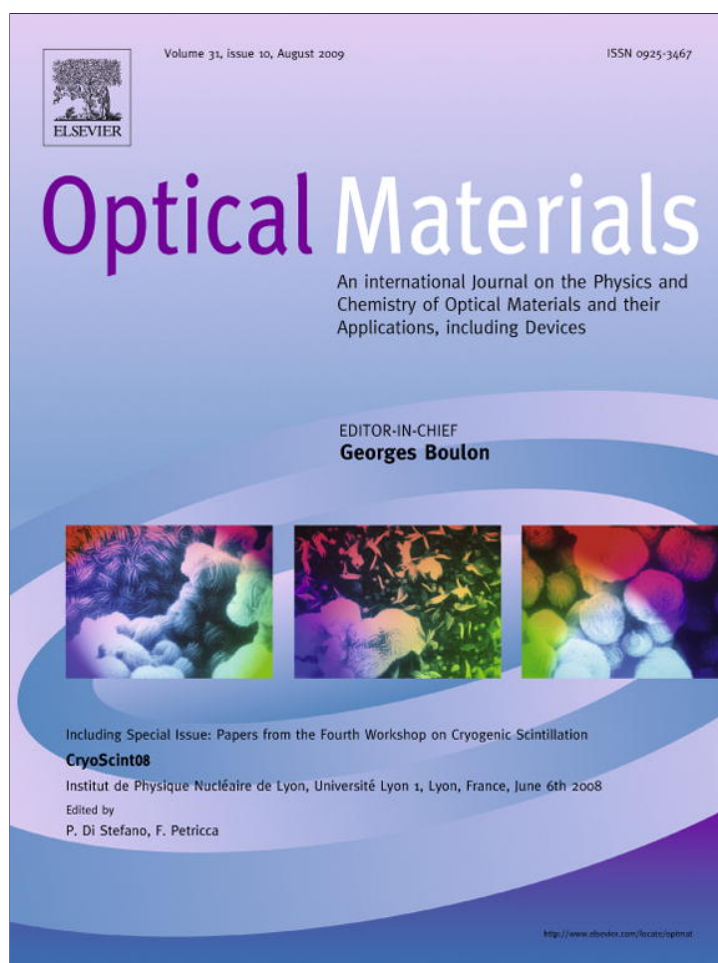




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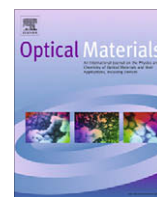
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Optical Materials

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Theoretical analysis of optical characteristics of the alpha spodumene in ultraviolet region

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ARTICLE INFO

Article history:

Received 10 February 2009

Accepted 11 February 2009

Available online 18 March 2009

PACS:

78.20.Ci

78.40.Ha

71.20.Ps

Keywords:

Spodumene

Optical axes

Dielectric tensor

Optical constants

ABSTRACT

It is presented an analysis of some important optical characteristics of the natural spodumene crystal, based on the first-principles calculations of its electronic structure and complex dielectric tensor. The optical absorption spectrum is interpreted in terms of electronic band structure for incident radiation energy up to 35 eV. The orientation of the three orthogonal principal optical axes is determined relative to the crystallographic axes, and expressed as function of the incident radiation wavelength. Reflectivity and electron energy loss are calculated along the three principal axes. All calculated optical properties are found to be highly anisotropic.

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1. Introduction

Spodumene ($\text{LiAlSi}_2\text{O}_6$) is a natural crystal of significant technological interest. It is a principal source of lithium and is widely used in glass and ceramic industry. There are three varieties (triphane, kunzite and hiddenite) of beautiful coloration that are considered as semi-precious gemstones. Their color is due to light absorption by various impurities commonly found in the material, mostly Mn, Fe and Cr. The relation between the color and position, coordination and concentration of impurities is still not fully understood. Process of irradiation can change the color, turning the spodumene an interesting material for a jewel industry. Because of these interesting properties the spodumene has been subject of many investigations of physicists and mineralogists [1–8].

Recently we reported a brief theoretical study of electronic and optical properties of the pure spodumene [9]. There we presented the spodumene electronic structure and some of its optical constants (absorption, refraction index and extinction coefficient) calculated along the three principal optical axes, for the case when the incident radiation energy ranges from 0 to 25 eV [9]. In this paper we complete this study by calculating orientation of the spodumene principal optical axes with respect

to its crystallographic axes. We also characterize the origin of the absorption peaks on the basis of the calculated electronic structure. Finally, we present the reflectivity and electron energy loss spectra of the spodumene. According to author's knowledge all experimental studies about the natural spodumene treat either impure or irradiated samples, thus the direct comparison with our results is not possible. Therefore, all the physical quantities calculated in this work should be understood as theoretical predictions.

2. Computation method, crystalline structure and the electronic bands

As a computational tool we employed the first-principles, full potential linear augmented plane wave (FP-LAPW) method [10], based on density functional theory (DFT) [11] and implemented into the WIEN2k computer code [12]. The technical details of calculations were the same as previously reported [9].

The α -spodumene adopts the monoclinic crystal structure with the space group number 15, with the two possible settings of crystallographic axes: $C2/c$ or $B2/b$. In our calculations the unit cell of the spodumene was fully optimized, i.e. the lattice parameters and all the atomic positions were relaxed in order to reach the values that correspond to energy minimum in our computer experiment. The electronic bands, presented in Fig. 1, refer to this equilibrium structure.

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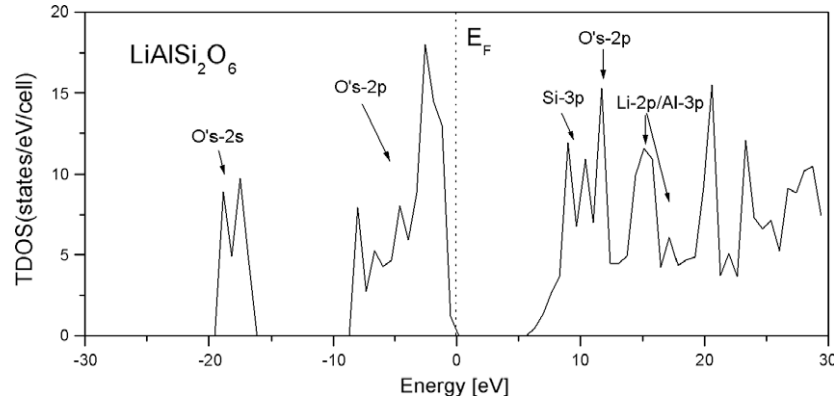


Fig. 1. Total electronic density of states (TDOS) of the pure spodumene crystal in the vicinity of the Fermi level (dashed line). The dominant orbital characters of bands are also indicated.

The valence region is consisted of two separated bands, the lower one being dominated by the 2s, and the higher one by the 2p states of the three crystallographically inequivalent oxygen atoms (O_1 , O_2 and O_3). At the bottom of the conduction band the prevalent states are the Si-3p, followed by the Li-2p and Al-3p states at higher energies. In the same energy region the oxygen's 2p states are also present in a non-negligible amount. At the energies higher than 20 eV the Si states dominate the conduction band. The fundamental gap is found to be indirect, with the calculated value of the 5.5 eV [9].

3. Determination of the principal optical axes of spodumene

Optical properties of the spodumene were determined on the basis of calculated imaginary part of dielectric tensor which describes the linear response of the electronic system to an external electromagnetic perturbation:

$$\text{Im}\varepsilon_{ij}(\omega) = \frac{4e^2}{\pi m^2 \omega^2} \sum_{v,c} \int_{\text{BZ}} d\vec{k} |\langle \phi_{c\vec{k}} | p_i | \phi_{v\vec{k}} \rangle \langle \phi_{c\vec{k}} | p_j | \phi_{v\vec{k}} \rangle| \delta(\varepsilon_c - \varepsilon_v - \hbar\omega) \quad (1)$$

The formula (1) is derived within the random-phase approximation, where the local-field and lifetime effects are neglected. It accounts for the interband electronic transitions from a filled initial state $|\phi_{v\vec{k}}\rangle$ of energy ε_v to an empty final state $|\phi_{c\vec{k}}\rangle$ of energy ε_c with the same wave vector $\vec{k}$. ω is the frequency of the incident radiation, m is the electron mass and p_i is the electronic momentum projection along the i direction of the electric field.

Knowing the eigenvectors of filled and empty states from the band-structure calculations, we computed all components of the dielectric tensor for the photon energies ranging from zero to $\hbar\omega = 35$ eV. Due to monoclinic symmetry of the spodumene the resulting tensor is not diagonal in the arbitrary Cartesian coordinate system $\{x, y, z\}$. However, it can be reduced to its diagonal form by transforming this coordinate system into another one $(\vec{n}_1, \vec{n}_2, \vec{n}_3)$, which is also orthogonal and usually called the principal axes system. This transformation is illustrated below,

$$\text{Im}\varepsilon(\omega) = \begin{bmatrix} \varepsilon_{11}(\omega) & \varepsilon_{12}(\omega) & 0 \\ \varepsilon_{21}(\omega) & \varepsilon_{22}(\omega) & 0 \\ 0 & 0 & \varepsilon_{33}(\omega) \end{bmatrix} \\ \Rightarrow \text{Im}\varepsilon'(\omega) = \begin{bmatrix} \varepsilon'_{11}(\omega) & 0 & 0 \\ 0 & \varepsilon'_{22}(\omega) & 0 \\ 0 & 0 & \varepsilon'_{33}(\omega) \end{bmatrix}$$

where $\varepsilon_{ij}(\omega)$ and $\varepsilon'_{ij}(\omega)$ stand for $\text{Im}\varepsilon_{ij}(\omega)$ and $\text{Im}\varepsilon'_{ij}(\omega)$ for the reason of shorter notation. The eigenvalues $\varepsilon'_{ij}(\omega)$ are expressed in terms of the calculated $\varepsilon_{ij}(\omega)$ components by formulas:

$$\left. \begin{aligned} \varepsilon'_{11}(\omega) &= \frac{1}{2} \left[(\varepsilon_{11} + \varepsilon_{22}) + \sqrt{(\varepsilon_{11} - \varepsilon_{22})^2 + 4\varepsilon_{12}^2} \right] \\ \varepsilon'_{22}(\omega) &= \frac{1}{2} \left[(\varepsilon_{11} + \varepsilon_{22}) - \sqrt{(\varepsilon_{11} - \varepsilon_{22})^2 + 4\varepsilon_{12}^2} \right] \\ \varepsilon'_{33}(\omega) &= \varepsilon_{33} \end{aligned} \right\} \quad (2)$$

They are directly proportional to the intensity of the optical absorption of the material along its three principal optical axes, which are determined by the eigenvectors $\vec{n}_1$, $\vec{n}_2$ and $\vec{n}_3$, respectively:

$$\left. \begin{aligned} \vec{n}_1 &= x(\omega)\vec{e}_x + \vec{e}_y \\ \vec{n}_2 &= y(\omega)\vec{e}_x + \vec{e}_y \\ \vec{n}_3 &= \vec{e}_z \end{aligned} \right\} \quad (3)$$

$\vec{e}_x$, $\vec{e}_y$ and $\vec{e}_z$ denote the orts of the x, y and z directions of the original coordinate system, and

$$x(\omega) = \frac{\varepsilon_{11} - \varepsilon_{22} - 2\varepsilon_{12} + \sqrt{(\varepsilon_{11} - \varepsilon_{22})^2 + 4(\varepsilon_{12})^2}}{\varepsilon_{11} - \varepsilon_{22} + 2\varepsilon_{12} - \sqrt{(\varepsilon_{11} - \varepsilon_{22})^2 + 4(\varepsilon_{12})^2}} \quad (4)$$

$$y(\omega) = \frac{\varepsilon_{11} - \varepsilon_{22} - 2\varepsilon_{12} - \sqrt{(\varepsilon_{11} - \varepsilon_{22})^2 + 4(\varepsilon_{12})^2}}{\varepsilon_{11} - \varepsilon_{22} + 2\varepsilon_{12} + \sqrt{(\varepsilon_{11} - \varepsilon_{22})^2 + 4(\varepsilon_{12})^2}} \quad (5)$$

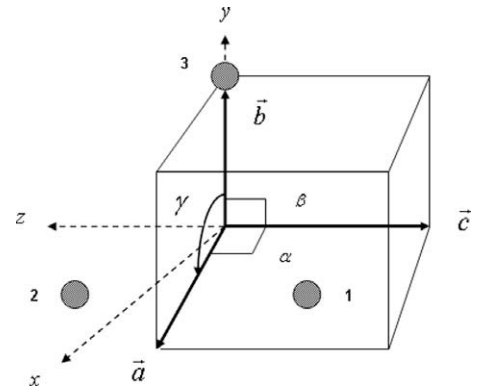


Fig. 2. Base centered monoclinic unit cell of the spodumene with the B2/b setting of the crystallographic axes. The angles α and β are the right angles, while the γ is 110.13° . The coordinate system in which the dielectric tensor is calculated is denoted as $\{x, y, z\}$ and crystallographic axes as a, b and c . The x -axis lies in the a - b plane, inclined by the angle $\gamma - 90^\circ$ with respect to the a -axis. The primitive vectors of the Bravais lattice connect the points 1, 2 and 3 of the lattice.

Our objective is to determine the principal axes directions relative to the directions of the monoclinic crystallographic axes a , b and c . The spodumene has the base centered monoclinic unit cell, and the WIEN2k program accepts the $B2/b$ settings of its axes. In this setting, the three primitive vectors of the Bravais lattice have the following coordinates: $(0, b, 0)$, $(\frac{a}{2} \sin \gamma, \frac{a}{2} \cos \gamma, -\frac{c}{2})$ and $(\frac{a}{2} \sin \gamma, \frac{a}{2} \cos \gamma, +\frac{c}{2})$, expressed in the $\{x, y, z\}$ coordinate system (Fig. 2).

From Fig. 2 one can easily establish a connection between the original coordinate system $(\vec{e}_x, \vec{e}_y, \vec{e}_z)$ and the system of crystallographic axes $(\vec{e}_a, \vec{e}_b, \vec{e}_c)$:

$$\left. \begin{aligned} \vec{e}_x &= \vec{e}_a / \sin \gamma - (ctg \gamma) \vec{e}_b \\ \vec{e}_y &= \vec{e}_b \\ \vec{e}_z &= -\vec{e}_c \end{aligned} \right\} \quad (6)$$

Combining this result with the formula (3) we determine the orientation of the principal optical axes of the spodumene in terms of its crystallographic directions:

$$\left. \begin{aligned} \vec{n}_1 &= \frac{x(\omega)}{\sin \gamma} \vec{e}_a + [1 - x(\omega) ctg \gamma] \vec{e}_b \\ \vec{n}_2 &= \frac{y(\omega)}{\sin \gamma} \vec{e}_a + [1 - y(\omega) ctg \gamma] \vec{e}_b \\ \vec{n}_3 &= -\vec{e}_c \end{aligned} \right\} \quad (7)$$

The principal axis $\vec{n}_3$ is found to be parallel to the crystallographic c -axis, while the other two principal axes ($\vec{n}_1$ and $\vec{n}_2$) lie in the plane defined by the other two crystallographic axes (a and b). It can be verified that the $\vec{n}_1$ and $\vec{n}_2$ are mutually orthogonal for any value of the frequency ω of incident radiation. Their orientation with respect to the axes a and b , however, depend on the radiation wavelength, i.e. $\vec{n}_1$ and $\vec{n}_2$ rotate around the c -axis as a function of wavelength.

Since direction of the $\vec{n}_3$ is fixed along the c -axis and the angle between the $\vec{n}_1$ and $\vec{n}_2$ is always 90° , the orientation of the principal axes is determined by just one angle, θ , between the axis a and the principal axis $\vec{n}_1$. On the basis of the formula (7) it is easy to verify that this angle depends on frequency as:

$$\cos \theta = \frac{x(\omega) \sin \gamma + \cos \gamma}{\sqrt{1 + x^2(\omega)}} \quad (8)$$

The dependency of θ with respect to the incident radiation wavelength is shown in Fig. 3. The values of the angle θ range from approximately 21° to the 180° , exhibiting very sharp changes with respect to the slight variation of the wavelength.

Fig. 4 shows the orientation of the principal axes for the specific radiation wavelength of $\lambda = 125.5$ nm, at one of which the spodu-

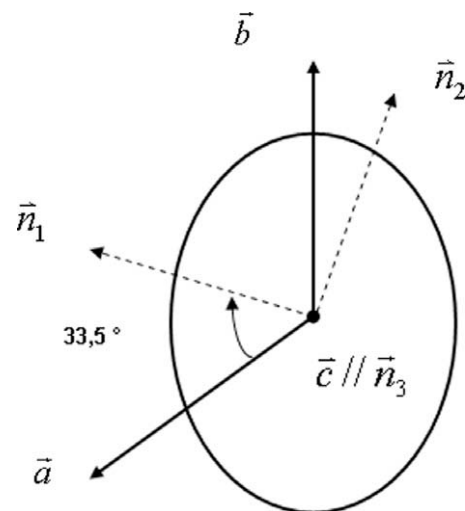


Fig. 4. Optical ellipsoid of $\text{LiAlSi}_2\text{O}_6$ for incident radiation wavelength of $\lambda = 125.5$ nm.

mene suffers a major absorption. The angle between the principal axis $\vec{n}_1$ and the crystallographic axis a in this case is 33.5° in the clockwise direction, when the positive end of the c -axis is pointing towards the observer. The formula (8), together with the data shown at Fig. 3, enables one to determine the orientation of the principal axes for arbitrary wavelength of the incident light.

4. Optical constants of the spodumene along its principal optical axes

Fig. 5 shows the optical absorption of the spodumene along its three principal optical axes. The absorption peaks are interpreted on the basis of the electronic structure presented in Fig. 1, by analyzing all possible transitions from valence to conduction band and taking the corresponding matrix elements into account (1).

In its long-wavelengths range (approximately from 100 to 200 nm) the spectrum is clearly dominated by the electronic transitions from O's-2p to the Si-3p states. The same transitions are responsible for the absorption on the other side of the spectrum, for the wavelengths from 50 to 60 nm. In the range of 60–100 nm the spectrum is determined by three types of electron transitions whose contributions are superposed: (1) O's-2p to the O's-2p states (involving electron transfer between oxygens of dif-

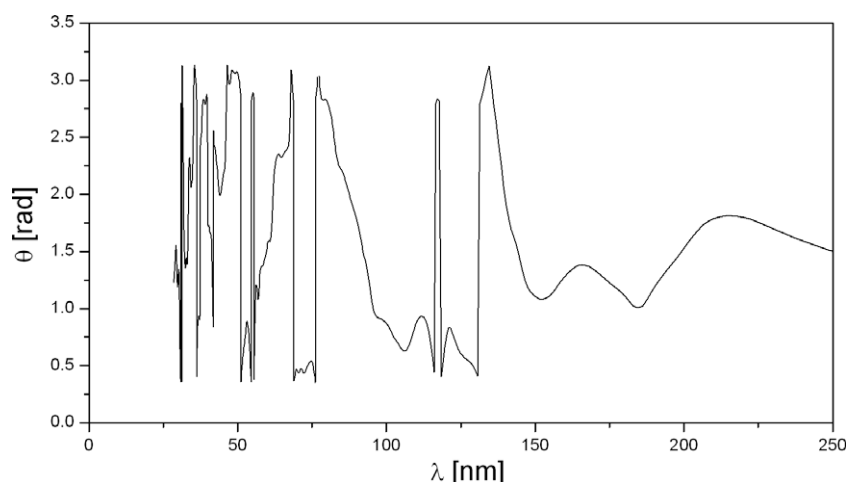


Fig. 3. The angle θ between the principal axis $\vec{n}_1$ and crystallographic axis a of the spodumene as a function of the incident light wavelength.

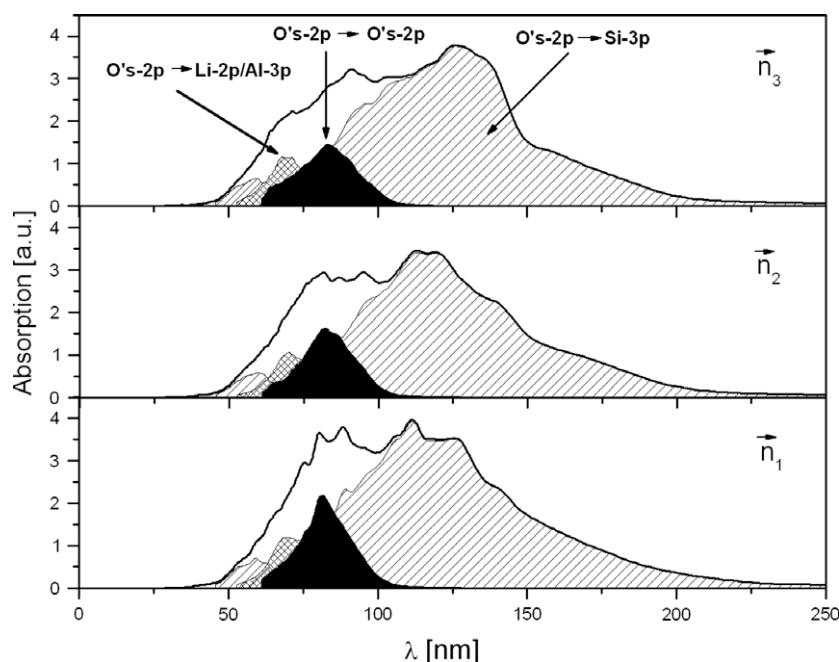


Fig. 5. Optical absorption spectrum of the spodumene (in arbitrary units) along the principal axis $\vec{n}_1$ (bottom), $\vec{n}_2$ (middle) and $\vec{n}_3$ (top). It is decomposed according to dominant electronic transitions from valence to conduction band.

ferent crystallographic types like $O_1 \rightarrow O_2$, $O_1 \rightarrow O_3$ and $O_2 \rightarrow O_3$), (2) O's-2p to the strongly hybridized Al-3p and Li-2p states and (3) O's-2p to the Si-3p states. In conclusion, the major absorption occurs due to O's-2p to the Si-3p transitions causing significant energy transfer from oxygen atoms to the silicon atoms during irradiation of the spodumene in the ultraviolet region. Fig. 5 also shows the different forms of absorption curves along the three principal axes, confirming a high optical anisotropy of the material.

The real part of the dielectric tensor is calculated on the basis of its imaginary part using Kramers–Kronig relations. It is diagonalized in the same way as the imaginary part. All the optical con-

stants are then calculated by combining the real and imaginary part of dielectric tensor [13], and refer to the principal optical axes. Fig. 6 presents the calculated real part of dielectric tensor, reflectivity and electron energy loss in α -spodumene, all as functions of the incident radiation wavelength.

The long-wavelength limit of the real part of dielectric tensor is a static dielectric constant of the material. Its extrapolated value (not shown in Fig. 6) is found to be very similar along all the three principal axes: 2.86 ($\vec{n}_1$), 2.92 ($\vec{n}_2$) and 2.90 ($\vec{n}_3$). Reflectivity spectra exhibit anisotropic behavior, being very different along the principal axes. When incident light is polarized along the $\vec{n}_3$ direction,

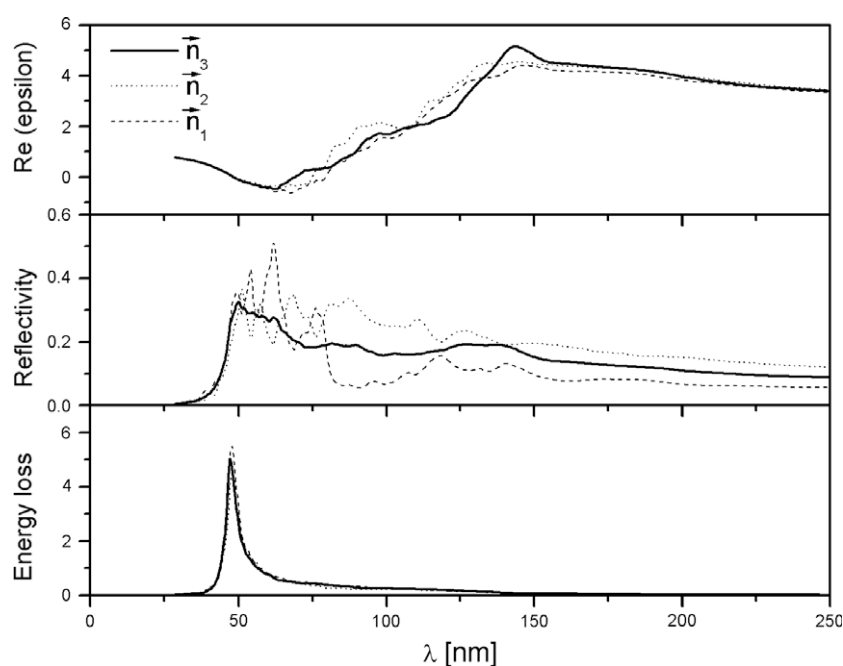


Fig. 6. Real part of dielectric tensor (top), reflectivity (middle) and electron energy loss (bottom) for α -spodumene, as calculated by the FP-LAPW method.

the spodumene reflects mostly the wavelengths from 50 to 70 nm. The same is true for the light polarized along the $\vec{n}_1$, but in this case the reflection is more intense and characterized by the three prominent peaks. Reflection of the radiation polarized along the $\vec{n}_2$ axis occurs in a broader range of wavelengths: from 50 to 120 nm with the more or less similar intensity. In the case of energy loss function it is observed a less anisotropic behavior. This function is proportional to the probability that a fast electron moving across a medium loses energy per unit length. The most prominent peak in the spectrum is identified as the energy of plasmon oscillation, signaling the collective excitations of the electronic charge density in the crystal. For the pure spodumene this energy is found to be approximately 48 nm, along any of the three principal axes (Fig. 6).

5. Conclusion

This work was focused on determination of the orientation of the principal optical axes of the pure α -spodumene, as well as on interpretation of its optical absorption spectrum. It is found that one principal axis ($\vec{n}_3$) is parallel to the crystallographic c -axis and the other two ($\vec{n}_1$ and $\vec{n}_2$) rotate around this axis in the plane defined by the crystallographic axes a and b , as functions of the incident light wavelength. We concluded that the O's-2p $\rightarrow$ Si-3p transitions are responsible for major part of the absorption, indicating an energy transfer from oxygen to silicon atoms. All the calculated optical properties are found to be highly anisotropic. It is especially true for reflectivity, which exhibits very different behavior when incident light is polarized along $\vec{n}_3$ axis in comparison with the light polarized along $\vec{n}_1$ and $\vec{n}_2$ axes. We predict that the plasmon oscillations in spodumene should be provoked by light

of the wavelength of about 48 nm, polarized along any of three principal axes. All calculations were performed by the first-principle, DFT based, FP-LAPW method.

Acknowledgement

The authors gratefully acknowledge the CNPq and FAPITEC for financial support.

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