Helical X-Rays Probe Crystal Chirality

Handedness or chirality is found in many complex materials such as proteins, sugars and pharmaceuticals as well as in simpler materials like low quartz and tellurium. They have two crystalline forms that are mirror images of each other, like our right and left hands. Often, the two structures of these so-called enantiomers can have very different chemical and biological properties. For example, thalidomide has two forms: right (R)-thalidomide is effective against morning sickness, on the other hand, left (S)-thalidomide is teratogenic and causes birth defects.

Linearly polarized visible light typically changes its polarization direction depending on whether it passes through a 'left'- or 'right'-handed form of an enantiomer, providing a convenient means of distinguishing them. This phenomenon is known as optical activity, which is effective only for transparent and thin materials. On the other hand, simple X-ray Bragg diffraction, a popular material analysis technique, cannot differentiate between the two, unfortunately.

Our team at the RIKEN SPring-8 Center in Harima and the UK have shown that right and left circularly polarized (RCP and LCP) X-rays of right energy can distinguish 'left' from 'right' low quartz [1].

When the energy of X-rays is tuned to a specific value, that of the silicon *K* absorption edge, X-ray scattering is able to distinguish the particular symmetry of unoccupied states of silicon ion. This process is called resonant scattering, in which the selection rules in diffraction are different from those of normal X-ray scattering. It is known that resonant scattering is sensitive to the crystal symmetry [2], for example, the screw axis, and that forbidden diffraction in normal scattering can become allowed in resonant scattering. We have applied this feature to low quartz with circularly polarized X-rays.

Quartz is the most abundant mineral on earth and has a screw axis in its crystal structure. The screw axis determines the handedness of quartz depending on its form, right screw or left screw, as shown in Fig. 1. Our experiments, carried out at RIKEN beamline **BL17SU**, show that the "forbidden" reflection 001 is observed at the resonant energy of the silicon *K* absorption edge (Energy = 1.85 keV). In addition, the intensity depends on the crystal form (right- or left-handed) as well as the helicity of the X-ray beam, as shown in Fig. 2. Another important aspect of resonant X-ray diffraction is that the intensity depends on the rotational angle of the sample, i.e., the azimuthal angle. The intensity of the diffracted X-ray beam is independent of the azimuthal angle for normal X-ray diffraction, however, it changes according to the crystal structure in resonant scattering. Figure 3 shows the intensities of the diffracted beam of 001 reflection for right and left quartz and for right and left circularly polarized X-rays as a function of

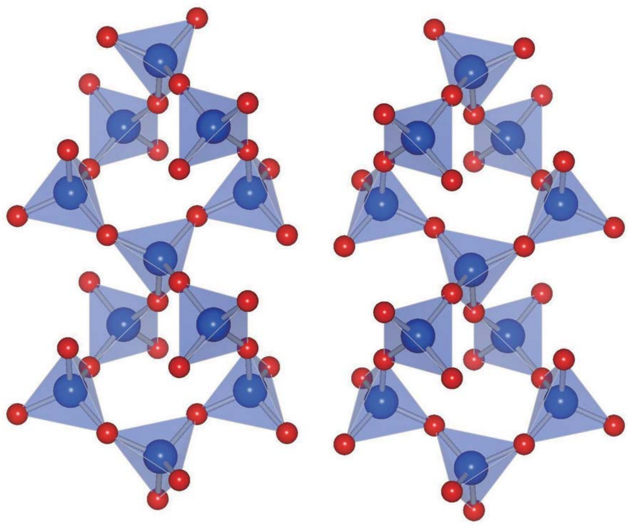

Fig. 1. Views of atomic structures of R-quartz (right) and L-quartz (left) along the a*- and b*- axes, respectively. Blue and red spheres represent silicon and oxygen atoms, respectively.

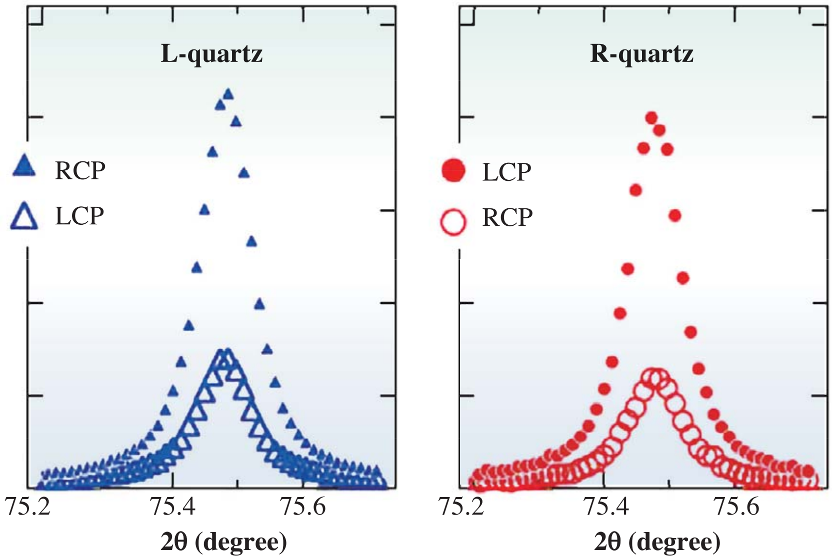

Fig. 2. Reflection profile of 001 of R-quartz and L-quartz measured with a left circularly polarized (LCP) incident beam and a right circularly polarized (RCP) incident beam.

the azimuthal angle. The results clearly show that the helicity of the X-ray beam couples with the handedness of the crystal. The periodicity of 120 degrees in each azimuth scan corresponds to the screw structure in quartz. This technique is expected to be useful for studying the chirality of other materials in general, including biomaterials, liquid crystals and multiferroics.

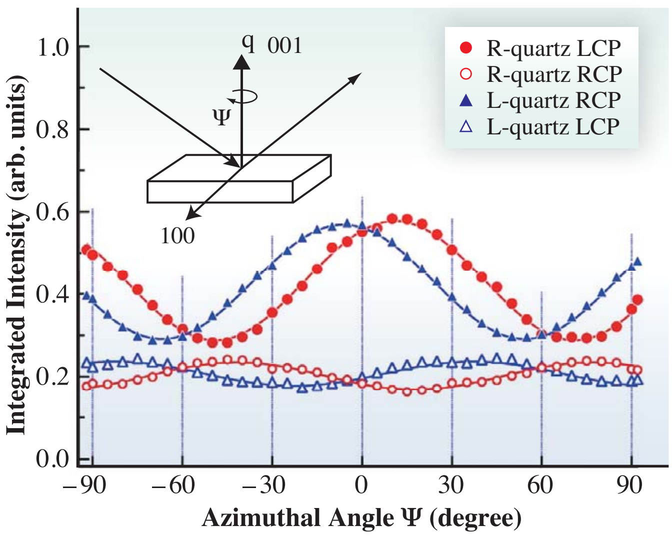

Fig. 3. Integrated intensity of reflection 001of R-and L-quartz as a function of azimuth angle Ψ. Filled (open) circles represent the intensity of reflection 001 of R-quartz measured with LCP (RCP) incident beam, and filled (open) triangles represent the intensity of reflection 001 of L-quartz measured with RCP (LCP) incident beam.

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