

OPTICAL ANISOTROPY OF CUPRITE CAUSED BY POLISHING

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ABSTRACT

It has long been well known that polished sections of cuprite, Cu_2O , space group $Pn\bar{3}m$, show strong anomalous anisotropy under the microscope. Optical investigations on bulk samples, as well as on oriented single crystals, confirm that all diamond-polished sections except (111) and (100) are anisotropic. Electron channeling patterns obtained on a scanning electron microscope reveal that these mechanically polished surfaces of cuprite are always extremely deformed. Consequently, an alternative chemomechanical polishing procedure with alkaline silica solutions was applied, and resulted in isotropic sections without exception. These samples then showed an undeformed surface-layer in the electron channeling image. Thus, the optical behavior of cuprite corresponds to that expected of a cubic crystal-structure.

Keywords: cuprite, optical anisotropy, polishing methods, surface analysis, SEM methods, electron channeling pattern (ECP) images.

SOMMAIRE

Il est clair depuis longtemps que les sections polies de cuprite, Cu_2O , groupe spatial $Pn\bar{3}m$, observées au microscope montrent les effets d'une forte anisotropie. Les études optiques faites sur échantillons massifs, aussi bien que sur cristaux uniques orientés, confirment que toutes les sections préparées avec pâte de diamant sauf (111) et (100) sont anisotropes. Une étude effectuée par microscopie électronique à balayage avec canalisation des électrons révèle que les surfaces de cuprite polies mécaniquement sont inmanquablement fortement déformées. C'est ce qui a motivé le développement d'une méthode alternative de préparer les sections. Il s'agit d'un protocole de polissage avec solutions siliceuses alcalines. Les sections qui en résultent contiennent la cuprite à l'état isotrope sans exception. La couche de surface dans ces cas est sans déformation, selon l'image obtenue par canalisation des électrons. C'est donc dire que le comportement optique de la cuprite correspond tout à fait à sa structure cristalline cubique.

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Mots-clés: cuprite, anisotropie optique, méthodes de polissage, analyse de surface, microscopie électronique à balayage, canalisation des électrons.

INTRODUCTION

The anomalous optical anisotropy noted in polished sections of cuprite has been described by many authors since the early days of ore microscopy. Schneiderhöhn & Ramdohr (1931) and Ramdohr (1975) stated that all investigated samples of cuprite are considerably anisotropic, that the colors of anisotropy are ink-blue to olive-green, and that the effect could be better observed in air than in oil owing to the intense internal reflections in oil immersion. Uytendogaardt & Burke (1971) claimed that cuprite always shows strong anomalous anisotropy and that the colors of anisotropy are grey-blue to olive-green. Picot & Johan (1982) wrote that in spite of its cubic symmetry, the mineral is distinctly polarized and that the anisotropy shows green to blue tints. Even recent

papers on ore microscopy comment that anomalous anisotropy in cuprite is common (Peckett 1992), and that it can be used as a diagnostic feature, even though the effect is unusual, as the mineral is cubic (Ineson 1989).

Klemm (1962) investigated several cubic but optically anisotropic ore-minerals. He found all samples of cuprite to be distinctly anisotropic. He suggested that cuprite might in fact depart from cubic symmetry. Criddle & Stanley (1986) published a set of reflectance data for cuprite (with minimum and maximum values), which showed a bireflectance of up to 2%. The strongly anomalous anisotropy was mentioned as well.

The cubic structure of cuprite ($Pn\bar{3}m$) was determined by Bragg & Bragg (1915). Even if some hemihedrally shaped crystals suggested a lower cubic

symmetry, physical experiments (etch figures, lack of optical activity) confirmed the holohedral structure (Bragg & Bragg 1915). A recent refinement of cuprite, which also confirmed space group $Pn\bar{3}m$, was given by Restori & Schwarzenbach (1986).

The present work was initiated by the extremely contradictory results of optical and structural investigations of cuprite. Moreover, since the author investigated a similar problem on pyrite recently (Libowitzky 1994a), a polishing effect was suspected as the cause of the anomalous optical anisotropy of cuprite.

EXPERIMENTAL

A synthetic polycrystalline sample of cuprite provided by Giester (1992), a polycrystalline bulk sample of cuprite from Siberia, as well as oriented single crystals of cuprite from Cornwall (octahedra), Siberia (octahedra) and Banat, Romania (cubes), were embedded in cold epoxy resin. They were carefully ground on abrasive paper, mesh 1000, until a smooth, scratch-free surface was obtained. Two methods of polishing were applied.

In the standard procedure (simply called the "standard polish"), the ground samples were polished with 9, 6, 3, and 1 μm diamond pastes on a nylon polishing cloth using polishing oil as a lubricant. The final step in polishing was performed with 0.25 μm diamond paste on Microcloth[®] (Buehler Ltd.). Samples were held by hand pressing them gently against the rotating disk of a polishing machine. Every step of the procedure was applied until scratches and other visible deformations on the surface had been removed (usually 5 to 15 minutes). At present, this "standard polish" procedure is the accredited method to prepare sections for optical microscopy (Laflamme 1990). It is also known to be the safest method to achieve mirror-like surfaces on nearly any material (Fynn & Powell 1988). Nevertheless, as the present investigation and the papers of Libowitzky (1994a, b) show, surface deformations cannot be avoided if mechanical methods of polishing only are used.

The successful procedure of polishing by which the structure of the surface was not deformed, because deformed surface-layers were removed, was as follows: The Microcloth[®] lined bowl of a small polishing machine (Buehler Ltd.) was filled up to about 5 mm with an alkaline silica solution (Mastermet[®], Buehler Ltd.). The previously "standard polished" samples were polished in this bowl, with minimum pressure applied for at least 60 minutes. Finally, they were flushed thoroughly with sufficient water to avoid crystallization of the very concentrated, alkaline polishing agent. This technique (which will be simply called the "Mastermet" finish) combines chemical and soft mechanical abrasion. It was recommended by Lloyd (1987) for SEM applications and by Fynn & Powell

(1988) for preparation of sections of sensitive semi-conductors.

In addition, two thin sections of cuprite from Siberia were prepared to check for anisotropy in transmitted light. Optical investigations were performed on a Reichert ore microscope equipped with a halogen lamp and several objectives. As the anisotropy of cuprite is very strong, no special settings of the microscope were necessary. The polarizers were slightly uncrossed, and the blue daylight filter was removed, to intensify the optical effects for a test of the isotropy of the (111) and (100) sections as well as of the "Mastermet" finished samples.

Electron channeling pattern (ECP) images were recorded on a JEOL JSM-6400 scanning electron microscope (SEM) at 30 kV and 8 mm distance from the objective lens. Since cuprite is a semiconductor, samples were not carbon-coated but only enclosed with a carbon suspension for electrical connection to the sample holder. All ECP images were recorded with a semiconductor detector of back-scattered electrons. The rocking angle of the beam was about $\pm 20^\circ$, the analyzed area was about 0.2 mm diameter. The ECP gives a picture of the crystallographic contrast of the uppermost surface-layer. The depth of penetration (and information) depends on the atomic number of the material investigated; in cuprite, it amounts to about 40 nm. A description of the ECP technique is given by Reimer & Pfefferkorn (1977) and by Lloyd (1987).

A chemical analysis by means of a LINK energy-dispersion X-ray analyzer connected to the SEM showed that the samples of cuprite contain no foreign elements above detection limits (0.1 wt.%).

RESULTS

Since optical anisotropy has been described as a general feature of polished sections of cuprite (see above), only two diamond-polished bulk samples (from Siberia and the synthetic one) were examined under the microscope. In almost all grains, the distinct to strong anisotropy, with blue to green colors, was verified, even where the anisotropy effects interfered with intense but variable internal reflections. A very weak bireflectance could be observed at the contact of some grains with obviously different orientations. This effect has been quantified with a set of reflectance values by Criddle & Stanley (1986). The sample from Siberia also showed numerous tiny inclusions of native copper, which appeared scratched and rough, though the samples had been polished with 0.25 μm diamond.

The diamond-polished (111) and (100) sections of the oriented single crystals proved to be isotropic without exception. On rotating the stage, even with slightly uncrossed polarizers and daylight filter removed, no variation in the color and brightness of

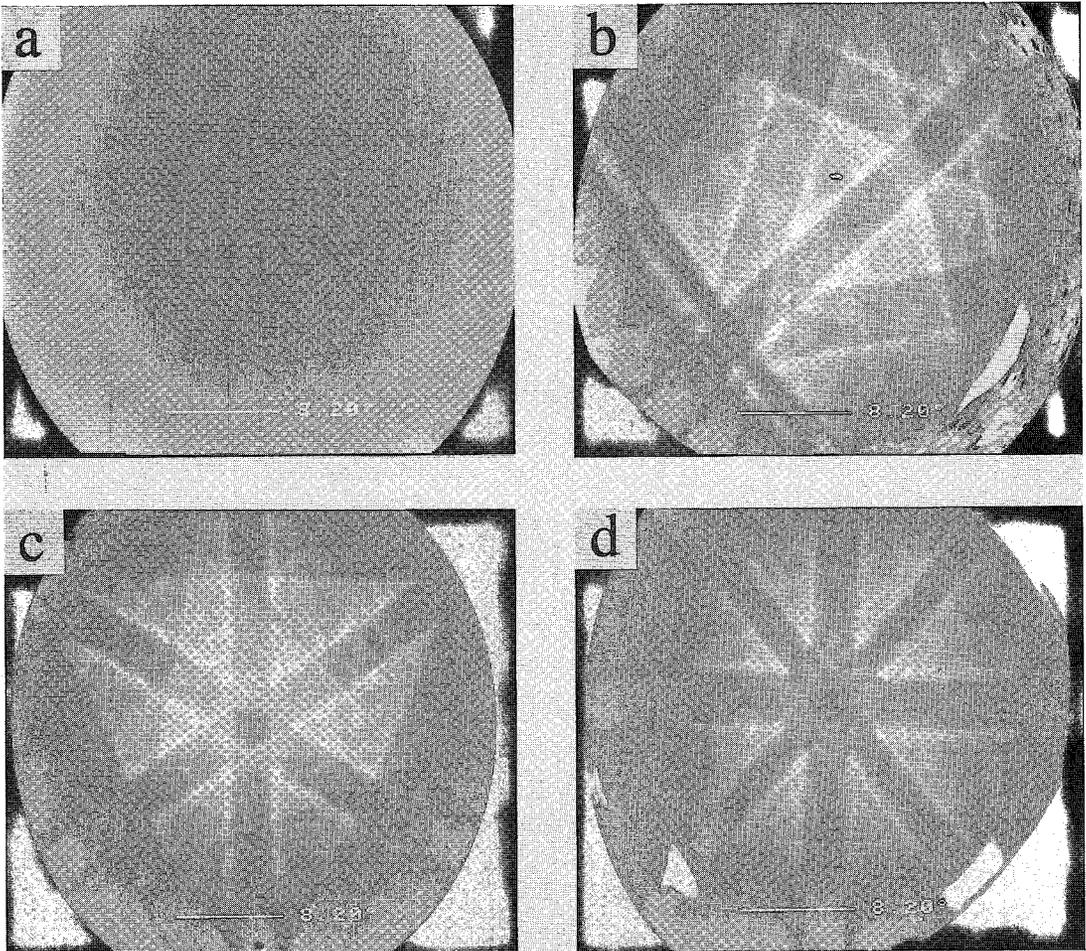


FIG. 1. ECP images of cuprite. Operating conditions: 30 kV, objective distance 8 mm. a) Standard polished sample of cuprite from Siberia; optically anisotropic. b) The same, randomly oriented sample as in a) after a "Mastermet" finish; isotropic. c) (111) section of a cuprite octahedron from Cornwall after a "Mastermet" finish. d) (100) section of a cuprite cube from Banat, Romania after a "Mastermet" finish.

the grains could be observed (except for the changing red internal reflections). ECP images revealed that all diamond-polished samples had an extremely deformed surface-layer, *i.e.*, an ordered, cubic crystal structure could not be observed at the surface (Fig. 1a). Since the information of the electron channeling pattern stems from the uppermost surface layer (about 40 nm thick in cuprite), knowledge about further propagation of the deformation cannot be obtained. Also, differences in the intensity of deformation between random orientations and the (111) and (100) sections could not be verified. A summary of observations is presented in Table 1.

On the other hand, all samples that had been finished with the "Mastermet" procedure for 60 minutes proved to be isotropic under the microscope.

Even with delicate adjustments of the microscope (polarizers slightly uncrossed, daylight filter removed), anisotropy was not observed. The weak bireflectance of the bulk samples had disappeared as well. However, the grain boundaries in the bulk samples of cuprite were clearly visible owing to the enhanced relief caused by the 60 minutes of "Mastermet" finish. This chemomechanical method of polishing even produced perfect, scratch-free surfaces in the very soft inclusions of native copper in the sample from Siberia. Besides, an experiment with only 30 minutes of the "Mastermet" finish in the case of the bulk sample from Siberia resulted in very weak, but still visible, anisotropy effects.

ECP images show a perfect, undisturbed surface in all samples subjected to 60 minutes of the

TABLE 1. SUMMARY OF OBSERVATIONS ON CUPRITE

Sample description	optical behavior	SEM study
Cuprite bulk samples with randomly oriented grains, standard polish	anisotropic	no ECP
Standard polished cuprite, (111)	isotropic	no ECP
Standard polished cuprite, (100)	isotropic	no ECP
Cuprite bulk samples with randomly oriented grains, "Mastermet" finish	isotropic	perfect, sharp ECP
"Mastermet" finished cuprite, (111)	isotropic	perfect, sharp ECP
"Mastermet" finished cuprite, (100)	isotropic	perfect, sharp ECP
Cuprite bulk sample, thin sections	isotropic	----

ECP: electron channeling pattern.

"Mastermet" procedures. The patterns of a random section of cuprite (Fig. 1b), a (111) section of an octahedral crystal from Cornwall (Fig. 1c), and a (100) section of a cuprite cube from Banat, Romania (Fig. 1d) show sharp zones that reflect the symmetry of the respective face. The pictures are only disturbed by a few black spots and lines that stem from holes or grain boundaries in the surface of the polished sections. Differences in the quality of the surface of different sections could not be observed.

A final investigation of two thin sections of the bulk sample from Siberia also confirmed that cuprite is cubic and hence isotropic: with crossed polarizers, the samples appear dark; the extinction does not change upon rotation of the stage.

DISCUSSION

The results of the present work clearly prove that the real optical behavior of undeformed cuprite is isotropic, and hence consistent with its cubic structure. Solely mechanical methods of polishing (like careful diamond-polishing) can cause severe damage in the surface structure of solid materials, which may result in unexpected and misleading effects. In the case of cuprite, these effects are responsible for the strong anomalous anisotropy. Polishing with alkaline silica solutions avoids or removes surface deformations and allows the study of the undisturbed structure of the surface.

Concerning chemomechanical polishing with strongly alkaline media, there seems to be only limited knowledge of this method in the literature on ore microscopy, even though the topic of sample preparation is dealt with on a broad scale (*e.g.*, Laflamme

1990). Even in an investigation of the influence of the different methods of polishing on the reflectance of silicon (Pauly 1986), one finds only mechanical methods competing for the ultimate result. Polishing with alkaline silica solutions is usually only described in the literature on material sciences [*e.g.*, preparation of electrical and optical materials: Fynn & Powell (1988), specimen preparation for the SEM: Lloyd (1987)], and it is known to provide perfect, undisturbed surfaces, even of soft materials. Since this method works with colloidal silica dispersed in a medium of pH \approx 9.8, it may be possible that chemically sensitive materials are affected by etching, dissolution, *etc.* This phenomenon was observed in the case of aurostibite, AuSb₂, which shows an almost perfect surface after the standard polish, but which became considerably anisotropic and in which the surface became deformed after the "Mastermet" finish (Libowitzky 1994a). Consequently, since polishing with alkaline solutions is not always successful, resulting surfaces should always be examined by ECP or other surface-sensitive methods. Of course, the "Mastermet" finish cannot be applied routinely to sections for ore microscopy, since this will result in high relief, which is not desirable for studies of ore parageneses. But the method should be considered for special purposes such as quantitative measurements of reflectance on ore minerals, and other investigations (like the present one), which require a structurally undisturbed surface.

Why do mechanical methods of polishing cause anisotropy effects in cuprite? One might well suggest that deformation of the surface layer of a crystal will result in a randomly distorted, isotropic surface-structure. But since the mechanical properties of a crystal face (*e.g.*, scratch hardness) mirror the crystal symmetry, and since the deformation caused by mechanical polishing conforms to the mechanical properties of that face, there is strong evidence that randomly oriented crystal faces (*hkl*) show an anisotropic deformation of the surface, thus resulting in optical anisotropy effects. This also explains why the (111) and (100) sections of cuprite appear isotropic. In space group *Pn3m*, the (111) face has a three-fold axis of symmetry (*3m*), and the (100) face has a four-fold axis of symmetry (*4mm*). Both the threefold and the fourfold symmetry preclude anisotropic optical phenomena, even if the surface is deformed according to the symmetry of the face. In pyrite (Stanton 1957, Libowitzky 1994a), which belongs to a lower space-group (*Pa3*), only the (111) face (face symmetry 3, trimetric) is isotropic, whereas the (100) section (face symmetry *2mm*, disymmetric) is considerably anisotropic. In the spinel group, *Fd3m* (Libowitzky 1994b) the isotropic faces are (111) and (100) as in cuprite, which strongly confirms the rule of mechanical deformation of the surface conforming to the face symmetries of a crystal.

The deformed layers of the cuprite surface obviously do not represent a new "single-crystal phase"; otherwise, the ECP images would show an ordered structure. Rather, the unstructured ECP images of standard polished cuprite indicate that the deformed surface-layer is composed of extremely small domains of cuprite in different (but not "random", as this might suggest "isotropic") orientations.

A more difficult question concerns the high intensity of the optical anisotropy effect. Whereas anomalous anisotropy effects are weak and not always visible in most cubic ore minerals (Klemm 1962), the effect can always be observed with high intensity in cuprite. The only minerals described by Klemm (1962) as considerably anisotropic without exception are cuprite and cobaltite. The latter has been refined in space group $Pca2_1$ (Fleet & Burns 1990), but all crystallographic work on cuprite has confirmed the cubic symmetry (Restori & Schwarzenbach 1986), even though Klemm (1962) suggested that it might deviate from cubic symmetry. One possible explanation for the strong anisotropy might be that cuprite is extremely brittle. Thus mechanical defects propagate easily into the upper layers of the surface. It is interesting to note that similar, but weaker effects of anisotropy occur in standard polished spinel-group minerals (chromite, magnetite, franklinite; Libowitzky 1994b), as well as in standard polished sections of pyrite and sperrylite (Libowitzky 1994a). One common feature among these minerals is the rather low amount of metallic bonding in their structures, even where these minerals conform to the usual "ore mineral" properties and they absorb visible light to a considerable extent. Another feature is their poor behavior during grinding: even soft grinding produces a considerable proportion of holes in the surface of these materials. One difference between cuprite and pyrite or spinel is that cuprite shows a cleavage along (111), whereas the latter do not. Another difference is that cuprite is rather weak in comparison with the hard minerals of the pyrite and spinel groups.

The anomalous anisotropy effects have also been attributed to second-order phenomena of spatial dispersion in cuprite (Agranovich & Ginzburg 1966). On the other hand, these authors claimed that these effects are usually small and negligible in classical crystal optics. Only in the case of anomalous effects like anisotropy in cubic crystals, which cannot be explained by other optical theories, can spatial dispersion be considered as a cause for visible effects.

Finally, it should be noted that surface deformations may be deleterious not only to precise optical investigations, but also to other fields of research on crystalline materials, like in X-ray structure analyses of spherically ground single crystals (Fetisov & Zhukov 1992). This is of special interest, since the most recent refinement of cuprite, which focused on calculation of charge density (Restori & Schwarzenbach 1986), was

made on spherically ground crystals. It seems worthwhile to check for the possible influence of deformed surface-layers on the observed X-ray intensities of cuprite. However, surface deformations also may be deleterious to orientation contrast images with the SEM (Lloyd 1987) and to the preparation and investigation of sensitive semiconductor materials (Fynn & Powell 1988). Consequently, surface-sensitive methods like ECP should be used to ensure that the material itself is investigated rather than the disturbed layers at the surface.

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