Application Note

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Investigation of Dichroism by Spectrophotometric Methods

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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*).

Pleochroism is caused by optical anisotropy of the crystals (*1-3*). The absorption of light in the optically anisotropic crystals depends on the frequency of the light wave and its polarization (direction of the electric vector in it) (*3, 4*).

Generally, any ray of light in the optical anisotropic crystal is divided into two rays with perpendicular polarizations and different velocities (v_1, v_2) which are inversely proportional to the refractive indices (n_1, n_2) (*4*).

In uniaxial crystals there is a single direction governing the optical anisotropy whereas all directions perpendicular to it (or at a given angle to it) are optically equivalent. Thus, rotating the material around this axis does not change its optical behavior. This special direction is known as the optic axis of the material (*5*). This direction is parallel to the axis of symmetry of highest order: 6 for hexagonal, 3 for trigonal, 4 for tetragonal (*6*). Light whose polarization is perpendicular to the optic axis is governed by a refractive index n_o (for "ordinary"). Light whose polarization is in the direction of the optic axis sees an optical index n_e (for "extraordinary"). For any ray direction there is a linear polarization direction perpendicular to the optic axis, and this is called an ordinary ray. However, for ray directions not parallel to the optic axis, the polarization direction perpendicular to the ordinary ray's polarization will be partly in the direction of the optic axis, and this is called an extraordinary ray. The ordinary ray will always experience a refractive index of n_o, whereas the refractive index of the extraordinary ray will be in between n_o and n_e, depending on the ray direction as described by the index ellipsoid. (*5*)

So, if the light travels through the crystal along the optical axis there would be no change of color or shade with the rotation of the sample around the direction of light.

If light travels in the direction perpendicular to the optical axis then we may observe change of color or shade with the rotation of the sample around the direction of light – this is dichroism.

The main points of the dichroism are the following (*2, 7, 8*):

- dichroism may be observed only in uniaxial crystals
- colored uniaxial crystals may not be dichroic (or dichroism may be so small that it can't be observed by naked eyes but can be detected by highly precise optical instruments)
- colorless in visual wavelength range crystals may demonstrate dichroism in UV or IR wavelength ranges

Dichroism is an evidence of the anisotropy of the absorbing centers (*7*).

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 the examined for dichroism.

Experimental

Equipment

To investigate dichroism we used an Agilent Cary 5000 UV-Vis-NIR spectrophotometer equipped with a Universal Measurement Accessary (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 (*9, 10*):

$$\Delta = \frac{D_1 - D_2}{D_1 + D_2} \qquad (1)$$

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

or

$$\Delta = \frac{\mu_{\max} - \mu_{\min}}{\mu_{\max} + \mu_{\min}} \qquad (2)$$

where μ_{max} is the maximum spectral attenuation coefficient for the experimental wavelength and μ_{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:

$$\mu(\lambda) = -\frac{1}{d}\lg \tau_i(\lambda), \qquad (3)$$

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

Internal transmittance $\tau_i(\lambda)$:

$$\tau_i(\lambda) = \sqrt{\left[\frac{1}{T(\lambda)}\cdot\frac{8n^2(\lambda)}{(n(\lambda)-1)^4}\right]^2 + \left[\frac{n(\lambda)+1}{n(\lambda)-1}\right]^4} - \frac{1}{T(\lambda)}\cdot\frac{8n^2(\lambda)}{(n(\lambda)-1)^4}, \qquad (4)$$

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

Results

Oriented cubes of $CaMoO_4$ 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).$CaMoO_4$ belongs to the tetragonal symmetry and is characterized by two refractive indices *No* and *Ne*.

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

Dichroism by naked eye

Dichroism in the samples of $CaMoO_4$ single crystals can be observed by naked eye, as shown in Figure 1.

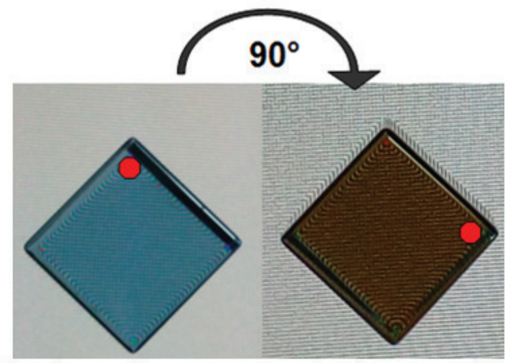

Figure 1. Image of a $CaMoO_4$ sample in two orientations; crystals x-axis parallel to optical axis (left) and (X + 90°) crystals x-axis perpendicular to the optical axis.

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).

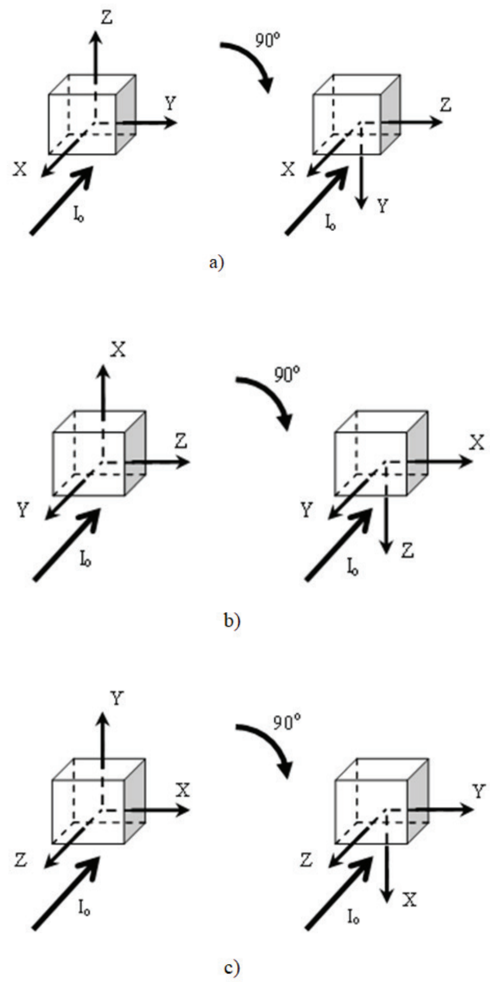

Figure. 2. The measurement scheme of $CaMoO_4$ samples: a) measurements along the X-axis and (X + 90°); b) along the Y-axis and (Y + 90°); c) along the Z-axis and (Z + 90°); (X + 90°), (Y + 90°), (Y + 90°) - sample is rotated by 90° around the X, Y and Z axes respectively

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):

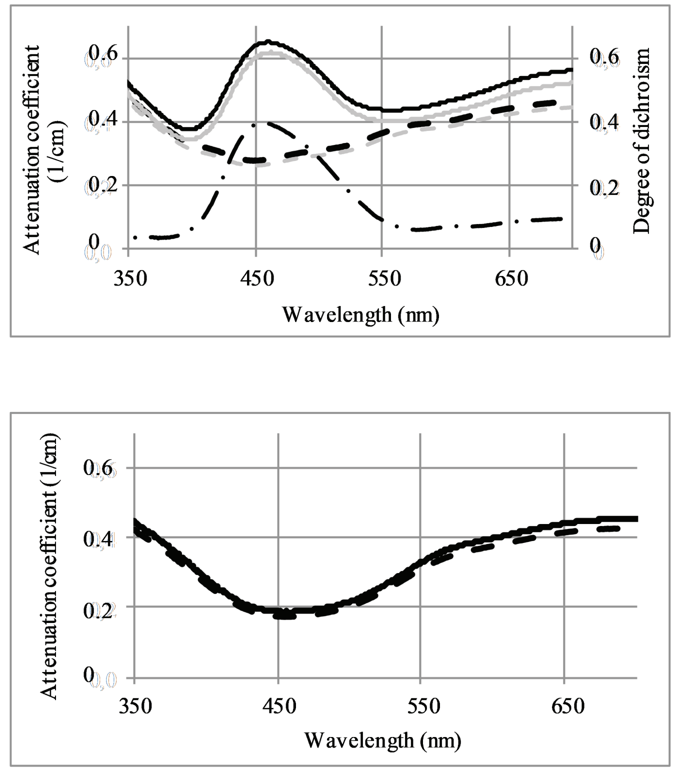

Figure 3. The spectral dependence of $\mu(\lambda)$ of $CaMoO_4$ single crystal and the degree of dichroism Δ:
Upper graph: Along X and Y axis, black and grey solid and dotes lines refer to left axis: black – crystallography X axis, grey – crystallography Y axis, solid line – initial position, dotes – sample was turned at 90° around the incident light ray; dash point curve refers to right axis;
Lower graph: Along the optical axis Z solid line – initial position, dotes – sample was turned at 90° around the incident light ray

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 perpenticular 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.

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