Investigation of Dichroism by Spectrophotometric Methods

Introduction

Pleochroism (from ancient Greek πλέον «more» + χρόμα «color») is an optical phenomenon when a transparent crystal will have different colors if it is viewed from different angles (1). Sometimes the color change is limited to shade changes such as from pale pink to dark pink (2).

Crystals are divided into optically isotropic (cubic crystal system), optically anisotropic uniaxial (hexagonal, trigonal, tetragonal crystal systems) and optically anisotropic biaxial (orthorhombic, monoclinic, triclinic crystal systems).

The greatest change is limited to three colors. It may be observed in biaxial crystals and is called trichroic. A two color change may be observed in uniaxial crystals and called dichroic. Pleochroic is often the term used to cover both (2).
Dichroism can be observed in non-polarized light but in polarized light it may be more pronounced if the plane of polarization of incident light matches plane of polarization of light that propagates in the crystal—ordinary or extraordinary wave. The difference in absorbance of ray lights may be minor, but it may be significant and should be considered both when reporting optical properties and when using the crystal. This is why any uniaxial crystal should be examined for dichroism.

Experimental

Equipment
To investigate dichroism we used an Agilent Cary 5000 UV-Vis-NIR spectrophotometer equipped with a Universal Measurement Accessory (UMA). This system allows us to carry out experiments in wavelength ranges for:
- non-polarized light - 190-2800 nm
- polarized light - 250-2500 nm.

To carry out experiments using polarized light, the system is equipped with an automatic polarizer controlled by the computer.

The accuracy of the Cary 5000 instrument is high enough to provide data on dichroism even in cases when dichroism is very small and the sample seems to be transparent and colorless when viewed with the naked eye.

Samples
Samples should have 2 plane-parallel polished surfaces parallel to the optic axis. The best sample is the oriented sample—when you exactly know where crystallographic axes (axes related to the elements of symmetry) X and Y are located.

Method
Investigation of dichroism phenomenon consists of obtaining two spectra in the same region of the sample:
- in case of non-polarized light, the sample should be rotated in the sample holder by 90 degrees around the light ray;
- in case of polarized light, two spectra are measured with polarizer in the 0 degree and then the 90 degree position.

The Cary 5000 allows the measurement of transmission or absorption spectra. In addition, data obtained can be recalculated to any other demanded values.

Dichroism is characterized by the degree of dichroism (8, 10):
\[ \Delta = \frac{D_1 - D_2}{D_1 + D_2} \]  

where
\[ D_1 \] is the optical density of the light transmitted through the sample in the sample position 1; \[ D_2 \] is the in the position 2.

or
\[ \Delta = \frac{\mu_{\text{max}} - \mu_{\text{min}}}{\mu_{\text{max}} + \mu_{\text{min}}} \]  

where \( \mu_{\text{max}} \) is the maximum spectral attenuation coefficient for the experimental wavelength and \( \mu_{\text{min}} \) is the minimum spectral attenuation coefficient for that wavelength.

Spectral attenuation coefficient \( \mu(\lambda) \) with consideration of multiple reflection is determined by calculations from measurements of spectral transmission \( T(\lambda) \) using material refractive index \( n(\lambda) \):
\[ \mu(\lambda) = \frac{1}{d} \log T(\lambda), \]

where \( d \) is the specimen thickness, cm, \( T(\lambda) \) is the spectral coefficient of the internal transmission of the sample, arbitrary units.

Internal transmittance \( T(\lambda) \):
\[ T(\lambda) = \frac{1}{1 - \frac{\mu_{\text{max}}^2}{\mu_{\text{max}}^2 - \mu_{\text{min}}^2}} \left( n(\lambda)^{\mu_{\text{max}}^2} - 1 \right) - \frac{1}{1 - \frac{\mu_{\text{max}}^2}{\mu_{\text{max}}^2 - \mu_{\text{min}}^2}} \left( n(\lambda)^{\mu_{\text{min}}^2} - 1 \right), \]

where \( T(\lambda) \) is the spectral transmission measured on the spectrophotometer, \( n(\lambda) \) is the refractive index of the material.

Results
Oriented cubes of CaMoO₄ were measured with the Cary 5000 UMS instrument. The planes of the cubes were perpendicular to the optical axis (Z or axis of symmetry of 4th order) and the axis of 2nd order (X and Y). CaMoO₄ belongs to the tetragonal symmetry and is characterized by two refractive indices \( n_3 \) and \( n_4 \).

The experiment was carried out along X, Y and Z axis.

Dichroism by naked eye
Dichroism in the samples of CaMoO₄ single crystals can be observed by naked eye, as shown in Figure 1.

The cubic sample was rotated by 90 degrees relative to the axis of light passing along the direction perpendicular to the optical axis of the crystal. In one position the sample is blue, and in other is grey-orange.

The phenomenon is pronounced along axis of 2nd order (X, Y) and along axis of 4th order (Z) no change of color is observed.

Dichroism by spectrophotometer
We measured the optical transmission in the different positions of the sample in regard of incident light according to the scheme (Figure 2).
According to the formula (3) we calculated the attenuation coefficients, according to formula (2) - the degree of dichroism, and plotted their spectral dependences (left-hand and right-hand scale in Figure 3 respectively):

If you compare the 2 solid or 2 dotted lines you will see that anisotropy of attenuation is insignificant: values in the X axis coincide values in Y (Figure 3, upper). But if you compare 2 black (measurements along X axis) or two grey lines (measurements along Y axis) you will see the difference between the attenuation in two positions - attenuation changes with the rotation by 90° around the incident light ray. This difference achieves its maximum 0.3 cm$^{-1}$ at 450 nm (dot-dash curve, Figure 3, upper). This is dichroism on the spectral dependences.

Also with the rotation of the sample, the maximum of the attenuation bands shift and this result in the change of color.

Along Z-direction (parallel to the optical axis), there is no significant changes in the attenuation in two positions of the sample (Figure 3, lower).
This phenomenon also may occur in any other birefringent materials. For example, dichroism in trigonal crystals is reported by Kozlova N. S., Buzanov O. A., Zabelina E. V., Kozlova A. P., Bykova M. B. in "Point Defects and Dichroism in Langasite and Langatate Crystals" (Crystallography Reports. – 2016. - Vol. 61. - No. 2. - p. 275–284.)

Conclusions
The Cary 5000 UV-Vis-NIR spectrophotometer fitted with a Universal Measurement Accessory (UMA) provided the required measurement flexibility, and S/P polarization control determine the degree of dichroism of birefringent materials.

Measurements of %R and %T were made along crystal axes (X, Y, Z), with non-polarized light and polarized light (parallel to, and perpendicular to, the optical axis). Spectrophotometric measurements afforded by being able to automatically position the UMA detector at any point in a 340° arc around the sample.

Dichroism should be taken into account in the investigation, and interpretation, of the optical properties of birefringent materials. The Cary 5000 with UMA has proven to be a capable and convenient tool for such analysis.

References
3. Sears F.W., Zemansky M.W., Young H.D., University Physics 6th ed, Pearson,

www.agilent.com/chem

This information is subject to change without notice.