American Mineralogist, Volume 93, pages 751–764, 2008

Quantitative absorbance spectroscopy with unpolarized light: Part I. Physical and mathematical development

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Abstract

A new approach to the use of spectroscopic absorbance measurements for anisotropic crystals allows results to be extracted using unpolarized light incident on random crystal orientations. The theory of light propagation in anisotropic absorbing crystals is developed from Maxwell's equations to devise an expression for the transmittance of linearly polarized light traveling in an arbitrary direction in weakly absorbing media. This theory predicts the distribution of transmittance and absorbance as a function of direction and polarization angle of incident light. It is shown how a previously deduced empirical expression, commonly used in infrared spectroscopy, is a good approximation to the full theory under a wide range of conditions. The new theory shows that principal polarized absorbances correspond to the eigenvalues of an absorbance ellipsoid. An expression is derived for the unpolarized absorbance as a function of the angles describing incident light direction, $A_{unpol}(\phi,\psi)$, and the principal polarized absorbances, A_a, A_b, A_c in an anisotropic crystal

$$A_{unpol}(\phi,\psi) = ½[A_a(\cos^2\phi\cos^2\psi + \sin^2\psi) + A_b(\cos^2\phi\sin^2\psi + \cos^2\psi) + A_c\sin^2\phi].$$

Integration of this expression over all incident angles leads to a simple relationship between total measured unpolarized absorbance and the three principal polarized absorbances. Using this theory, a procedure is proposed for estimating both total ($A_a + A_b + A_c$) and principal absorbances from spectroscopic measurements of absorbance using unpolarized light on a set of randomly oriented crystals.

Keywords: Absorption index theory, anisotropic media, unpolarized light, spectroscopy