

ANOMALOUS BIREFRINGENCE-BASED DIAGNOSTICS OF DIAMOND ORIGIN

Anomalous birefringence is peculiar to almost all diamonds (both natural and synthetic) and serves as an indirect diagnostic feature.

Anomalous birefringence in natural and synthetic diamonds

- Those diamonds showing strong anomalous birefringence (manifested as intense interference coloring) are, as a rule, natural, while weak anomalous birefringence is typical of synthetics.
- Patterns arising due to anomalous birefringence may serve as another diagnostic feature. In natural diamonds, these patterns consist of thin dashes intersecting with one another (in some directions, anomalous birefringence is manifested as mosaic interference coloring). A black cross pattern is typical of synthetics.

Recommended procedure for studying anomalous birefringence:

- Carefully clean the sample under study before starting the tests.
- Test the sample in accordance with the recommended procedure for working with a [polariscope](#).
- Analyze the observed features using the description of anomalous birefringence in natural and synthetic diamonds.

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Abstract

Optical anomalies (deviations of the symmetry of optical properties from the ideal symmetry of the crystal) occur in many minerals and synthetic compounds and have been under investigation since the last century. An important feature of optically anomalous mixed crystals is a high degree of optical inhomogeneity, whereas the optical patterns of mixed crystals without anomalies are usually rather uniform. This work is devoted to the study of this phenomenon. As a model object we have chosen mixed alum crystals, which were known for their anomalous birefringence and which revealed the following types of optical inhomogeneities: (1) sector zoning; (2) concentric zoning; (3) subsector zoning; (4) stripes normal to growth front.

The inhomogeneity of anomalous birefringence of mixed crystals of alums can be explained by superposition of several effects: mismatch strain, strain along dislocations and growth ordering of isomorphous components. Optical inhomogeneities due to the sector zoning of crystals and their dislocation structure arise even under stationary growth conditions and stationary micromorphology of the growing face. Both variable growth conditions and the relief of the growing face strongly intensify the optical inhomogeneity due to three interrelated factors: (1) a significantly inhomogeneous mismatch strain; (2) a variable degree of ordering of isomorphous components due to the compositional inhomogeneities; (3) different degrees of ordering of isomorphous atoms caused by different orientations, heights and velocities of growth steps. These effects lead to the formation of subsector zoning and zoning superimposed on the optical sector zoning. These optical structures are crossed by birefringent stripes arising from dislocations.

Key words Optical anomalies Alum Dissymmetrization Mismatch strain

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A. G. Shtukenberg · Yu. O. Punin
E. Haegele · H. Klapper

On the origin of inhomogeneity of anomalous birefringence in mixed crystals: an example of alums

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Key words Optical anomalies · Alum · Dissymmetrization · Mismatch strain

Introduction

Optical anomalies occur in many minerals and synthetic compounds. This phenomenon is well known and has been under investigation since the last century (e.g. Brauns 1891). Under optical anomaly we understand the deviation in the symmetry of optical properties from the ideal symmetry of the crystal. Several sources of optical anomalies are known so far (Shtukenberg and Punin 1996). For mixed crystals, two of them are the most important:

1. Ordering of mixing atoms during crystal growth.
2. Optical inhomogeneities due to the piezooptic effect (stress birefringence).

Both effects result in a local degradation of crystal symmetry. Optical inhomogeneities by stress birefringence associated with crystal defects (e.g. dislocations) are common also in pure (i.e. non-mixed) crystals.

The ordering of structural units (atoms, ions, radicals, molecules) during growth is typical for mixed crystals. The main idea of the origin of this phenomenon was suggested by Shubnikov (1975); it was first applied by Tsinober and coworkers to quartz crystals (Tsinober and Samoilovich 1975), some years later by Bulka to $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (Bulka et al. 1980), and independently by Akizuki to adularia (Akizuki and Sunugawa 1978) and to many other minerals (e.g. to garnets: Akizuki 1984). The various aspects of the phenomenon were discussed by Tsinober et al. (1977), Bulka et al. (1980) and also recently by the present authors (Shtukenberg and Punin 1996; Shtukenberg et al. 1994, 1998, 2000).

A. G. Shtukenberg (✉) · Yu. O. Punin
Department of Crystallography,
St. Petersburg State University, Universitetskaya nab. 7/9,
199034 St. Petersburg, Russian Federation
e-mail: sasha@as3607.spb.edu

E. Haegele · H. Klapper
Mineralogisch-Petrologisches Institut, University of Bonn,
Poppelsdorfer Schloß 53115 Bonn, Germany

The essence of growth ordering is as follows. The positions of structural units, which are strictly equivalent in the bulk of a crystal, are geometrically and energetically non-equivalent in the surface of a growing crystal. This gives rise to an ordered distribution of isomorphous atoms. The ordered state arising at the surface is then buried in the bulk of the crystal in the course of its growth. The state is metastable but it can be preserved in a crystal for a long time due to the very low diffusion rates in solids. Thus, the symmetry of a crystal is reduced, leading to optical anomalies. Traditionally, this origin of optical anomalies is called growth dissymmetrization of crystals.

Mixed crystals of the continuous series of solid solutions of alums have been well known for their optical anomalies since the last century (Brauns 1891). They present convenient model objects for studying these phenomena. The crystals can be easily grown from aqueous solution under controlled conditions. Our earlier studies have shown that growth dissymmetrization and mismatch strain contribute considerably to optical anomalies (Shtukenberg et al. 1994, 1998, 2000). Birefringence caused by growth dislocations is also known (Van Enkevort 1982). Thus, all kinds of optical anomalies occurring in mixed crystals may be found in alum crystals.

The anomalous birefringence in mixed crystal is, as a rule, highly inhomogeneous. Specifically, in mixed alum crystals the following types of optical inhomogeneities are distinguished:

1. Sectoral zoning (regions grown on different habit faces).
2. Concentric zoning parallel to the growth face (striations).
3. Subsectoral zoning (regions grown on different vicinal faces within one growth sector).
4. Stripes normal to growth front.

A study of these optical peculiarities is the aim of the present paper.

Experimental

α -Alums $A^+M^{3+}(SO_4)_2 \cdot 12H_2O$ ($A^+ = K, NH_4, Rb, \dots$, $M^{3+} = Al, Fe, Cr, Ga, \dots$) form a continuous series of solid solutions with isomorphic replacements in both cation positions, A^+ and M^{3+} . They belong to the cubic system (space group $P\bar{2}1$) and should be optically isotropic. In most cases the end members of the series are isotropic, but the mixed crystals display pronounced anomalous birefringence (Brauns 1891).

The crystals were grown from aqueous solutions in the temperature range of 25–60 °C and at supersaturations $\Delta C/C = 0-0.5$ by temperature lowering. The series of $(K, NH_4)Al(SO_4)_2 \cdot 12H_2O$, $K(Al, Cr)(SO_4)_2 \cdot 12H_2O$ and, to a less extent, of $(K, Rb)Al(SO_4)_2 \cdot 12H_2O$ and $NH_4(Al, Fe)(SO_4)_2 \cdot 12H_2O$, were studied.

The following techniques of growth on seed crystals were applied:

- Growth on the bottom of a small vessel (300–500 ml) under free convection (i.e. without stirring). The final size of these crystals was 1–3 cm in diameter.

- Growth in large vessels (5 l) on a horizontal platform under strong stirring with reversal of rotation. The rotation rate was 40–60 rpm in each direction during 1 min with a stop of 3–5 s. The final size of crystals was 2–10 cm in diameter.
- Growth in medium-sized vessel (2.5 l) on a vertical platform under strong stirring (rotation rate 30 rpm). The crystal was fixed either to the platform or to the bottom of the vessel, with the platform working as a stirrer. The final size of the crystals was 2–5 cm in diameter.

The crystals exhibited the following forms: dominant octahedron $\{111\}$, small rhombo-dodecahedron $\{110\}$ and cube $\{100\}$.

The crystals were cut parallel to $\{110\}$ or $\{111\}$ planes, and the plates were studied with a polarization microscope. The values of birefringence were measured using a Berek compensator with an accuracy of 3–15%, depending on the magnitude of the birefringence and the thickness of the sample.

X-ray diffraction topographs were recorded on the X-ray film D4 (Agfa Gevaert) by means of the Lang technique (Mo-K α radiation) applying reflections 220, 004, 111 and 333.

The compositions of the crystals of the isomorphous series $(K, NH_4)Al(SO_4)_2 \cdot 12H_2O$ were determined by means of flame photometry, and those of the series $(Al, Cr)(SO_4)_2 \cdot 12H_2O$ by colorimetry. Lattice constants were evaluated from the reflections angles 2θ measured from growth faces using a conventional powder diffractometer DRON-2.0 with Co-K α radiation.

Results

The results of all growth experiments and evaluations are collected in Table 1.

Observed optical effects

Optical sectoral zoning

This is always observed in the mixed crystals of alums (Table 1; Fig. 1a, b). The optical index ellipsoids of symmetrically equivalent growth sectors have the same shape, but different orientations, corresponding to the symmetry relations between these sectors. Such crystals appear in polarized light as twin intergrowths. The growth sectors of different growth faces exhibit ellipsoids, which, in general, differ in shape and orientation.

The growth sectors of octahedron $\{111\}$ faces (which have the largest volume in alum crystals) exhibit the highest birefringence Δn , i.e. $\Delta n_{\{111\}} \gg \Delta n_{\{110\}} \geq \Delta n_{\{100\}}$. Its index ellipsoid is a biaxial, nearly uniaxial ellipsoid with the approximate rotation axis normal to the growth front (Fig. 1a, b). This axis is n_x (optical sign $-$) if the replacement takes place in the A^+ position, and it is n_z (optical sign $+$) if in the M^{3+} position. The maximum observed birefringence reaches 1×10^{-4} . The birefringences as well as the optical signs are additive when replacement occurs simultaneously in both positions.

Growth sectors of rhomb-dodecahedron $\{110\}$ show small birefringences: $\Delta n < 2 \times 10^{-5}$ (usually 5×10^{-6}). The orientation of the indicatrix is not so strictly related to the orientation of the growth front as it is in the $\{111\}$ growth sectors. In the $\{110\}$ cuts, n'_x ($K \leftrightarrow NH_4$ and $K \leftrightarrow Rb$ substitutions) or n'_z ($Al \leftrightarrow Cr$