Anisotropic Small-Angle X-ray Scattering in Quartz

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Small-angle scattering using X-rays (SAXS) is a powerful technique to investigate the structure and the size distribution of heterogeneities with nanometric sizes in solutions, biological systems and polymeric materials. On the other hand, small-angle neutron scattering (SANS) has been more adopted to investigate second-phase precipitates in metals and alloys. Double Bragg Scattering (DBS) and high absorption due to heavy elements are often the restrictions to use SAXS in inorganic materials with polycrystalline structure. In case of single crystals, DBS can be normally avoided but an anisotropic pattern around the incident beam is expected. In this case, the direction of the scattering vector should be taking into account in data analysis \cite{1}.

Recently, the problem of the clustering of OH-related defects in crystalline quartz was studied by SAXS and infrared spectroscopy (IRS) in synthetic \cite{2} and natural \cite{3} single crystals. It was observed that even those samples without any heat treatment scattered X-rays at low angles. The scattering was attributed to fine-scale water aggregates that were visualised by transmission electron microscopy \cite{4}. However, it was not possible to clearly notice the effect of the heat-treatment on the clustering of water aggregates in SAXS profiles. This difficulty was explained by the short duration of the isothermal heat-treatments performed and the anisotropy of the scattering pattern. This report describes our further attempts to investigate the small-angle scattering of quartz single crystals taking into account the effect of the crystal anisotropy.

Two natural quartz single crystals were selected for this study. The first crystal is an euhedral rock crystal (colourless) with about 100 mm long in [0001] direction taken from Brumado (BA), a mine district located in a pegmatite environment in Brazil. The second crystal is an euhedral amethyst with about 60 mm long grown in the hydrothermal environment of São Gabriel district (RS, Brazil). SAXS were carried out at the Soft Condensed Matter A2 beamline of HASYLAB using a X-ray wavelength of 1.5 Å. Plates parallel to the (0001) plane were cut with a diamond saw and lapped mechanically with fine SiC grits to reach thickness < 200 \(\mu\)m in order to get \(\mu t \leq 2.0\); where \(\mu\) is the linear absorption coefficient and \(t\) is the thickness. The scattering intensities were collected in vacuum at room temperature with sample-to-detector distance of 2565 mm. A solid-stated CCD detector (MAR 185\textsuperscript{®}) was used to collect two-dimensional (2D) high resolution images with 2048x2048 pixels. The 2D data analysis was performed by using the FIT2D software. The angular range of the scattering curves were 0.15nm\(^{-1}\) \(\leq q \leq 1.25\)nm\(^{-1}\), where \(q\) is the scattering vector. All curves were scaled to the incident beam and then corrected for sample absorption and parasitic scattering. To complement the investigation with quartz, samples of layered agate, a chalcedony quartz that forms in concentric layers in a wide variety of colours and texture, were prepared and measured in the same conditions.

Figure 1 shows three typical SAXS patterns collected from quartz and agate. Figures 1(a) and 1(b) reveals that the SAXS pattern of quartz are anisotropic, clearly showing the symmetry of the basal plane. The hexagonal pattern is always present and moves with the same angle when the sample itself is rotated. The cut angle from one sample to the other varies around \(\pm 1^\circ\) in relation to the basal plane. DBS can not be satisfied for all conditions considering the rotating and the tilting of the sample. Thus, the contribution of DBS to the formation of the hexagonal patterns can be ruled out. On the other hand, streaks like those in Figure 1(b) sometimes appeared superposed or dispersed from the hexagonal pattern. These streaks are sensitive to sample position in the holder and depends of the specimen itself. Probably, these streaks come from DBS due to small deviation of the incident beam by surface flaws that can act as diffracting planes. The isotropic SAXS pattern of agate in figure 1(c) is explained by its microcrystalline structure.
The anisotropy of the scattering intensities in quartz was evaluated by using two procedures. Figure 2(a) corresponds to the projection of the scattered intensities on [11\(\bar{2}0\)] and [10\(\bar{1}0\)] directions lying in the basal plane. The scattering profiles shown in Figure 2(b) were obtained by integrating a slice of 6° around each direction. For both cases one observes that the scattering intensity is higher along the [11\(\bar{2}0\)] direction in the q range from 0.2 to 0.7 nm\(^{-1}\). This fact indicates that the inhomogeneities related to small-angle scattering are dispersed in the SiO\(_2\) matrix with a preferential orientation. Therefore, these results show that the anisotropic behaviour of the SAXS patterns should be taken into account in the study of the clustering of OH-related defects in quartz single crystals.

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References