# ELECTROLYSIS OF SYNTHETIC QUARTZ WITH A NONSTRUCTURAL IMPURITY

CRYSTALLOGRAPHY

1967

SovietRxiv

## Abstract

## Full Text

UDC 549.514.5-114 : 541.135.4

*CRYSTALLOGRAPHY*

**V. G. LUSHNIKOV, V. E. KHADZHI**

# ELECTROLYSIS OF SYNTHETIC QUARTZ WITH A NONSTRUCTURAL IMPURITY

*(Presented by Academician N. V. Belov, April 19, 1966)*

As is known, the passage of a direct current through crystalline and fused quartz heated to high temperatures lowers its electrical conductivity and is accompanied by a change in light absorption in the ultraviolet and visible regions of the spectrum. In a number of works ([1–3]) it was shown that the effects arising in electrolyzed quartz are associated either with the removal of impurities from it or with contamination by the electrode material.

In recent years, studies of the diffusion processes of impurities in single crystals of natural and synthetic quartz under the application of thermal and constant electric fields have attracted attention in the study of the nature of the centers of smoky ([4,5]), blue ([6]), green, and brown coloration ([7,8]). Removal of impurities from crystalline quartz during electrolysis contributes to a change in some of its physical properties ([9]), in particular to an improvement of piezoelectric characteristics, in connection with which the electrocleaning method has been used to prepare piezoquartz for the manufacture of heat-resistant resonators ([10,11]).

The present article considers phenomena accompanying the process of electrocleaning of single crystals of synthetic quartz with an increased sodium content. In synthetic quartz, sodium is usually present as an interstitial impurity or so-called "nonstructural impurity" ([12,13]). Such crystals, when heated to a temperature of 700–750°, usually acquire a milky-white color, with the intensity of light scattering, other conditions being equal, increasing with increasing sodium concentration ([14]). Possible mechanisms of this process are discussed in works ([13,15]). However, experimental data confirming the connection of light-scattering centers with impurities migrating in synthetic quartz during electrolysis have not yet been presented. The present work was intended to carry out such an investigation.

Specimens for electrocleaning, in the form of plates parallel to the plane (0001), about 3 mm thick, were cut from the pinacoidal pyramid of crystals synthesized in aqueous solutions of sodium carbonate. For heating, an electric resistance furnace was used, in which a current-supplying device was mounted. Electrodes made of various materials were used. The temperature was recorded with an electronic automatic potentiometer. Before and after the experiments, the specimens were subjected to spectral, spectrophotometric, and optical investigations. Electrocleaning was carried out at temperatures of 500–700° in a constant electric field with a voltage from 400 to 1000 V for various periods of time. As a rule, after the passage of current, on the cathode side the surface of the polished quartz plates exhibited traces of corrosion due to the action of alkaline ions. Therefore, for subsequent investigations it was necessary to grind and polish the surfaces. It was noted ([16,17]) that the process of electrolytic cleaning is accompanied by diffusion of the electrode material into crystalline quartz.

To the article by V. T. Lyshnikov and V. E. Khadzhi, p. 1072

[Figure 1]

**Fig. 1.** Separation of chains of microscopic copper crystallites in synthetic quartz after electrolysis. Native coal replica. 50 000×

[Figure 2]

**Fig. 2.** Effect of electropurification on centers of milky-white coloration obtained in synthetic quartz after annealing. *a*—after electropurification; *b*—after electropurification and subsequent annealing; *c*—after annealing, but without electropurification. The plane of the plates is parallel to (0001). 2×

with the formation of dendritic and layered inclusions. We found that the morphology of the precipitates of metal ions in synthetic quartz is affected by the textural features of the crystal, caused by the nonuniform distribution of the "nonstructural impurity" in the growth layers. In experiments using copper electrodes, preferential introduction of copper was observed in areas of intensive development of the macromosaic, associated with secondary sectoriality. Depending on the duration of electrolysis, there was first the appearance of a yellow coloration (chains of microscopic copper crystals, see Fig. 1, inset, p. 1071), and then layered macroinclusions of copper. The boundaries of the region colored by copper usually extended beyond the zone covered by the electrodes. To prevent contamination of the specimens during electrocleaning, platinum and graphite electrodes were used. The results of spectral analyses are presented in Table 1.

**Table 1**

**Results of spectral analysis of synthetic quartz before and after electrocleaning**

| Sample treatment | $Na_2O$ | $Al_2O_3$ | $Fe_2O_3$ |
|---|---|---|---|
| Quartz before heat treatment and electro-cleaning | $3 \cdot 10^{-3}$ | $8 \cdot 10^{-3}$ | $1.8 \cdot 10^{-3}$ |
| Quartz after electrocleaning and subsequent annealing: a) marginal (uncleaned) regions of the specimen | $2 \cdot 10^{-3}$ | $8 \cdot 10^{-3}$ | $1.0 \cdot 10^{-3}$ |
| Quartz after electrocleaning and subsequent annealing: b) central region of the specimen, located between the electrodes during electrocleaning | $< 4 \cdot 10^{-4}$ | $4 \cdot 10^{-3}$ | $6.0 \cdot 10^{-4}$ |

Electrocleaning was applied to quartz specimens with a sodium oxide content on the order of $(3—4) \cdot 10^{-3}$ wt. %. Quantitative determinations of sodium were carried out by the flame photometry method.* After heat treatment at a temperature of 750°, the specimens of this series became irreversibly cloudy (Fig. 2b). After electrocleaning at a temperature of 500° and a field strength of up to 1000 V/cm$^2$ for several hours, no light scattering was observed (Fig. 2a), and, when the spectrum was recorded on an SF-4 instrument, it was possible to detect a change in the degree of transparency of the specimen in the cleaned zone. At the same time, a slight decrease in absorption was observed in the short-wavelength region of the spectrum (220–280 mμ) in the central cleaned part of the specimen. During subsequent annealing of the specimen at a temperature above 700°, the milky-white coloration appeared mainly in its marginal parts, outside the area covered by the electrodes (Fig. 2b). It is characteristic that in all cases the specimens that had first been heat-treated and had become cloudy showed no changes in the density of the milky-white coloration during subsequent electrocleaning.

From consideration of the spectral-analysis data it is seen that, in the cleaned central part of the specimen (Fig. 2b), the sodium content decreases by a factor of 3 in comparison with the marginal zones. Along with sodium, impurities of aluminum and iron are also removed from the quartz. The decrease in the aluminum concentration in the cleaning region is also confirmed by the results of $\gamma$-irradiation. When the specimen was exposed to a dose of $6 \cdot 10^6$ roentgens (Fig. 2b), "development" of smoky-color centers was observed only in the marginal, uncleaned zones. Infrared absorption spectra of quartz subjected to electrolysis reveal a substantial increase in the concentration of hydrogen in the cleaned region.

* Analyst L. Z. Kurtasova.

It should be noted that the experiments described here can be reproduced on crystals with a sodium content of not more than $5 \cdot 10^{-3}$ wt.%. At higher impurity concentrations, brightening of the near-electrode region after electro-purification is not observed, because the formation of milky-white coloration centers occurs at lower temperatures, apparently before the onset of alkali diffusion. The absence of a brightening effect in specimens that had been preliminarily annealed is probably explained by the fact that, during the organization of the milky-white coloration centers, the main components of the nonstructural impurity—sodium and aluminum—promote the formation of submicroscopic precipitates of a new phase. In addition, part of the light is scattered by microscopic cracks that are intensively developed in the zones of clouding ([13]).

All-Union Scientific-Research Institute
of Mineral Raw-Material Synthesis

Received
11 IV 1966

## CITED LITERATURE

[1] A. A. Kalenov, *Optiko-mekhanicheskaya promyshlennost'*, **6**, 1 (1958).
[2] V. Garino-Canina, *C. R.*, **240**, 1765 (1955).
[3] V. Garino-Canina, *Verres et Refract.*, **10**, 2, 63 (1956).
[4] L. G. Chentsova, N. E. Vedeneeva, *Tr. Inst. kristallogr. AN SSSR*, **7**, 191 (1952).
[5] I. Lietz, M. R. Hänisch, *Naturwiss.*, **46**, 67 (1959).
[6] V. G. Lushnikov, *Zap. Vsesoyuzn. mineralog. obshch.*, **93**, 6, 735 (1964).
[7] L. I. Tsinober, L. G. Chentsova, A. A. Shternberg, in: *Rost kristallov*, **2**, 1959, p. 81.
[8] V. G. Lushnikov, *Zap. Vsesoyuzn. mineralog. obshch.*, **92**, 5, 619 (1963); **94**, 6, 740 (1965).
[9] H. H. Pfenninger, F. Laves, *Naturwiss.*, **48**, 1, 22 (1961).

[10] *J. Electrochem. Soc.*, **109**, 2, 44c–45c (1962).
[11] *Times Rev. Industry*, **16**, 187, 56 (1962).
[12] A. J. Cohen, *J. Phys. Chem. Solids*, **13**, 3-4, 321 (1960).
[13] L. I. Tsinober, V. E. Khadzhi et al., in: *Rost kristallov*, **6**, 1965, p. 22; V. G. Lushnikov, V. E. Khadzhi, *Tr. Inst. p' ezooptich. syr' ya*, **5**, 87 (1961).
[14] V. E. Khadzhi, Yu. P. Sazonov, Author' s certificate 167837, 1965.
[15] J. A. Bastin, E. W. Mitchell, *Am. Mineral.*, **46**, 1227 (1961).
[16] E. V. Tsinzerling, *Zap. Vsesoyuzn. mineralog. obshch.*, **93**, 3, 342 (1964).
[17] E. V. Tsinzerling, *Kristallografiya*, **10**, 3, 368 (1965).

*Note: Figure translations are in progress. See original paper for figures.*