Insights to crystal chemistry of defects during industrial processing from ESEEM spectroscopy

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The ubiquitous presence of point defects in quartz and in other silica polymorphs has been recognized since many years. Since many point defects are associated with trapped electrons or holes, the most specific technique employed in these studies was Electron Paramagnetic Resonance (EPR). In this study, we are aimed to verify through pulsed EPR (in particular, through Electron Spin Echo Envelope Modulation experiments) if defect species in natural quartz powders can be used as proxy to trace crystal chemical changes involving surface paramagnetic species, induced by specific mechanical processing. The study, carried out on laboratory standard and on industrial quartz-bearing samples, compares the effects due to dust granulometry, chemical impurities, mechanical milling and interaction with associated mineralogical phases.

During a first stage of the investigation, reference quartz dusts, both bulk and breathable, were analyzed before and after a laboratory mechanical milling procedure, in order to sort out if structural changes are occurred. By c.w. and Echo-EPR, the samples exhibit a clear signal due to oxygen point defects associated to the Al substitutional centers: these can be formally described as $[AlO_4]^0$ species, where charge neutrality is achieved through a hole in a bonding oxide anion. Moreover, from three-pulse ESEEM this species is found to closely interact with a proton, situated in the channels parallel to the c-axis: the center can be thus better described as $[AlO_4]H^+$. Mechanical milling induces only distortion in the geometry of the mutual relationships between the Al center and the proton, or in the number of centers per unit of volume (of the order of magnitude of 10^{20} centers per cm^3). Accordingly, mechanical milling induces just a minor effects in the centers' population and features.

In the second stage, samples belonging to industrial processes (ceramic and casting of iron alloys) were analyzed. Pair of samples, before and after a specific processing step, were considered for the investigation. The pulsed EPR measurements reveal a common starting point for all the industrial and reference samples, i.e. the $[AlO_4]H^+$ centers. On the contrary, after each industrial processing, the final samples present specific paramagnetic species, markedly different from the initial one. In particular, ceramic samples contain radical species centered on the Si ion, which closely interact with Al nuclei external to the quartz framework, and namely provided by the abundant kaolinite intimately mixed with quartz during the process. The casting sample is characterized by the presence of abundant carbonious radicals, closely interacting with protons, which are the trace of a robust reaction occurred among the quartz of the mould, the carbon species expelled during the quenching of the Fe alloys, and the moisture.