in modeling the temperature dependence of optical properties. An increase in quality results could reveal the individual cases. Research will be developed by including combined interpolation methods using Chebyshev polynomials.

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