

## Optical properties of alpha spodumene: orientation of its principal optical axes

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**Abstract.** We studied the orientation of the three orthogonal principal optical axes of the alpha spodumene crystal. This orientation is determined relative to the crystallographic axes, and expressed as function of the incident radiation wavelength in ultraviolet region. The calculations were performed by density functional theory based, full potential augmented plane wave method.

### 1. Introduction

The 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. Since considered as semi-precious gemstone, it is interesting for a jewel industry as well. Due to all these characteristics the spodumene has been subject of many investigations of physicists and mineralogists [1-5].

Recently we reported a brief theoretical study of electronic and optical properties of the pure spodumene [6]. There we discussed its electronic structure and several optical properties (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 [6]. In the present paper we continue this study by focusing our attention to the orientation of the spodumene principal optical axes with respect to its crystallographic axes. This orientation is determined for any wavelength of the incident light ranging from zero to 35 eV.

### 2. Calculations

All the calculations were performed by the first-principles, full potential linear augmented plane wave (FP-LAPW) method [7], based on density functional theory (DFT) [8] and implemented into the WIEN2k computer code [9]. The technical details of calculations were the same as reported in our recent paper [6].

The  $\alpha$ -spodumene adopts the monoclinic crystal structure with the space group number 15, with the two possible settings of the 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 minimum of energy.

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Optical response of the spodumene is determined by calculating its complex dielectric tensor  $\epsilon$ . Imaginary part of this tensor is directly proportional to the optical absorption spectrum of the material. It is computed on the basis of the calculated electronic band structure, in the limit of linear optics, neglecting electron polarization effects and within the frame of random phase approximation [6]. The  $\text{Im}(\epsilon)$  is computed for the photon energies ranging from zero to  $\hbar\omega = 35$  eV, with a mesh of 55 k-points in the irreducible wedge of the first Brillouin zone.

### 3. Orientation of the principal optical axes of the spodumene

Due to monoclinic symmetry of the spodumene the dielectric 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,

$$\text{Im } \epsilon(\omega) = \begin{bmatrix} \epsilon_{11}(\omega) & \epsilon_{12}(\omega) & 0 \\ \epsilon_{21}(\omega) & \epsilon_{22}(\omega) & 0 \\ 0 & 0 & \epsilon_{33}(\omega) \end{bmatrix} \Rightarrow \text{Im } \epsilon'(\omega) = \begin{bmatrix} \epsilon'_{11}(\omega) & 0 & 0 \\ 0 & \epsilon'_{22}(\omega) & 0 \\ 0 & 0 & \epsilon'_{33}(\omega) \end{bmatrix} \quad (1)$$

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

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

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:

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

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

Our objective is to connect the principal axes directions with 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 (figure 1).

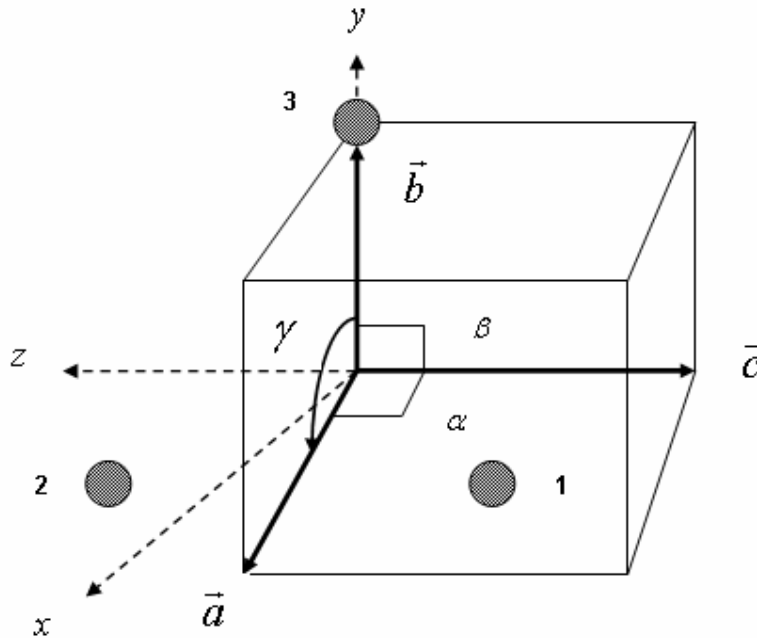


Figure 1: The monoclinic unit cell of the spodumene with the  $B2/b$  setting of its crystallographic axes. The angles  $\alpha$  and  $\beta$  are the right angles, while the  $\gamma$  is  $110,13^\circ$ . The coordinate system in which the dielectric tensor is calculated is denoted as  $\{x,y,z\}$  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.

From the figure 1 it can be easily established a connection between the original coordinate system  $(\vec{e}_x, \vec{e}_y, \vec{e}_z)$  and the system of crystallographic axes  $(\vec{e}_a, \vec{e}_b, \vec{e}_c)$ :

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

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

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

The principal axis  $\vec{n}_3$  is 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 arbitrary value of the frequency  $\omega$  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 the incident photon 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  $90^\circ$ , the orientation of the principal axes is determined by just one angle,  $\theta$ , between the axis  $a$  and the axis  $\vec{n}_1$ . Manipulating 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  $\theta$  with respect to the incident radiation wavelength is shown in the figure 2.

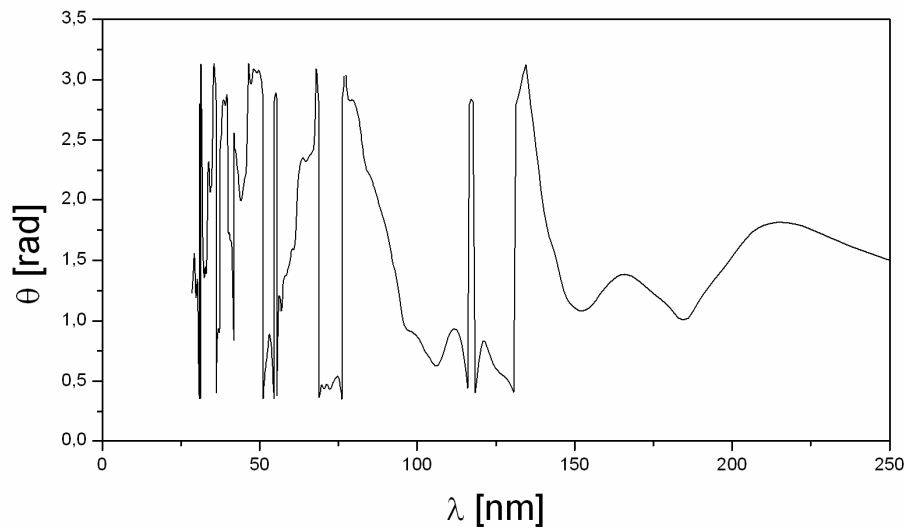


Figure 2: The angle  $\theta$  between the principal axis  $\vec{n}_1$  and crystallographic axis  $a$  of the spodumene as a function of the incident photon wavelength.

The figure 2 finally determines complete orientation of the principal optical axes of the pure spodumene, along which the optical absorption and other optical characteristics have been discussed in ref. [6]. It is seen that the values of the angle  $\theta$  range from approximately  $21^\circ$  to the  $180^\circ$  and exhibit very sharp changes with respect to the slight variation of the wavelength. The reason for such abrupt changes lies in the fact that the off-diagonal dielectric tensor component  $\epsilon_{12}(\omega)$  (1) (not shown in this paper) is very small and frequently reverses its sign as function of wavelength. Each time when the sign reversal occurs, the denominator of  $x(\omega)$  (4) becomes extremely small, also reversing its sign. Thus, the small variation of incident wavelength can cause extreme variation of  $x(\omega)$ : when  $\epsilon_{12}$  is positive, the  $x(\omega)$  is very large and positive, and when  $\epsilon_{12}$  is negative, the  $x(\omega)$  is very large and negative. The abrupt changes of  $x(\omega)$  provoke the abrupt changes on the angle  $\theta$  within the range which can be estimated on the basis of the formula (8). For  $x(\omega)$  very large and positive,  $\sqrt{1+x^2} \approx x$  and (8) simplifies at  $\cos \vartheta \approx \sin \gamma$ , which approximately determines the lower limit  $\theta \approx 21^\circ$ . On the other side, for  $x(\omega)$  very large and negative,  $\cos \vartheta \approx -\sin \gamma$  and  $\theta \approx 160^\circ$ .

#### 4. Conclusions

The present work was focused on determination of the orientation of the principal optical axes of the pure  $\alpha$ -spodumene. It is found that one principal axis ( $\vec{n}_3$ ) is parallel to the crystallographic axis  $c$  and the other two ( $\vec{n}_1$  and  $\vec{n}_2$ ) rotate around the  $c$  in the plane defined by the crystallographic axes  $a$  and  $b$ , as functions of the incident light wavelength. The orientation of these axes is precisely determined for each wavelength in the ultraviolet range (up to 35 eV). All calculations were performed by the first-principle, DFT based, FP-LAPW method.

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