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The orthorhombic ferroelastic domains of $K_3Fe_5F_{15}$, with prototypic tetragonal W bronze (TTB) structure and mixed valence $3Fe^{2+}/2Fe^{3+}$, were studied at R. T. in polarized light on single crystals grown by high temp. soln. growth with subsequent quenching from 973 K. The birefringent ferroelastic domains exhibit a remarkable linear dichroism. The principal refractive indexes and the principal extinction coeffs. were measured along the crystallog. axes, identified by x-ray measurements on a single domain. The correlation between the refractive indexes, the extinction coeffs. and the cell parameters was established. The change of orientation of the vibration ellipse of the transmitted light due to dichroism was obsd.

**Reference**


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Polarized Light Studies of the Ferroelastic Domains of K₃Fe₅F₁₅

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Abstract The orthorhombic ferroelastic domains of K₃Fe₅F₁₅, with prototypic tetragonal tungsten bronze (TTB) structure and mixed valency 3Fe²⁺/2Fe³⁺, have been studied at R.T. in polarized light on single crystals grown by high temperature solution growth with subsequent quenching from 973K. The birefringent ferroelastic domains exhibit a remarkable linear dichroism. The principal refractive indices and the principal extinction coefficients have been measured along the crystallographic axes, identified by means of x-ray measurements on a single domain. The correlation between the refractive indices, the extinction coefficients and the cell parameters has been established. The change of orientation of the vibration ellipse of the transmitted light due to dichroism has been observed.

INTRODUCTION

In the past years there has been increasing interest in the properties of TTB fluorides as well as TTB oxides. The TTB structure is characterized by straight anion octahedra chains being aligned parallel to the fourfold axis and by a variety of tunnels between the chains: triangular, tetragonal and pentagonal tunnels, in which each octahedron shares all the corners with others.

Initially K₃Fe₅F₁₅(KFEF) was synthesized by solid state reaction. X-ray measurements on a single crystal revealed that KFEF crystallizes in the orthorhombic space group Pba2 with lattice parameters a=12.750, b=12.637 and c=3.986 Å at R.T.. Recently, it was predicted that KFEF should be both ferroelastic and ferroelectric at R.T. with a phase transition at 535K. Subsequently, it was confirmed that orthorhombic ferroelastic domains are present at R.T. and that there exists a phase transition to tetragonal symmetry at about 490K, accompanied by a dielectric anomaly, which was discussed in terms of an order-disorder type phenomenon taking place on the octahedral cation sites of Fe²⁺ and Fe³⁺.

With a view to studying the orthorhombic ferroelastic domains of KFEF we synthesized single crystals by high temperature solution growth in order to increase the dimensions of the crystals.
Not only spontaneous linear birefringence but also remarkable linear dichroism was observed under a polarized light microscope on the ferroelastic domains. By combining optical analysis with x-ray measurements we have established the correlation between the principal refractive indices and the principal extinction coefficients in the orthorhombic crystallographic system. By referring to classical theory, we also dealt with the potential influence of the pronounced dichroism of KFEF on the measurement of optical birefringence.

SAMPLE PREPARATION

KFEF single crystals have been synthesized by high temperature solution growth as follows: The melting composition (KF=38.71, FeF₂=38.71 and FeF₃=22.58 mole%) was sealed in a platinum tube after ball milling and baking at about 413K in vacuum. First, the temperature was increased up to 1073K in 9 hours and maintained at 1073K for 5 hours, followed by cooling to 973K at a rate of 1°C/hour. Finally, the tube was quenched in water from 973K.

KFEF single crystals produced in this process grew in an elongated form along the [001]_orth direction, showing very good cleavage parallel to the {001}_orth planes. The dominant growth facets were parallel to the {110}_orth planes. The maximum dimensions of a single crystal were 1.9x1.7x1.2 mm³. By x-ray measurement on a CAD-4 diffractometer the cell parameters were found to be orthorhombic with a=12.745, b=12.647 and c=3.985 Å. The transition temperature, at which the crystal symmetry would change to tetragonal, was identified to about 490K by differential scanning calorimetry (DSC).

Two kinds of platelet were prepared for optical studies; one had faces parallel to the {001}_orth planes and another one parallel to the {100}_orth and/or {010}_orth planes. Each platelet was polished carefully to a thickness of less than 40 μm using alumina powder (θ=3μm) and oil lubricant with a view to avoiding any adsorption of water traces and herewith hydrolysis of the fluoride.

OPTICAL STUDIES

Polarized light studies were performed in transmitted light on ZEISS Axioplan and LEITZ Orthoplan Pol microscopes. The domain structure was analysed on two different kinds of platelet of single crystals, both between crossed polars and without analyzer, and correlated with the crystallographic axes identified previously by x-ray measurements on a single domain.

Domain Patterns

Fig. 1 (a) shows a domain pattern observed in diagonal position between crossed polars on the {001}_orth plane, i.e. the plane perpendicular to the c axis, the traces of the
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Figure 1 Domain patterns of a single crystal of K₃Fe₅F₁₅ on the {001}₉₀° plane (d = 23 μm), (a): in diagonal position under crossed polars, (b): dichroism without analyzer.

Figure 2 Schematic representation of morphology and domain patterns of a K₃Fe₅F₁₅ single crystal.

domain walls running parallelly to the polars. By rotation of 45° from the diagonal position, all domains came to extinction simultaneously. Linear dichroism of the orthorhombic ferroelastic domains was observed with a polarizer alone, as shown in Fig. 1 (b). The domain walls are parallel to orthorhombic (110)₉₀° planes, linking 90°-ferroelastic domains. The extinction coefficient along the a axis is found to be larger than that along the b axis.

In addition to observations on (001)₉₀°, domain patterns were also studied on {100}₉₀° and/or {010}₉₀° planes, i.e. parallel to the c axis. The platelet was cut in order that the domain walls observed on the plane perpendicular to the c axis should across the faces of this platlet at an angle of 45°.
A striking contrast was formed without analyzer between the domains viewed on the \{100\}_{orth} / \{010\}_{orth} planes containing the c axis, when the polarizer was perpendicular to the c axis. However, the contrast disappeared when the polarizer was parallel to the c axis. It was also observed between crossed polars in the diagonal position. The domain patterns observed on the two platelets are schematically represented in Fig. 2.

**Refractive Indices**

The principal refractive indices were measured at 294K by means of an oil-immersion technique, commonly called the "Becke method"\(^8\), using certified refractive index liquids (Cargille oil, Series:RF). Monochromatic light (\(\lambda = 589\)nm) was used as light source. For measuring the Becke line, a crystal was mounted on a spindle stage and immersed in an oil chamber. After changing the oils, we observed the behaviour of the Becke line under a polarized light microscope without analyzer and measured the principal refractive indices along the direction parallel to the polarizer in asymptotic manners, by selecting two oils, one with a refractive index a little larger and another one with an index a little smaller than that of the crystal. The values of the certified refractive index were corrected for the deviation from the standard temperature, 25°C, according to the factor attached to each of them.

The principal refractive indices are indicated in Table 1, together with the lattice parameters and the principal extinction coefficients, where the conventional notation of biaxial crystals was used as \(n_\alpha < n_\beta < n_\gamma\). The optic axial angle, \(2V_x\)\(^9\), was calculated to be 62° by using the measured principal refractive indices. Thus, it was revealed that the indicatrix of KFEF is biaxially negative at \(\lambda = 589\)nm.

**Extinction Coefficients**

The principal extinction coefficients were measured on a twinned platelet containing the a, b and c axes in the plane at R.T. A microscope equipped with a microphotometer served for measuring the extinction coefficients in monochromatic radiation of \(\lambda = 551\) and 643nm. No analyzer was used. The measurement of the light intensity was performed on a spot of about 30 \(\mu\)m in diameter on a single domain. The platelet had a thickness of 10 \(\mu\)m.

If we neglect the influence of reflection on the crystal surface, the extinction coefficient, \(k, ^a\) along the direction parallel to the polarizer is given by

\[
k = \frac{\lambda}{4\pi d} \cdot \ln \left( \frac{I}{I_0} \right),
\]

where \(\lambda\) is the wavelength of the light and \(d\) is the thickness of the crystal; \(I\) and \(I_0\) are the intensities of the transmitted light with and without the crystal.

\(^a\): The extinction coefficient is defined as the imaginary part of the complex refractive index as follows:

\[n^* = n - ik.\]
Measuring the optical density, \( \log(I_0/I) \), along the a, b and c axes, we obtained the principal extinction coefficients (Table 1). The measured values of the principal extinction coefficients were remarkably large and very anisotropic, in particular at \( \lambda = 551 \text{nm} \).

Thus, it was revealed that \( k_b < k_a < k_c \), corresponding to the sequence of the principal refractive indices in the following way: \( n_{\alpha} (//b) < n_{\beta} (//a) < n_{\gamma} (//c) \).

Figure 3 shows the correlation between the principal refractive indices and the principal extinction coefficients in the orthorhombic crystallographic system, indicating the anisotropic optical feature of KFEF schematically.

Table 1 Lattice parameters, principal refractive indices and principal extinction coefficients of \( K_3\text{Fe}_5\text{F}_{15} \)

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Refractive Indices</th>
<th>Extinction Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T = 298 \text{K} )</td>
<td>( \lambda = 589 \text{nm}, T = 294 \text{K} )</td>
<td>( \lambda = 634 \text{nm}, \lambda = 551 \text{nm} )</td>
</tr>
<tr>
<td>( a = 12.745 \text{Å} )</td>
<td>( n_{\beta} = 1.502 )</td>
<td>( k_a = 8.9 \times 10^{-3}, k_a = 23 \times 10^{-3} )</td>
</tr>
<tr>
<td>( b = 12.647 \text{Å} )</td>
<td>( n_{\alpha} = 1.494 )</td>
<td>( k_b = 6.2 \times 10^{-3}, k_b = 16 \times 10^{-3} )</td>
</tr>
<tr>
<td>( c = 3.985 \text{Å} )</td>
<td>( n_{\gamma} = 1.505 )</td>
<td>( k_c = 10 \times 10^{-3}, k_c = 31 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Figure 3 Schematic representation of the correlation between refractive indices and extinction coefficients in the orthorhombic crystallographic system of \( K_3\text{Fe}_5\text{F}_{15} \). As for the extinction coefficients, the larger crosses represent those at \( \lambda = 551 \text{nm} \) and the smaller ones those at \( \lambda = 643 \text{nm} \).

**DISCUSSION**

In a conventional optical measurement under a polarized light microscope, a compensator is used between crossed polars in order to identify the domain orientation by compensating the phase difference between ordinary and extraordinary ray. Since the extinction coefficient is usually negligible in many crystals, this technique is applicable to the analysis of domain structures without respect to absorption. According to classical theory, however, the effect of reflectivity and absorption should be taken into account in general. As for KFEF, the extinction coefficients, compared with the refractive indices are not negligible at all as shown in Table 1. In fact, we have
observed a rotation of the vibration ellipse. In an extreme case we were unable to observe any phase difference on a comparatively thick platelet in spite of the crystal exhibiting birefringence, because the crystal itself had become a linear polarizer owing to remarkable anisotropic absorption. We calculated the biextinction, $\Delta k_{a,b}$, by measuring the angular difference of analyzer position between normal and real extinction positions,$^7$ on a platelet perpendicular to the c axis and of 20$\mu$m thickness. Comparing $\Delta k_{a,b}$ with the difference of the principal extinction coefficients, $k_a - k_b$, which we measured, we found good consistency between two values of biextinction.

CONCLUSIONS

(1) K$_3$Fe$_5$F$_{15}$ single crystals, large enough to be used for optical, electric, magnetic, and other measurements, were synthesized by high temperature solution growth followed by subsequent quenching.

(2) There occur two domain states and two mutually perpendicular domain walls in single crystals of K$_3$Fe$_5$F$_{15}$, as is expected according to Aizu.$^{10}$

(3) The orthorhombic ferroelastic domains exhibit not only spontaneous linear birefringence but also remarkable linear dichroism. The indicatrix of K$_3$Fe$_5$F$_{15}$ is biaxially negative at R.T., corresponding to the extinction coefficients as follows;

$$n_\alpha (//b) < n_\beta (//a) < n_\gamma (//c) \quad \text{and} \quad k_b < k_a < k_c.$$

(4) The change of state and orientation of the vibration ellipse of the transmitted light due to biextinction, has been observed.

ACKNOWLEDGEMENTS

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