ELECTRON-MICROSCOPIC INVESTIGATION OF SYNTHETIC QUARTZ WITH A NONSTRUCTURAL IMPURITY

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Abstract

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CRYSTALLOGRAPHY

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ELECTRON-MICROSCOPIC INVESTIGATION OF SYNTHETIC QUARTZ WITH A NONSTRUCTURAL IMPURITY

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One of the characteristic properties distinguishing synthetic quartz crystals from natural ones is Tyndall scattering of light, observed most often in specimens obtained at high growth rates. Attention was first drawn to this phenomenon in work ([1]), where it was established that an increase in the intensity of opalescence is accompanied by a decrease in the refractive index and a simultaneous increase in the magnitude of the diffuse maximum in the region of 3 μ. They suggested that the scattering of light occurs on submicroscopic inclusions of the mother solution captured by the crystals during growth.

Subsequent investigations showed that in opalescent regions an increased concentration of sodium is detected, reaching in individual cases tenths of a percent ([2]). Synthetic quartz enriched with sodium becomes irreversibly cloudy after heating to 600° ([3]), with the greatest density of centers of milky-white coloration being observed in the pinacoidal growth pyramid. As a result of microscopic study of preparations from crystals subjected to high-temperature annealing, it was established that colonies of regularly oriented microcracks arise in the clouded regions and promote the scattering of light ([2,4]). It was also suggested that the centers of the milky-white coloration are particles of a new phase (lithium aluminosilicate), which separate out at 573° in quartz previously heated above the point of the $\alpha \rightleftarrows \beta$ transformation ([5]). However, X-ray structural studies did not confirm this conclusion. In annealed milky-white quartz it was not possible to reveal new phases ([6]) or to record a change in the lattice parameters ([7]). Therefore the impurity causing opalescence and milky coloration in quartz was conventionally called nonstructural ([2,7]). King ([8]) and Nelson ([9]) came to the conclusion that in defective synthetic quartz there exist amorphized disordered regions (unbonded oxygen atoms in the lattice) enriched with an alkali silicate. Two known attempts to estimate the sizes of the defects causing Tyndall scattering in synthetic quartz were based on indirect data. Dodd and Fraser ([6]) determine the sizes of inclusions as 0.2–1 μ. N. M. Melankholin and I. N. Guseva ([10]), noting the polarization effect of the Tyndall cone in quartz and referring to the work of K. S. Shifrin ([11]), conclude that the impurity is included in the crystal in the form of the finest uniformly oriented colloidal particles of elongated and flattened shape. As a result of investigation of natural milky-white quartz crystals by the method of diffraction electron microscopy, voids in the form of polyhedra with diameters of 200–1000 Å and with a density of the order of 10^{14} cm^3 were found in them ([12]). In the opinion of the authors ([12]), the milky color of the natural crystals studied is associated with the scattering of light on these voids, the source of whose origin is not clear.

Synthetic single crystals of quartz grown on seeds parallel to the (0001) plane, in sodium carbonate solutions at growth rates of about 0.6 mm per day per side, were investigated. The specimens were prepared from the pinacoidal growth pyramid, in which Tyndall scattering was observed. On a freshly prepared cleavage in a vacuum of $1 \cdot 10^{-4}$ mm Hg.

Fig. 1. Fracture surfaces of a synthetic quartz crystal without a nonstructural impurity (*a*) and with an impurity (*b*), as well as of a crystal with a nonstructural impurity etched in 40% hydrofluoric acid for 1 min (*c*). Self-shadowed carbon replica

Fig. 2. Fracture surfaces of an annealed quartz crystal with a nonstructural impurity: *a*—before etching; *b*—after etching in 40% hydrofluoric acid for 1 min. Self-shadowed carbon replica

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A replica was deposited by simultaneous evaporation of platinum and carbon at a definite angle. The replica was separated from the specimens by gelatin or by dissolving the substance of the specimen in a solvent. The replicas obtained were mounted in a GEM-6A electron microscope and examined over a magnification range from 4000 to 50,000.

As a standard, use was made of synthetic quartz which does not become cloudy after annealing and does not give Tyndall scattering. The fracture surface of this crystal is characterized by the absence of any inhomogeneities (Fig. 1a). After etching the fractures of the standard specimen in hydrofluoric acid, no defects were detected under the electron microscope (therefore a photograph of the etched fracture surface is not given). An entirely different picture is observed in specimens containing an unstructured impurity (Fig. 2b). Here, inclusions of isometric shape are clearly revealed, uniformly distributed in the plane of the preparation. The size of the inclusions varies within the limits 0.02—0.04 μ. The slight scatter in sizes is probably explained by the different positions of the inclusions relative to the fracture plane. The number of inclusions varies within the limits $1.1—1.3 \cdot 10^9$ cm^{-2}.

Fractures of the specimens were etched in hydrofluoric acid (1 min, 10% solution). The etching patterns make it possible to reveal the detected defects more clearly. The positions of the etch pits correspond to the character of the distribution of inclusions on fresh fractures of unetched and unannealed specimens (Fig. 1b). The number of etch pits is equal to the number of inclusions. More prolonged etching, as well as the use of more concentrated hydrofluoric acid (40%), leads to growth of the pits tangentially and to their acquiring an elongated form; moreover, they are all oriented mutually parallel, and no other defects arise upon prolonged etching.

Fractures of specimens previously annealed at 700° for 1 hour were also studied. Annealed cloudy crystals are characterized by the presence of globules (voids) of isometric (nearly spherical) shape (Fig. 2a). The relief of the fracture surface of an annealed crystal, as compared with the fracture surface of an unannealed preparation, is characterized by strain and by the presence of microcracks. A correspondence is observed between the distribution of inclusions in unannealed crystals and of globules in annealed ones. The number of voids is $(7.6 \div 8.0) \cdot 10^8$ cm^{-2}. The size of the voids varies within the limits 0.03—0.1 μ. Etching of annealed specimens with hydrofluoric acid first transforms the voids into trihedral flat-bottomed pits (Fig. 2b). Increasing the etching exposure, as in the case of etching inclusions, causes further widening of the pits and an increase in the number of faces. Since the observed pits are flat-bottomed, the defects associated with them are evidently not channels of the kind found in quartz by Pfenninger and Laves [13]. This is further confirmed by the fact that on fractures of different orientation the form of the defects does not change in any case.

The observations carried out indicate that opalescent synthetic quartz contains a colloidally dispersed impurity phase uniformly distributed throughout the volume of the crystal.

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