

Determination of Layer Thickness of Ammonium Nitrate and Potassium Nitrate Using Polarized Light Microscope

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Abstract

The Polarized Light Microscope (PLM) has been used to estimate the layer thickness of ammonium nitrate and potassium nitrate by analyzing the optical properties. The polarized images of the surface of each sample prepared by fusion method have been taken using PLM under the extinction position together with the retarder. The results show that the polarized images have various interference colors. The difference of each color depends on layer thickness. The thickness of each area that has different colors could be estimated by using the Michel Lévy chart when the birefringence of ammonium nitrate and potassium nitrate are 0.224 and 0.171, respectively. The thickness of NH_4NO_3 is between 4.018 and 6.473 μm , the thickness of KNO_3 is between 5.848 and 8.187 μm . The thickness of NH_4NO_3 obtained from considering the optical properties has the error of 4.79% from the thickness measured by the Scanning Electron Microscope (SEM).

Keywords: Polarized Light Microscope: Extinction Position: Ammonium Nitrate: Potassium Nitrate: Michel Lévy Chart

Introduction

Magnus, M. [1] studied the optical properties of unknown minerals to identify the type of the minerals. He used Polarized Light Microscope (PLM) to determine the birefringence of mineral sample by taking photos of sample when it is oriented 45° from the position of extinction (the darkest position). Then, he compared the colors of this image with the colors from the Michel Lévy Chart. The Michel Lévy Chart displays the birefringence as a function of the thickness and the optical path difference. An example of a mineral sample with a thickness of 25-30 μm gives birefringence of 0.024; and the mineral has been identified as an augite. In our research, PLM will be used to estimate the layer thickness of chemical compounds prepared by fusion method [2] when we

know their birefringence. PLM is composed of the basic components from the general microscope with 2 additional polaroids, a polarizer and an analyzer. Both polaroids are used to change unpolarized light to polarized light which gives the single vibrational direction of electric field. The polarizer is located between the light source and the sample stage while the analyzer is located between the sample stage and the objective lens. When the light passes through the polarizer, its vibrational direction of electric field is in the same direction as the axis of the polarizer, e.g. East-West (E-W). Then the polarized light passes through the sample before travelling to the analyzer which is oriented in the perpendicular direction to the polarizer, e.g. North-South (N-S). Normally, the polarized light from the polarizer could not pass the

analyzer if they are oriented in the crossed position. If some materials are placed between the polarizer and the analyzer, the polarized images of these materials will have various interference colors which are called "birefringence" materials. [3-4]

Theory

When light enters a birefringence material, it is usually split into two rays; an ordinary and an extraordinary rays. Both rays are characterized by different propagation speeds due to the difference of refractive indices, known as birefringence (B) defined by

$$B = n_e - n_o, \quad (1)$$

where n_e and n_o are the refractive indices of the extraordinary and the ordinary rays, respectively. The vibrational planes of the electric field of these two rays are perpendicular to each other. The superposition of the two rays causes the interference which can be either constructive or destructive. The colors of the sample's surface which appear under the crossed position of the polaroids are called interference colors. Normally, the light cannot pass from the polarizer to the analyzer that having the transmission axes aligned perpendicularly to each other. However, when a birefringence material is inserted to the light path between them, the light can pass through. When the sample stage is rotated, the brightness on a certain area will change. With this phenomenon, we rotate the samples stage till the polarized image of the considered area becomes dark. This position is called the "extinction position", where the optical axis of the material is parallel to the axis of either polarizer or analyzer. The sample is continuously rotated to complete 360°, the darkest position appears four times at 90°, 180°, 270° and 360° from the extinction position indicating that there is no interference light.

When a birefringence material is rotated 45° from the extinction position, the image shows the brightest interference colors. This implies that the optical axis of the material is now 45° to the axis of

polarizer and analyzer. This position is called the "diagonal position".

When the polarized light from the polarizer enters a birefringence material, it is split into two polarization components which generally are governed by different refractive indices. The so-called "slow ray" is the component for which the material has the higher refractive index, while the "fast ray" is the one with a lower refractive index. These two rays travel with different speeds causing the difference in distance, known as the "optical path difference" or "retardation".

Now we consider two birefringence materials one on top of each other (e.g. the chemical compounds and the retarder in this research). If the O-ray of the chemical compounds is parallel to the O-ray of the retarder, the total optical path difference (R) is defined as the numerical sum of the optical path differences as shown in Equation (2).

$$R = R_1 + R_2. \quad (2)$$

R_1 and R_2 denote the optical path differences of the chemical compounds and the retarder, respectively. This state is called "addition". In contrast, if the O-ray of the chemical compounds is perpendicular to the O-ray of the retarder, the optical path difference (R) will be decreased as shown in Equation (3). This state is called "subtraction".

$$R = R_1 - R_2. \quad (3)$$

Either addition or subtraction can be determined from the changes in the interference colors when the two birefringence materials are placed on top of each other. Shifting of the interference color toward the increase of retardation is addition, and vice versa for subtraction.

Materials and Methods

The standard chemical compounds used in this study are ammonium nitrate (NH_4NO_3) with molecular

weight of 80.04 g/mol and melting point of 169 °C, and potassium nitrate (KNO₃) with molecular weight of 101.11 g/mol and melting point of 334 °C.

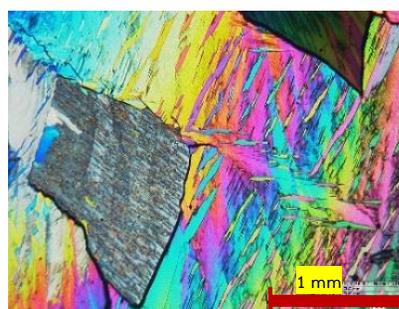
The chemical compounds of NH₄NO₃ or KNO₃ of 3.5 mg is placed on glass slide that pre-cleaned using ethyl alcohol. For fusion preparation, the glass slide is placed on a temperature-controlled hot plate with the temperature of heating set to its melting point. While chemical compound is melting, a cover glass is put on top of it and the sample is then taken out from the hot plate. Finally, the sample is allowed to cool to room temperature for few hours to ensure stabilization of the crystal structure. The polarized images were taken by a high-resolution digital PLM (model KH-7700, Hirox Co. Ltd., Japan) with the magnification of 100 times. Since the interference lights produces various colors on the images of the sample, the Berek-type variable retarder [4] and a Michel Lévy interference color chart are used in conjunction with the PLM to measure with high accuracy the path differences introduced by the sample. For the thickness measurement procedures, firstly, the interested grain is located at diagonal position or the brightest position then the PLM image of the grain is taken. Next, the retarder, priorly adjusted to a known retardation, is inserted between the sample and the analyzer. As a result, the color of the interested grain is modified. The second PLM image is taken. Then the interested grain is rotated by 90° further and the image is taken by PLM. After that, all three images of the interested grain are considered together with the Michel Lévy Chart to identify the path difference. Finally, the interested grain thickness is calculated by using

$$R = Bd, \quad (4)$$

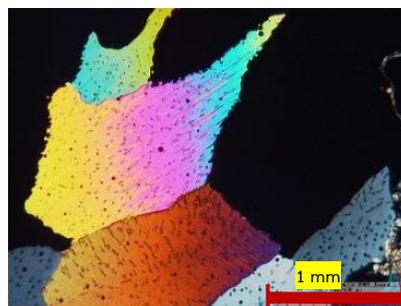
where R is the retardation or the optical path difference obtained from the Michel Lévy Chart, B is the birefringence of the sample, and d is thickness of the sample.

Results and Discussion

The interference patterns with varying colors are obvious on both recrystallized NH₄NO₃ and KNO₃ samples as shown in Figure 1. Such observation is addressed to birefringence property of the crystals at room temperature. NH₄NO₃ in Figure 1(a) has more complicated crystal phases and are more sensitive to the temperature when compared to KNO₃ in Figure 1(a). At room temperature, however, they are quite stable in orthorhombic phase in which the crystal is optically biaxial. The variety of the colors directly relates to the thickness and the crystal orientation.



(a)



(b)

Figure 1 Polarized images of a) NH₄NO₃ and b) KNO₃ film on glass slide

Continuously shifting in color similar to rainbow series is usually caused by gradient of the thickness of the sample in that area. Abrupt shift in color between adjacent areas implies the difference crystal orientation. A group of crystals showing the same color or showing slowly and continuously varying in color will be resolved as a grain. During cooling-down process, there is thermal expansion mismatch

between the sample and the glass slide. This is very serious in NH_4NO_3 as evidenced by the cracks observed in the image.

The effects of sample-stage rotation are demonstrated in Figures 2(a) – 2(d). The PLM images of a grain are taken at different angle of rotation. In Figure 2(a), the interested grain (marked in red circle) is dark as its optical axis is either parallel to the axis of the polarizer or that of the analyzer). In Figure 2(b), however, after rotating the sample clockwise by 45° , the brightness of the interested grain increases to maximum and the grain become pink. At this position, the optical axis of the crystals in this grain makes an angle of 45° to the axis of the polarizer (and the analyzer). In Figure 2(c), the grain turns dark again after rotating the sample further by 45° . Finally, in Figure 2(d), the grain becomes pink after rotating further by 45° .

We observe that turning the sample affects only the brightness but not the hue of the image. One complete turn will produce four periods of dark-to-bright variation on the image. The boundary of a grain of interest can be highlighted by rotating the sample stage when viewing the sample under PLM.

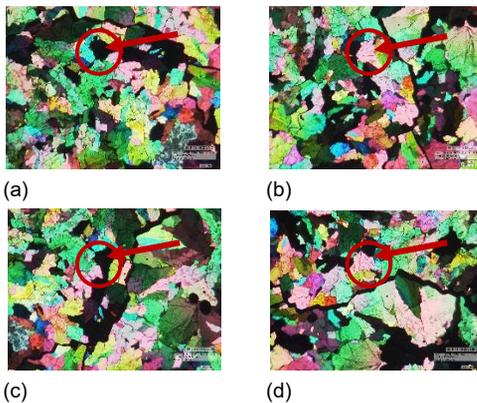


Figure 2 Polarized images of ammonium nitrate (a) extinction position, (b) rotates clockwise by 45° from extinction position, (c) rotates clockwise by 90° from extinction position and (d) rotates clockwise by 135° from extinction position.

Figure 3(a) displays a section of the PLM image where the grain of interest is locating on. The image is

taken when the sample is at the extinction position and the grain turns dark in the figure. To evaluate the thickness on the grain using the Michel Lévy chart, the sample must be oriented to the diagonal position to ensure maximum brightness as shown in Figure 3(b). The example of thickness determination will be performed on small areas appearing green (b1) and yellow (b2), on the grain in this figure.

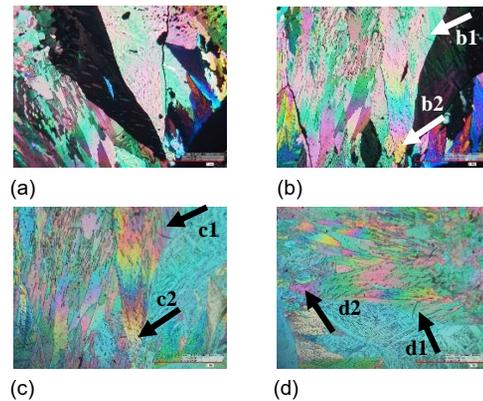


Figure 3 Using the retarder to estimate the optical path difference of NH_4NO_3 , (a) the extinction position, (b) rotating the sample clockwise by 45° from the extinction position, the image shows green (b1) and yellow (b2) colors, (c) insert retarder between the sample and the analyzer, the image shows purple (c1) and yellowish white (c2) colors, (d) rotating the sample further by 90° shows green (d1) and purple (d2) colors

When comparing the green color (b1) to the colors in the Michel Lévy Chart in Figure 4, the color can be best matched to two regions either the third order green (with the optical path difference between 1200 and 1300 nm) or the fourth order green (with the optical path difference between 1750 and 1850 nm).

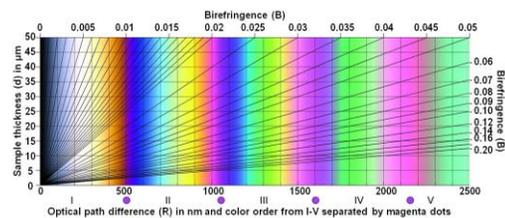


Figure 4 The Michel Lévy chart

To identify the actual one, the retarder with a path difference of 632.8 nm is inserted to the light

path in front of the sample. The green area (b1) in Figure 3(b) turns to purple color (c1) in Figure 3(c). This causes the shift of the interference color toward the decrease of the optical path difference which is the subtraction as in Equation (3). So the purple color (c1) has the optical path difference of approximately 617 nm ($1250 \text{ nm} - 632.8 \text{ nm} = 617 \text{ nm}$). Vice versa, when the sample is rotated further 90° clockwise, the grain appears in green color (d1) in Figure 3(d). This causes the shift of the interference color toward the increase of path difference known as addition as in Equation (2). Thus the green color (d1) has the optical path difference of approximately 1882.8 nm ($1250 \text{ nm} + 632.8 \text{ nm} = 1882.8 \text{ nm}$). This implies that the original interested grain with green color (b1) has the optical path difference approximately 1250 nm (the third order green). The layer thickness of the green color (b1) of NH_4NO_3 in Figure 3(b) can be calculated from Equation (4) using a path difference of 1250 nm and the birefringence of 0.224, and gives a thickness of $5.580 \mu\text{m}$.

Similarly, the yellow color (b2) in Figure 3(b) belongs to the second order yellow with the optical path difference of 900 nm, with the layer thickness of approximately $4.018 \mu\text{m}$. The layer thickness of other interference colors in the same grain in Figure 3(b) are estimated as shown in Table 1 and Figure 5.

Table 1 Examples of the interference colors, the order in the Michel Lévy Chart, the optical path difference and the layer thickness of one grain of NH_4NO_3

Colors at diagonal position (Fig.3b)	Order of Michel Levy	Optical path difference (nm)	Thickness (μm)
1 Yellow	2	900	4.018
2 Pink	2	1000	4.464
3 Green	3	1200	5.357
4 Yellow	3	1400	6.250
5 Pink	3	1450	6.473
6 Green	3	1250	5.580

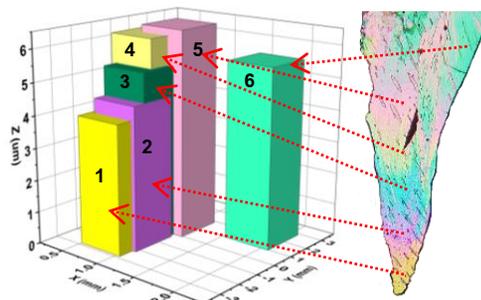


Figure 5 Distribution of the layer thickness of NH_4NO_3 in one grain

The estimation of layer thickness of KNO_3 can be done in the same way as NH_4NO_3 , but use the retarder of 500 nm wavelength to identify the optical path difference from the Michel Lévy Chart.

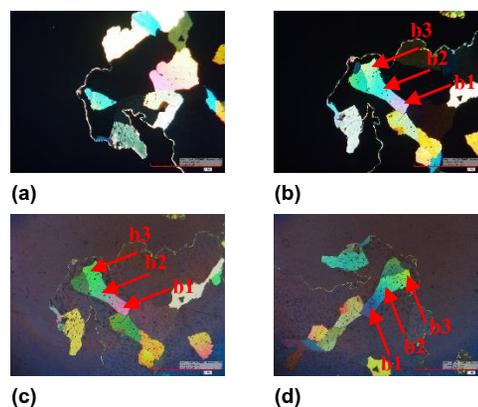


Figure 6 Using the retarder (500 nm wavelength) to estimate the optical path difference of KNO_3 , (a) the extinction position, (b) rotating the sample clockwise by 45° from the extinction position, the image shows pink (b1), blue-green (b2) and yellow (b3) colors, (c) insert retarder between the sample and the analyzer, the image shows pink (c1), purple (c2) and green (c3) colors, (d) rotating the sample further by 90° shows violet (d1), blue (d2) and yellow (d3) colors

At the extinction position, the interested grain of KNO_3 shows dark color as in Figure 6(a). At the diagonal position, the dark grain turns to maximum brightness with various interference colors as shown in Figure 6(b). These interference colors are pink (b1), blue-green (b2) and yellow (b3). Then these colors are compared with the Michel Levy's chart to identify the optical path difference and to calculate the

thickness as shown in Table 2 and Figure 7 when the birefringence of KNO_3 is 0.171.

Table 2 Examples of interference colors, the order in the Michel Lévy Chart, the optical path difference and the layer thickness of one grain of KNO_3

Colors at diagonal position (Fig.6b)	Order of Michel Levy	Optical path difference (nm)	Thickness (μm)
1 Pink	2	1000	5.848
2 Green	3	1200	7.018
3 Yellow	3	1400	8.187

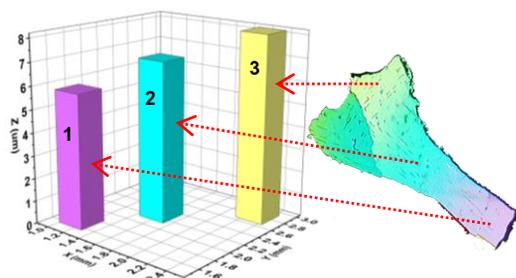


Figure 7 Distribution of the layer thickness of KNO_3 in one grain

Although, the polarized images of NH_4NO_3 and KNO_3 show the similar interference colors and the optical path difference, but the estimation of layer thickness are not the same due to the difference of their birefringences. The PLM with the retarder and the Michel Lévy Chart can be used to estimate the thickness of NH_4NO_3 and KNO_3 for thin layer samples. The thickness of NH_4NO_3 is between 4.018 and 6.473 μm . An error due to the estimation of the optical path difference from the Michel Lévy Chart is 5.53%. The thickness of KNO_3 is between 5.848 and 8.187 μm with an error of 3.57%.

To verify the thickness of the samples, the Scanning Electron Microscope (SEM) has been used. The thickness of NH_4NO_3 at b1 position (Figure 3) SEM is 5.861 μm while the thickness obtained from PLM is $5.580 \pm 0.223 \mu\text{m}$. The thickness obtained

from PLM is differed from the one measured from SEM by 4.79%.

Conclusions

The polarized images of chemical compounds prepared by fusion method have been taken using PLM. The layer thickness of the thin layer samples can be estimated by analyzing the optical properties. The results show that the polarized images of one grain with the same direction of optical axis have various interference colors that depend on the sample's thickness. For a particular grain of NH_4NO_3 , the thickness is between 4.018 and 6.473 μm , while the thickness of KNO_3 ranges from 5.848 to 8.187 μm . The thickness of a position of NH_4NO_3 obtained from PLM has error of 4.79% as compared to the thickness measured by SEM. The measurement of the layer thickness using PLM can be an alternative method which costs less than SEM. The limitations of this technique are the time taken for cooling the chemical compounds (samples) after fusion preparation and its hygroscopic property. After the sample is heated, if it is slowly cooled down then there will be air bubbles in the sample. These bubbles cause black dots on the images taken by PLM. To reduce these bubbles, we need to rapidly cool down the sample after fusion process by taking it out from the hot plate immediately after it completely melts. However, there are still some air bubbles in the sample. Moreover, due to the hygroscopic property, the samples need to be stored in desiccator.

Acknowledgments

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References

- [1] Magnus, M. (2011). Information on Polarization Microscopy, Carl Zeiss, 2-7.

- [2] Carl, Z.N. (2011). Identification of minerals in polarized light, 1-7.
- [3] McCrone, W.C. (1957). *Fusion Methods in Chemical Microscopy*. Interscience. New York and London.
- [4] Carlton, R.A. (2011). *Pharmaceutical Microscopy: Polarized Light Microscope*: Springer Science + Business Media.
- [5] Olympus. (2012). *Basics of Polarizing Microscopy*. University of California, Berkeley.
- [6] Paulding, P., et al. (1968). Identification of Crystals in Synovial Fluids from Gout and Pseudogout. *JAMA*, 203, 508-512.
- [7] Barbara, P.W. and Lori, J.W. (2008). *Practical Forensic Microscopy*. Wiley-Blackwell.